conformation of the transition states is activated for endocyclic and exocyclic cleavage. Pseudorotation of $(I_GN)^-$ or $(I_GX)^-$ to an intermediate with the methyl group equatorial and the hydroxyl group axial is energetically unfavorable.[20] Solvent effects do not alter the gas-phase reaction profile qualitatively since the solution free energy barrier for exocyclic cleavage is more than twice that for endocyclic cleavage, as in vacuum.[20]

The present and previous ab initio calculations in conjunction with molecular dynamics simulations of the RNase A complexes[11,21] and experimental data suggest a more detailed mechanism for the RNase A-catalyzed transphosphorylation step; this is summarized in Figure 5. In particular, the proposed mechanism shows that the precise alignment of three key active site residues; viz., His 12, His 119, and Lys 41, is crucial in determining the lowest energy pathway for the transphosphorylation step. His 12 is positioned to facilitate the transfer of the proton on O2′ in **1** to a phosphoryl oxygen to yield **3**. Lys 41 is in a position to stabilize **3** and the endocyclic cleavage transition state **4**; both **3** and **4** can be also be stabilized by active site residues (His 12, His 119, Phe 120, and/or Gln 11) and water molecules so that the barrier to phosphorane monoanion intermediate formation is reduced relative to vacuum or solution. The two active site histidines are positioned so that His 12 can remove the phosphoryl hydrogen in **5**, while His 119 protonates the phosphoryl oxygen to yield **6**, whose conformation is activated for exocyclic cleavage. His 119 is positioned to facilitate the transfer of the proton on a phosphoryl oxygen in **6** to O5′, thus stabilizing the developing charge on O5′ in the exocyclic cleavage transition state **8**; the phosphoryl and ring oxygens in **8** can be stabilized by interactions from His 12, Lys 41, Phe 120, and/or Gln 11 and water molecules. The stereochemistry of the proposed mechanism for transphosphorylation in RNase A catalysis is in-line, as observed experimentally.

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Localization Properties of π Electrons and the Validity of Independent-Particle Models for Hydrocarbon Compounds

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Abstract: The electronic localization properties in alternant and nonalternant hydrocarbon π compounds are quantified in terms of the mean-square deviation of the π electron density $\langle(\Delta n_i^2)\rangle$ around the corresponding mean value $\langle n_i\rangle$. To derive the correlated ground state, the method of the local approach (LA) is employed. The computational method for the π subspace is a simple Hückel-type operator for the one-determinantal wave function and a model Hamiltonian defined by Hartree–Fock hopping terms to evaluate the correlated ground state. The integrals are calculated ab initio in a single-ζ Slater-type basis. The π electrons in hydrocarbons are sizeably localized. This also holds for extended polyenes and $4n + 2$ monocycles. In addition to the electronic charge fluctuations $\langle(\Delta n_i^2)\rangle$, two atomic electron density localization parameters Δ_i and Σ_i are defined to analyze the π electron localization and the importance of the electron–electron interaction in π bonds. The respective atomic electron density localization depends on the topology of the selected "reference center". Bond length alternation leads to an enhancement of the π electronic charge fluctuations, i.e., they are better delocalized here. Interatomic sharing is enlarged. The latter enhancement accompanying bond alternation increases with enlarged electron–electron interaction. Bond length alternation and the uneven charge distribution in certain nonalternant hydrocarbons support the π electron delocalization in the respective networks. On the basis of the calculated π electron localization parameters Δ_i an instability index γ_{in} for nonalternant π systems is suggested. Calculated γ_{in} elements agree well with the known experimental status of the considered π systems. An analysis of the π correlation energy is given for polyenes and monocyclic annulenes as a function of the bond alternation. The competition between π and σ correlation effects is studied by a semiempirical INDO (intermediate neglect of differential overlap) model.

1. Introduction

The electronic structure properties of hydrocarbon π systems have absorbed the interest of theoretical chemists and physicists for more than 60 years. For a very long time it has been assumed throughout in the chemical community that π electrons, especially those in extended networks, are close to the free-electron behavior and highly delocalized. It has been and it is still common usage to characterize molecular geometries without bond length alternation as "delocalized" structures, while bondlength alternation universally is equated with "localized π electron systems". In this context it is remarkable that the two labels "delocalized versus localized π electron systems" have their roots in a purely descriptive language, but not in unambiguously defined quantum chemical expectation values. Only the following two statements can be extracted from static electron density distributions. Molecular structures without bond alternation indicate in the first place an even electron distribution. Spatial differences in the density distribution are present in structures with bond alternation. This and only this follows from molecular geometries and the associated electron density. Any argumentation beyond the latter statements, e.g., the widely assumed 1:1 correspondence between bond alternation and electronic localization, cannot be justified a priori as it violates a fundamental principle of quantum mechanics, i.e., the indistinguishability of electrons. The bottleneck in the above widely used interpretation will be explained in the present investigation intended to introduce a well-defined localization measure for electrons in chemical bonds.

The frequent adoption of free-electron approaches together with the use of descriptive labels for the interpretation of π electron properties had been possible in the past due to the remarkable success of simple one-electron theories. By using the well-known Hückel molecular orbital (HMO) model[1] or the free-electron (FE)

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theory of Kuhn[2] many experimental observations could be explained. However, it had been recognized already in the 1950s and 1960s that the latter model theories failed for many systems.[3] But nevertheless the HMO and FE as well as other simplified models allowed for the formulation of some useful ordering principles in the class of hydrocarbon π systems. The subclassification into alternant and nonalternant systems, e.g., had been one step in this direction.[4] In the present context one should carefully discriminate between bond length alternation and alternant/nonalternant π molecules. The alternancy symmetry in alternant materials leads to a common π electron density $\langle n_i \rangle$ of 1.0 at any center. Furthermore one finds pairwise symmetric arrangements of occupied and unoccupied canonical MOs around the atomic basis energy α.

Nevertheless theoretical investigations in the past years have shown that the above one-particle approaches correspond to an oversimplification or even wrong description.[5-11] We have used the label one-particle model to symbolize the single-determinantal character of an electronic wave function. It may be either of the simple Hückel/extended-Hückel type or of the SCF type. Although these differences are of fundamental importance in conventional quantum chemical studies, they are irrelevant for the purpose of the present work; see below. In a series of ab initio calculations Shaik and co-workers have shown that structures of π systems without bond alternation are only a byproduct of the σ frame.[12,13] Even for the π system of benzene, C_6H_6, bond alternation leads to a stabilization of the π energy. This result has been confirmed by Jug and Köster in a subsequent contribution.[14] They have demonstrated that the mutual competition between π and σ electronic effects is a function of the strength of the electron-electron interaction already in the SCF representation. This means that the gain in π energy due to bond length alternation in hexazine N_6 exceeds the corresponding stabilization in C_6H_6 where the electron-electron interaction is less strong. The important role played by π electron correlations, i.e., the electron-electron interaction that cannot be mapped in a single-determinantal formalism, on the bond length alternation in π systems has been studied extensively by several theoretical physicists.[15-19] Most of these contributions refer to polyacetylene, where finite size effects and topologic factors are irrelevant.

Guided by the above theoretical discussion, which is often quite controversial, we decided to investigate the atomic π electron density localization in alternant and nonalternant hydrocarbons. The delocalization/localization of the (π) electrons is quantified by the mean-square deviation $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ of the π electron density around the corresponding static mean value $\langle n_i \rangle$. In the next section it is demonstrated that the adoption of the charge fluctuations $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ leads to an unambiguously defined atomic π electron density localization parameter. The index corr in $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ indicates that the correlated ground-state wave function has to be used to evaluate the charge fluctuations. Calculations of $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ numbers provide straightforward access to the many-particle character of π electron bonding. By means of correlation-strength parameters Δ_i and Σ_i, which are defined in the next section, the importance of π electronic correlations can be expressed by quantities with well-defined boundary values. The two accessible limits are the free-electron boundary $\Delta_i = 0$ and $\Sigma_i = 0$ and the limit of perfect π correlations $\Delta_i = \Delta_i^{\max}$ and $\Sigma_i = \Sigma_i^{\max} = 1$, where the motion of the (π) electrons is only determined by the many-particle contributions to chemical bonding. In this limit, configurations with 2 e/π site are suppressed as much as possible. At this stage of our discussion it should also be intelligible that there exists a close conceptual proximity between many-particle interactions in a chemical bond and the resulting electronic localization properties. With increasing correlations the electrons tend to localize atomically.

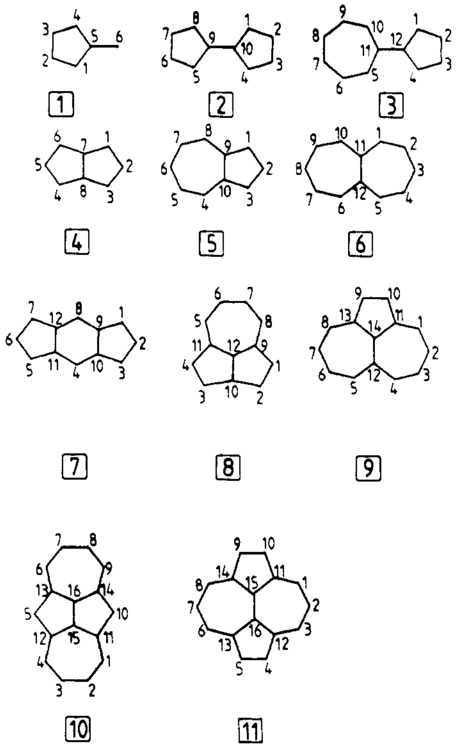

Figure 1. Studied nonalternant hydrocarbons 1-11 together with the employed atomic numbering scheme. Only the molecular topology is indicated.

In previous contributions of one of us[20-23] the different types of chemical bonds have been divided into characteristic classes according to the theoretically calculated $\langle(\Delta n_i^2)\rangle_{\text{corr}}$, Δ_i, and Σ_i numbers. For recent work on the atomic electron density localization in hydrocarbon π systems see refs 24-26. It is one purpose of the present study to relate the present results for π systems to the aforementioned previous findings covering many types of chemical bonds (i.e., σ versus π interactions, homopolar versus heteropolar bonds). Additionally we quantify the validity of one-electron models for π systems. Finally the variation of the π electron fluctuations $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ as a function of the bond length alternation is investigated. To derive the correlated ground state, the method of the local approach (LA)[27,28] has been adopted.

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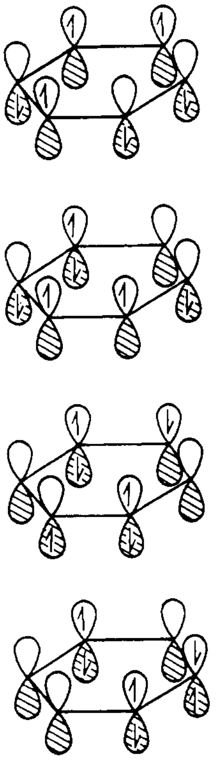

Figure 2. Possible electronic configurations in C_6H_6; schematic representation. From top to bottom: covalent configuration with all π centers singly occupied; ionic configuration with one anionic, one cationic, and four singly occupied π centers; four ionic centers; and completely ionic configuration.

The organization of the present contribution is as follows: The theoretical background of our model together with the computational conditions are presented in section 2. In the next section we demonstrate that the π centers in alternant and nonalternant hydrocarbons can be divided into characteristic classes on the basis of the above many-particle indices. In section 4 nonalternant π systems are discussed. The considered model compounds are summarized in Figure 1. As can be seen, all bi- and polycyclic π molecules have been studied extensively by experimentalists in the past years. For experimental work see refs 29–38. In section 5 the π localization properties in alternant molecules are analyzed. In section 6 the many-body influence due to the σ frame as well as the coupling between π and σ correlations are concisely touched. A general resume is then formulated in section 7.

2. Theoretical Background and Computational Conditions

Not only to employ qualitative delocalization parameters for electrons in chemical bonds, but also to explain reactivities, chemists often refer to so-called "tautomeric valence configurations" accessible in chemical systems. The latter expression is widely used in chemical textbooks. An important example is the keto–enol tautomery in carbonyl compounds. Possible "valence configurations" of benzene are shown schematically in Figure 2. In the top line one "covalent configuration" is indicated. Here each π center is singly occupied. Ionic configurations with an increasing transfer of (π) electrons to neighboring centers are shown from top to bottom. It is intelligible that the (π) electronic delocalization increases with increasing weight of the ionic configurations to the ground-state wave function as the latter require an electronic hopping process from one π center to a neighboring one. The probability of these events is enhanced with increasing hopping/resonance integrals. On the contrary the weight of ionic structures is reduced by the two-electron repulsion suppressing configurations where two electrons are found at the same center. Thus, we always have a competition between kinetic energy effects supporting the interatomic hopping processes and thus the delocalization of the (π) electrons, on one side, and two-electron repulsions, on the other. The latter tend to localize the electrons atomically. Perfect atomic localization is realized if the electronic ground state is completely described by convalent configurations as shown in the top line of Figure 2.

On the basis of the above interpretation it becomes intelligible that the (π) electronic delocalization cannot be measured by static (π) electron densities $\langle n_i\rangle$, but only by calculating the deviations in the (π) electron density around the respective mean value $\langle n_i\rangle$. For atomically localized electrons these charge fluctuations are completely suppressed. The mean value of the (π) density $\langle n_i\rangle$ is only determined here by configurations with singly occupied centers. Electronic delocalization lifts this 1:1 correspondence between the $\langle n_i\rangle$ numbers and the weight of single occupancies. The $\langle n_i\rangle$ elements are then given by a superposition of double, single and empty (π) occupancies. To put these findings into a quantitative basis we define in eq 2.1 the (π) electronic charge fluctuations at center i, i.e., the mean-square deviation of the charge around the respective mean value. Equation 2.1 indicates

$$\langle(\Delta n_i^2)\rangle_{\mathrm{corr}} = \langle\psi_0|n_i^2|\psi_0\rangle - \langle\psi_0|n_i|\psi_0\rangle^2 \tag{2.1}$$

that the mean-square deviations are given by the difference between the mean value of the number operator squared and the mean value squared of the number operator. $|\psi_0\rangle$ in the above relation stands for the correlated ground state, and n_i is the (π) electron number operator whose expectation value $\langle\psi_0|n_i|\psi_0\rangle$ gives simply the (π) density $\langle n_i\rangle$. The charge fluctuations in any single-determinantal ground state either of the SCF or one-electron type are defined by changing $|\psi_0\rangle$ in eq 2.1 into the respective single-determinal $|\psi_{\mathrm{SCF}}\rangle$.

$$\langle(\Delta n_i^2)\rangle_{\mathrm{SCF}} = \langle\psi_{\mathrm{SCF}}|n_i^2|\psi_{\mathrm{SCF}}\rangle - \langle\psi_{\mathrm{SCF}}|n_i|\psi_{\mathrm{SCF}}\rangle^2 \tag{2.2}$$

It has been mentioned in connection with Figure 2 that the charge fluctuations are suppressed by electron–electron repulsions in $|\psi_0\rangle$. One always has the inequality $\langle(\Delta n_i^2)\rangle_{\mathrm{SCF}} > \langle(\Delta n_i^2)\rangle_{\mathrm{corr}}$; constant density assumed. Small $\langle(\Delta n_i^2)\rangle$ numbers indicate atomic electron-density localization. Interatomic sharing and thus also the bonding capabilities of electrons are thereby reduced. Simply speaking, large $\langle(\Delta n_i^2)\rangle_{\mathrm{corr}}$ numbers indicate also high stability. Note that the $\langle(\Delta n_i^2)\rangle$ elements are local probes to quantify the atomic electron density localization at any π center i. The above picture, which perhaps is quite unusual for the chemical readership, is in line with the fundamental Heisenberg uncertainty principle. Large $\langle(\Delta n_i^2)\rangle$ numbers imply high spatial uncertainties. According to the uncertainty principle this must cause small momentum uncertainties. Small momenta then become of higher probability. But this leads to a reduction of the kinetic energy, the mechanism which is decisive for the formation of chemical bonds; see also below.

It is convenient to adopt the charge fluctuations in $|\psi_0\rangle$ and $|\psi_{\mathrm{SCF}}\rangle$ for the definition of a correlation-strength parameter Δ_i, which is a measure for the many-particle character of chemical bonding.

$$\Delta_i = \frac{\langle(\Delta n_i^2)\rangle_{\mathrm{SCF}} - \langle(\Delta n_i^2)\rangle_{\mathrm{corr}}}{\langle(\Delta n_i^2)\rangle_{\mathrm{SCF}}} \tag{2.3}$$

Δ_i has allowed values between $\Delta_i = 0$, indicating the validity of the single-determinantal description, and $\Delta_i = \Delta_i^{\max}$ in the limit

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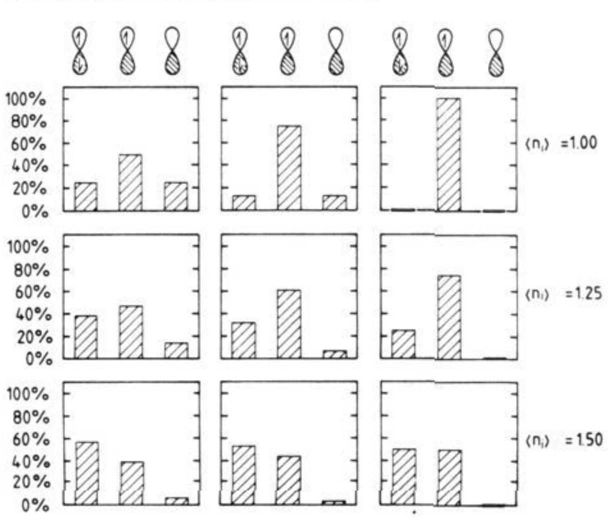

Figure 3. Atomic occupation probabilities $P_i(n)$ (n = 0, 1, or 2) as a function of the π electron density $\langle n_i \rangle$ and the strength of electronic correlations measured in terms of the correlation-strength parameter Δ_i. The atomic configurations are given in the first row. The considered π densities $\langle n_i \rangle$ amount to 1.00, 1.25, and 1.50 (from top to bottom). The Δ_i elements employed in Figure 3 are 0, $0.5\Delta_i^{\max}$, and $\Delta_i^{\max}$ (from left to right), i.e., left column symbolizes the independent-particle results.

of perfect correlations corresponding to the maximum suppression of anionic configurations. $\Delta_i^{\max}$ depends only on the atomic π electron density $\langle n_i \rangle$ and is defined in eq 2.4. The simple origin of this behavior will be clarified below. Equation 2.4 indicates

$$\Delta_i^{\max} = \frac{\langle n_i \rangle}{2 - \langle n_i \rangle} \quad \text{for } 0 \le \langle n_i \rangle \lesssim 1.0$$

$$\Delta_i^{\max} = \frac{2 - \langle n_i \rangle}{\langle n_i \rangle} \quad \text{for } 1 \le \langle n_i \rangle \lesssim 2.0 \qquad (2.4)$$

that the correlation-strength parameter has the largest width in alternant hydrocarbons with $\langle n_i \rangle = 1.0$ at any π center leading to an upper Δ_i boundary of $\Delta_i^{\max} = 1.0$. In nonalternant systems with $\langle n_i \rangle \neq 1.0$ the width in the accessible Δ_i range is reduced. This effect increases with increasing $\langle n_i \rangle$ deviations from the $\langle n_i \rangle = 1.0$ limit.

On the basis of the above correlation-strength parameter Δ_i it has been possible to arrange chemical bonds into characteristic subgroups; see refs 20–23. The Δ_i elements allow for a straightforward determination of the different atomic occupancies in the correlated ground state; the corresponding configurations are shown schematically in Figure 3. $P_i(2)$ stands for the anionic configuration (i.e., double occupancy) at center i and $P_i(0)$ for the cationic counterpart (i.e., empty occupancy). $P_i(1)$ is the single occupancy at center i and simulates a "covalent (sub)structure". With increasing strength of the electron–electron repulsion, the $P_i(2)$ configurations become more and more unfavorable. Any correlation in the motion of the electrons must lead to a suppression of $P_i(2)$. $P_i(2)$ and $P_i(1)$ are defined in eqs 2.5 and 2.6 in terms of the π density $\langle n_i \rangle$ and the Δ_i parameter. $P_i(0)$ is given in eq 2.7. The latter relation follows simply from the normalization condition. The single-determinantal values for the respective

$$P_i(2) = 0.25\langle n_i \rangle[\langle n_i \rangle - (2 - \langle n_i \rangle)\Delta_i] \qquad (2.5)$$

$$P_i(1) = \langle n_i \rangle(1 - 0.5\langle n_i \rangle)(1 + 0.5\Delta_i) \qquad (2.6)$$

$$P_i(0) = 1 - P_i(2) - P_i(1) \qquad (2.7)$$

atomic occupancies are simply derived by setting $\Delta_i = 0$ in the above equations.

A schematic representation emphasizing the interrelation between the strength of π electronic correlations and the π density $\langle n_i \rangle$, on one side, and the atomic occupation probabilities $P_i(n)$, on the other, is given in Figure 3. From top to bottom we have assumed π electron densities $\langle n_i \rangle$ of 1.0, 1.25, and 1.5, respectively. In the left-hand column the independent-particle values of the $P_i(n)$ are collected. On the right-hand side the pendants in the limit of perfect π correlations $\Delta_i^{\max}$ are displayed. The associated charge fluctuations are abbreviated by $\langle(\Delta n_i^2)\rangle_{\min}$ to symbolize that they correspond to the absolute minimum. The $P_i(n)$ numbers in the middle column refer to $\Delta_i = 0.5\Delta_i^{\max}$, i.e., 50% of the maximum accessible correlations. Figure 3 is simple to interpret. As already mentioned, electronic correlations lead to a suppression of π configurations with atomic double occupancies. This suppression increases with the strength of electronic correlations, which is generally given by the ratio between the π electron interaction and the kinetic energy of the electrons. In chemistry the latter matrix element is frequently called the "resonance integral", Hückel β. In the physical community the label "hopping integral" is widely employed. The upper right diagram in Figure 3 indicates that complete suppression of double occupancy $P_i(2)$ is only possible in neutral alternant hydrocarbons in the limit of perfect π correlations. The charge fluctuations are completely suppressed here, and the electrons are atomically localized. Residual fluctuations in the perfectly correlated regime also are possible in nonalternant systems at π centers with densities $\langle n_i \rangle \neq 1.0$. For a π density of 1.5, perfect correlations lead to 50% probabilities of $P_i(1)$ and $P_i(2)$ with complete suppression of the empty configuration. The alternancy symmetry encountered in alternant hydrocarbons leads furthermore to the identity $P_i(2) = P_i(0)$ between double and empty occupancy.

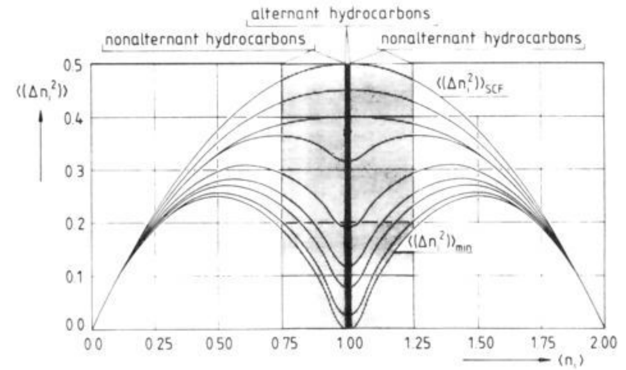

Figure 4. Charge fluctuations at the ith π center or any center built by a single atomic orbital as a function of the electron density $\langle n_i \rangle$ and the ratio X between the electron–electron interaction and the kinetic energy. The topmost curve corresponds to the fluctuations in the one-determinantal limit $|\psi_{SCF}\rangle$ and the lowest one to the minimum fluctuations $\langle(\Delta n_i^2)\rangle_{\min}$ for perfect π electron correlations. The X factors between these two boundary curves confined to the correlated ground state $|\psi_0\rangle$ amount to 0.2, 0.4, 0.8, 1.6, 2.4, 3.2, and 4.0, respectively; from top to bottom. The charge fluctuations accessible in alternant π systems with $\langle n_i \rangle = 1.0$ at any π center i are symbolized by the full vertical line. The shaded area in the domain of the nonalternant molecules symbolizes approximately the width in the π electron density $\langle n_i \rangle$ realized in conventional nonalternant hydrocarbons. For densities $\langle n_i \rangle < 1.0$ there exist even some centers outside the given $\langle n_i \rangle$ interval.

In Figure 4 we have portrayed again the interrelation between electronic localization properties, now measured by the mean-square deviations of the charge $\langle(\Delta n_i^2)\rangle$, the strength of electronic correlations, and the corresponding π density $\langle n_i \rangle$. The magnitude of the many-particle interactions is described by the parameter X, which is the ratio between the electron–electron repulsion and the resonance integral β. The $\langle(\Delta n_i^2)\rangle$ curves refer to the correlated ground state and are based on the exact treatment of a 2 × 2 problem for the correlations.[39,40] The solution is valid for any strength of the π electronic correlations, i.e., any magnitude of X. The two marginal dispersions correspond to the single-determinantal fluctuations (outermost curve) and the limit of perfect correlations (innermost one). The charge fluctuations allowed in alternant π systems are confined to the center of the $\langle(\Delta n_i^2)\rangle$ diagram. Figure 4 indicates immediately that the charge fluctuations in the one-determinantal limit are identical at all π

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centers of alternant molecules; in this case one has a common $\langle(\Delta n_i^2)\rangle_{SCF} = 0.5$. The Δ_i parameters reflect only modifications in the localization properties of the π electrons due to many-particle interactions. Characteristic π densities encountered in nonalternant molecules are indicated by the hatched area. The diagram visualizes in a transparent form the charge dependence of the π electron delocalization and the necessity to have densities $\langle n_i \rangle \neq 1.0$ in the perfectly correlated regime to conserve π electron delocalization.

As we have already mentioned the correlation-strength parameter Δ_i depends on the π electron density $\langle n_i \rangle$. To have a many-particle index with the same width for any $\langle n_i \rangle$ value we define a "density invariant" counterpart of Δ_i by dividing Δ_i by the allowed maximum $\Delta_i^{\max}$. As indicated in eq 2.2 $\Delta_i^{\max}$ depends only on the respective π density $\langle n_i \rangle$.

$$\Sigma_i = \Delta_i / \Delta_i^{\max} \tag{2.8}$$

For alternant hydrocarbons the relation $\Sigma_i = \Delta_i$ ($\Delta_i^{\max} = 1.0$) does of course hold. Σ_i has allowed values between 0 and 1.0. The former boundary indicates again the validity of the independent-particle picture, and $\Sigma_i = 1.0$ stands for perfect π electronic correlations.

To derive the many-particle results schematically shown in Figures 3 and 4 as well as the computational data presented in the subsequent sections we have employed the method of the local approach (LA).[27,28] For the above results, elements of the bond orbital approximation (BOA) have been used.[41,42] The LA has the large advantage that the local nature of correlation processes is explicitly taken into account. This allows for a sizeable reduction in the computational effort. The theoretical background of the LA in combination with ab initio basis sets[28,43,44] and semiempirical model Hamiltonians[8,20-23,41] is well documented in the literature. For detailed information we refer the reader to the corresponding references. In the following we give only a concise summary of the numerical conditions adopted in the subsequent model calculations. The matrix elements entering the suggested many-particle description are summarized in the Appendix. To simplify the determination of the correlated π electronic ground state $|\psi_0\rangle$ we have used a linearized version of the LA which corresponds to a CEPA-type (coupled electron pair approximation) formulation[45] of the LA. This setup is strictly valid only for not too strong electronic correlations; its applicability has been studied recently by one of us.[46] As an additional approximation in the correlation part of our investigation we have restricted the virtual two-particle excitations of the π electrons to the leading intraorbital ones. The simplifications and decouplings to derive the $\langle(\Delta n_i^2)\rangle_{corr}$ elements have been described in our recent work.[24]

The above correlation-strength parameters Δ_i and Σ_i are determined by the ratio of matrix elements mapping the two-electron interaction beyond single-determinantal wave functions of the SCF type and the kinetic (resonance) energy. Chemically the corresponding numerator measures the stiffness of the π electronic ground-state wave function. The denominator represents kinetic excitations from the occupied to the unoccupied π orbitals. The π correlation energy E_{corr}, however, depends on the interaction squared divided by the kinetic energy part. For further details see refs 24–26. In the present degree of sophistication the total (π) correlation energy E_{corr} can be given as a sum of individual pair elements $E_{corr,i}$, i.e., $E_{corr} = \Sigma_i E_{corr,i}$.

Next we have to define the matrix elements in the many-body part of our investigation together with the underlying single-determinantal precursor. To reduce the computational expenditure as much as possible we have adopted a simple Hückel-type Hamiltonian in an ab initio basis to derive the corresponding ground state $|\psi_{SCF}\rangle$. The only required input element from this step is the first-order density matrix. For alternant π systems the latter is completely defined by symmetry. The adoption of a Hückel-type operator is therefore sufficient for these π networks. Our previous computational experience has furthermore shown that the employed one-electron Hamiltonian with kinetic integrals calculated in a Slater basis also allows for the determination of reliable density matrices in nonalternant hydrocarbons.[26] To evaluate the two-electron interaction in the LA we have used a matrix defined by so-called Hartree–Fock hopping elements F_{ik}.[41] The latter are given by the Hückel-type "resonance integral" t_{ik} minus the product of 0.5 times the first-order density matrix and the two-electron interaction. In the definition of the Hückel-type matrix F_{ik} a strict nearest-neighbor approximation has been used. The different one- and two-electron integrals have been calculated ab initio in a single-ζ Slater-type basis.[47] Burns' rules[48] have been adopted to estimate the corresponding screening coefficient. Use of a minimal basis of π AOs restricts the many-body calculations to so-called interatomic correlations; for their definition see refs 8, 42, and 49. All matrix elements have been determined in the zero differential overlap (ZDO) approximation to conserve the alternancy symmetry in the orbital wave functions. The validity of the present simple setup has been discussed in detail in our previous contributions.[25,26] Finally we should mention that all calculations have been performed on a conventional personal computer. Determination of the correlated ground state $|\psi_0\rangle$ in π systems containing more than 60 carbon centers is possible without any difficulty. The time required for the many-body part always has been less than the time requirement to determine $|\psi_{SCF}\rangle$.

Table I. Characteristic Values for the Correlation-Strength Parameter Δ_{av} in Different Types of Chemical Bonds[a]

type of bond	second-row elements E	third-row element E
EE σ bonds	0.18–0.32	0.13–0.26
EE σ in double bonds	0.14 ± 0.02	0.12 ± 0.02
EE σ in triple bonds	0.10 ± 0.01	0.09 ± 0.01
EE π double bonds	0.49 ± 0.02	0.62 ± 0.03
EE π triple bonds	0.27 ± 0.02	0.42 ± 0.02
EH σ bonds	0.18 ± 0.02	0.20 ± 0.02
ME σ bonds	0.40–0.80	
synthetic metals	>0.80	

[a] E is a main-group element, H abbreviates hydrogen, and M a 3d transition metal. The computational results have been adopted from refs 20, 21, 50, and 51.

3. π Electronic Localization Properties in Alternant and Nonalternant Compounds

To derive values for the charge fluctuations $\langle(\Delta n_{av}^2)\rangle_{corr}$ and correlation-strength parameters Δ_{av}, which are characteristic for different types of π centers i, we have studied more than 100 model systems. The most important nonalternant molecules have been collected already in Figure 1. In the family of alternant hydrocarbons, we have considered linear polyenes, monocyclic rings of the $4n$ and $4n + 2$ type (n = number of carbon centers), as well as many other linear and polycyclic model systems. The index av in this section always represents averaging over a larger number of topologically equivalent π sites in different molecules. The subsequent data have been derived for structures with a common CC bond length of 140 pm. Bond length alternation is considered in the following two sections. Our model calculations have shown that the charge fluctuations $\langle(\Delta n_{av}^2)\rangle_{corr}$ and therefore also the correlation-strength parameters Δ_{av} and Σ_{av} are highly site-specific. They are determined by the topology of the corresponding π center, i.e., the number of bonded neighbors, and the bonding properties

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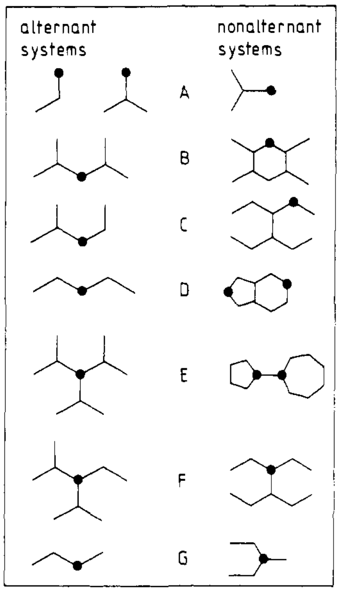

Figure 5. Topology of the π centers in alternant (left-hand column) and nonalternant (right-hand column) hydrocarbons which can be subdivided into characteristic subclasses A to G according to their charge fluctuations $\langle(\Delta n_{av}^2)\rangle_{corr}$ and correlation-strength parameters Δ_{av}. The reference center has been labeled by a filled dot.

realized at the direct neighbors of the "reference center".

The present π results become more transparent if we compare them with correlation-strength parameters Δ_{av} which have been derived previously by one of us for different types of chemical bonds.[20,21] In Table I Δ_{av} numbers for π and σ interactions are summarized. It is seen that the different types of bonds fall into characteristic classes according to their many-particle interactions. The given Δ_{av} numbers have been derived prevailingly for two-center, two-electron bonds. Rather weakly correlated are σ bonds formed by main-group atoms. Decreasing bond length allows for a reduction of the correlation strength, i.e., enhancement of the charge fluctuations = enhancement of interatomic sharing. The Δ_{av} numbers for σ bonding are reduced when going from second-row combinations to third-row ones. Table I indicates also that the π electrons in localized double/triple bonds are less delocalized and thus more strongly correlated than the associated σ electrons. The relative sequence in the correlation strength between second- and third-row elements is changed when going from σ bonds to π ones. The rather high correlation strength encountered for π bonds formed by third-row atoms is a simple many-particle demonstration of the remarkable instability of double/triple bonds formed by heavier main-group atoms. Note that there is a simple inverse relation between the strength of a chemical bond and the size of the associated Δ_{av} parameters. In the last line of Table I the rather strong correlations realized in the organic metals (intermolecular coupling) are quoted.[50,51]

Model calculations on alternant and nonalternant π systems have demonstrated that a subclassification as suggested in Table I is even accessible in the π subspace of hydrocarbons. The π centers can be divided into characteristic classes on the basis of their charge fluctuations and correlation-strength parameters. They are portrayed in Figure 5. The averaged charge fluctuations and Δ_{av} elements for the corresponding π atoms are summarized in Figure 6. The latter diagram contains an interesting result. Depending on the type of the π center, the localization properties and correlation-strength parameters cover the same width as indicated in Table I for different element combinations and bonds (i.e., σ versus π interactions). In the studied π systems the magnitude of the $\langle(\Delta n_{av}^2)\rangle_{corr}$ and Δ_{av} parameters is largely determined by the position/topology of or around the corresponding carbon center.

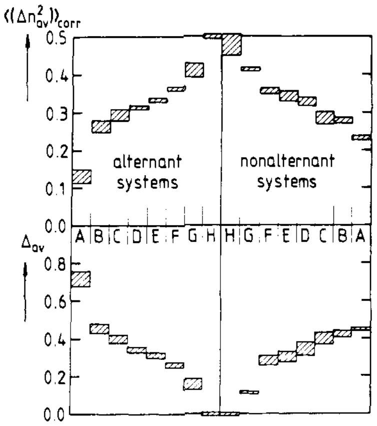

Figure 6. Charge fluctuations $\langle(\Delta n_{av}^2)\rangle_{corr}$ and correlation-strength parameters Δ_{av} at the π centers belonging to the classes A to G of Figure 5 in alternant and nonalternant π systems. H symbolizes the SCF/independent-particle limit. The width encountered here for nonalternant materials is caused by the possible scattering in the π density $\langle n_i \rangle$.

Terminal atoms are strong localization centers, where the charge fluctuations are sizeably suppressed (class A atoms). Next in the scale suggested in Figures 5 and 6 we predict π centers bonded to sites which always have three neighbors (type B and also C atoms). Our data indicate that the smaller charge fluctuations at the "reference center" allow for increasing π delocalization at the neighbors. This kind of "alternation pattern" is found throughout in the collection of Figure 6, i.e., π centers with a rather strong atomic electron density localization are bonded to centers with enhanced fluctuations. See the couple A/G, where this effect is maximized.

Intermediate between the strong localization centers of type A and type G atoms approaching the delocalized "free-electron limit" are sites belonging to the classes B, C, and D always bonded to two neighbors and type E and F functions which have three neighbors. The interatomic sharing is enhanced from the B, C, and D centers to the E and F ones. We believe that the topology dependence of charge fluctuations and correlation-strength parameters provides a microscopic explanation for the success of graph theory approaches to explain the stability of hydrocarbon π systems.[52,53] Note that increasing localization of the (π) electrons is equivalent with decreasing stability. The 1:1 correspondence between elements of graph theory and the present atomic many-body probes $\langle(\Delta n_{av}^2)\rangle_{corr}$ and Δ_{av} is of course a result of the local nature of electronic correlation processes. They are therefore a function of the topology of a given (π) center and its neighbor relations. We believe that such many-body information is hidden in conventional correlation models of molecular quantum chemistry.

The theoretical results given in Figure 6 can be summarized as follows: With rather sparse exceptions (i.e., π centers of class G) π electrons in hydrocarbon compounds are sizeably localized and by no means in the vicinity of the "free-electron" limit. This label has been used to indicate the validity of a single-determinantal description for the electronic wave function. Comparison with the data of Table I indicates that even the π electrons in extended polyenes and $4n + 2$ Hückel rings are more strongly correlated and therefore also more strongly atomically localized than σ electrons in bonds formed by main-group atoms.

The smaller width in the Δ_{av} numbers for nonalternant molecules in comparison to the alternant ones is a result of the alternancy symmetry violation in the former networks. $\langle n_i \rangle \neq 1.0$ restricts the accessible channels for π correlations. Numerically this effect is expressed by eq 2.4. The reduction in the width of the $\langle(\Delta n_i^2)\rangle_{corr}$ numbers in nonalternant systems should become intelligible by inspection of Figure 4. For weaker correlations

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deviations from the $\langle n_i \rangle = 1.0$ case result in an attenuation of the mean-square deviations of the (π) charge. In the limit of strong correlations the charge fluctuations are, however, less efficiently suppressed if $\langle n_i \rangle$ deviates from 1.0. Finally we should mention that the net width of the $\langle (\Delta n_{av}^2) \rangle_{corr}$ and Δ_{av} distributions in Figure 6 is slightly reduced when adopting a many-body formalism beyond the linearized LA variant; the general trends are, however, not changed.

4. π Electronic Fluctuations and Many-Particle Effects in Nonalternant Systems; Bond Length Alternation in Pentalene

We begin this section with an analysis of the charge fluctuations and correlation-strength parameters Δ_i and Σ_i in pentalene as a function of the bond length alternation δ, which measures the deviation in the CC bond length from 140 pm. Pentalenes are highly reactive molecules. Synthetically feasible derivatives require steric protection or electronic manipulation.[32] It is well-known that all characterized pentalene derivatives show remarkable bond length alternation.[32] In the chemical community this behavior is usually equated with a localization of the π electrons. The principal error in this interpretation is demonstrated in Figure 7, where we give the charge fluctuations of the π electrons together with the Σ_i elements as a function of δ. Below the upper two diagrams the mean value of $\langle (\Delta n_i^2) \rangle_{corr}$ and the two localization parameters Δ_i and Σ_i are shown, i.e., $\langle (\Delta n_m^2) \rangle_{corr}$, Δ_m, and Σ_m. Analysis of the many-particle ground state $|\psi_0\rangle$ indicates that the electronic correlations are remarkably strong at the $C_1 = C_3 = C_4 = C_6$ atoms of pentalene. The respective π density $\langle n_i \rangle$, however, allows for an enhancement of the fluctuations/delocalization.

Figure 7 demonstrates impressively that the charge fluctuations in pentalene are enhanced with increasing bond alternation δ. This effect is operative at $C_1 = C_4$ as well as at the bridging centers $C_7 = C_8$. The mean value of the density-dependent localization parameters Δ_m is only weakly δ-dependent. The invariant pendant Σ_m, however, is reduced with increasing bond alternation indicating that the correlations cover then less of the accessible maximum boundary. The latter dependence is prevailingly a π density effect. With increasing bond alternation the charge separation/imbalance between the π centers is attenuated; see bottom diagram in Figure 7. The $\langle n_i \rangle$ numbers approach the limit of an even π electron distribution. The averaged enhancement of the fluctuations with increasing δ is clearly seen in Figure 7. We believe that the increasing mean-square deviations of the π charge with increasing alternation are the microscopic origin of the distortive nature of hydrocarbon π frameworks. Comprehensive calculations already have shown impressively that π ribbons of Hückel rings are generally distortive.[12,13] The pentalene results can be summarized as follows: The key quantity allowing for the enhancement of the fluctuations is the bond alternation. A possible charge control is here overcompensated. In the above context it is opportune to comment on the widely employed mutual interconnection between bond length alternation and a falsely assumed increasing electronic localization. Whenever bond alternation takes place in the ground state, it leads to an energetic stabilization. For covalent bonds it has been proven that the corresponding energy gain is caused by a reduction of the kinetic energy, which becomes possible by a better delocalization of the electrons.[54] To summarize; π networks are distortive because bond length alternation is accompanied by increasing atomic π electron density delocalization.

The charge fluctuations and correlation-strength parameters in the studied nonalternant systems have been anticipated already in the last section; see Figure 6. The fluctuations $\langle (\Delta n_i^2) \rangle_{corr}$ are confined to an interval between ca. 0.24 (terminal π centers) and 0.42 (type G atoms). Most of the $\langle (\Delta n_i^2) \rangle_{corr}$ elements are found between 0.27 and 0.35. In connection with this width the charge fluctuations in a localized π bond deserve some interest. For ethylene at a hypothetical CC bond length of 140 pm we predict $\langle (\Delta n_i^2) \rangle_{corr} = 0.281$, $\Delta_i = 0.438$. These numbers are in sufficient agreement with the data reviewed in Table I. The latter couple can be considered as characteristic elements for π electrons in localized bonds. The many-particle indices derived for nonalternant π networks indicate thus the presence of π centers whose atomic electron density localization exceeds the one appearing in two-center, two-electron bonds.

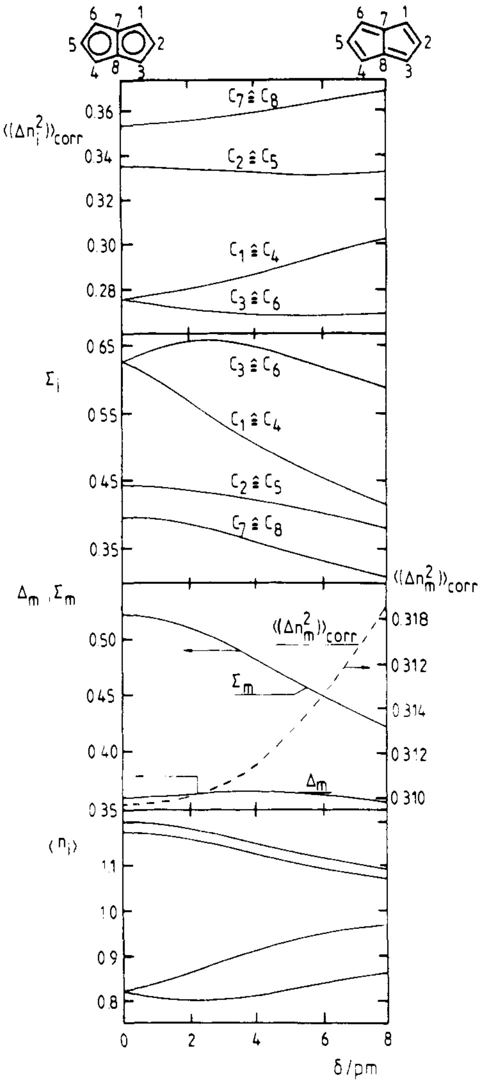

Figure 7. Variation of the charge fluctuations $\langle (\Delta n_i^2) \rangle_{corr}$ and normalized correlation-strength parameter Σ_i in pentalene as a function of the bond length alternation δ; upper two diagrams. The third representation down gives the mean values of the charge fluctuations $\langle (\Delta n_m^2) \rangle_{corr}$ and the two correlation-strength parameters Δ_m, Σ_m. In the lowest plot the δ dependence of the atomic π density $\langle n_i \rangle$ is shown. The four curves correspond to the following atom pairs: $C_7 = C_8$, $C_2 = C_5$, $C_1 = C_4$, $C_3 = C_6$ (from top to bottom). The atomic numbering scheme is given in the top line. For the equidistant pentalene conformation a common CC bond length of 140 pm has been employed. The C_7C_8 bond has been kept constant in the transition from the D_{2h} to the alternating C_{2h} structure.

Analysis of the computational results derived for the systems collected in Figure 1 demonstrates the formation of characteristic electronic substructures; see Figure 8. It is common to the polycycles 8, 9, 10, and 11, e.g., that they contain the azulene fragment, criterion $\langle (\Delta n_i^2) \rangle_{corr}$, and Δ_i elements. Possible $4n$ structures in 8 (=pentalene) or 9 (=heptalene) are not realized. For a discussion of such "memory effects" in alternant structures see our recent contribution.[25]

Perhaps the most interesting results that can be extracted from the model calculations on the selected nonalternant π systems is collected in Table II. Here we give the mean value $\langle (\Delta n_m^2) \rangle_{corr}$ of the charge fluctuations and the two correlation-strength parameters Δ_m and Σ_m for each of the π systems. For convenience we have added the corresponding elements for benzene, often

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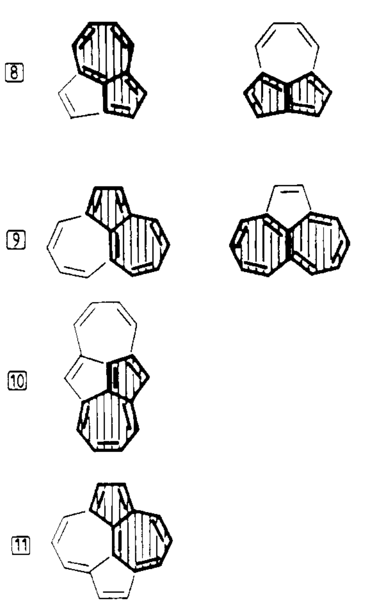

Figure 8. Possible fragmentations in the nonalternant systems 8, 9, 10, and 11 leading to simpler substructures in the corresponding molecules. The hatched area symbolizes a "connected" π unit; thin lines represent disconnections.

Table II. Mean Values of the Correlation-Strength Parameters Σ_i and Δ_i ($=\Sigma_m$ and Δ_m) as Well as the π Fluctuations $\langle(\Delta n_i^2)\rangle_{corr} = \langle(\Delta n_m^2)\rangle_{corr}$ for the Nonalternant π Systems 1–11[a]

system	$\langle(\Delta n_m^2)\rangle_{corr}$	Σ_m	Δ_m	γ_{in}	status
1	0.312	0.500	0.360	0.467	u
2	0.307	0.446	0.382	0.412	u
3	0.320	0.457	0.348	0.385	s
4	0.309	0.518	0.359	0.437	u
5	0.320	0.428	0.352	0.387	s
6	0.316	0.459	0.359	0.407	u
7	0.317	0.443	0.356	0.433	u
8	0.322	0.428	0.348	0.392	s
9	0.321	0.421	0.352	0.396	s
10	0.323	0.410	0.350	0.404	s
11	0.324	0.413	0.347	0.391	s
C_6H_6	0.323	0.354	0.354	0.354	

[a] Additionally we have given an "instability index" γ_{in} which is the sum of Δ_m and the mean-square deviation of the Δ_i. In the last column we give the experimental status of the considered nonalternant hydrocarbons. s stands for stable and u for unstable, highly reactive systems. We have used refs 29–38 for the experimental work. For convenience we have given the benzene data at the bottom of the table.

considered as the "standard example" for a highly delocalized π compound. In the table we define also an instability index γ_{in} for the nonalternant molecules. γ_{in} has been designed on the basis of chemical intuition. The corresponding element is given by the mean value of the correlation-strength parameter Δ_m plus the associated standard deviation σ_i; i.e., $\gamma_{in} = \Delta_m + \sigma_i$. The mean value of the localization parameter measures the net π electron localization in the system and σ_i the influence of individual localization centers reducing the stability of a system. High stabilities of π compounds require small γ_{in} numbers and vice versa. The γ_{in} elements will be correlated with the present experimental status of the systems 1 to 11. The index s in Table II abbreviates stable and u a rather unstable system. The averaged fluctuations $\langle(\Delta n_m^2)\rangle_{corr}$ in Table II indicate roughly comparable net π delocalization in all compounds. The atomic electron density delocalization in pentalene, e.g., differs not strongly from the π delocalization in benzene, if delocalization/localization is measured in terms of the charge fluctuations.

The Σ_m elements in Table II indicate, however, large differences between the nonalternant models and benzene. Although the density-dependent correlation-strength parameters Δ_m are found in a rather narrow window, the Σ_m elements show larger scattering. This indicates that the π electron delocalization in nonalternant systems is supported by the uneven charge distribution. As a result the π electron correlations in the nonalternant models cover a larger part of the accessible maximum ones; i.e., see the large Σ_m elements. Comparison of the suggested instability parameters γ_{in} with the present experimental status of the π systems demonstrates that γ_{in} reflects the relative stability of the selected systems. The stable compounds 3, 5, 9, 10, and 11 have throughout the smallest instability parameters γ_{in}. This number is enhanced in the highly reactive unstable nonalternant hydrocarbons 1, 2, 4, 6, and 7. Finally we should mention that γ_{in} is determined by local atomic properties; it does not depend on any definition of reference structures as encountered in traditional models to define resonance energies as a stability index of π systems. For further theoretical details concerning the new instability element γ_{in} we refer the reader to ref 24.

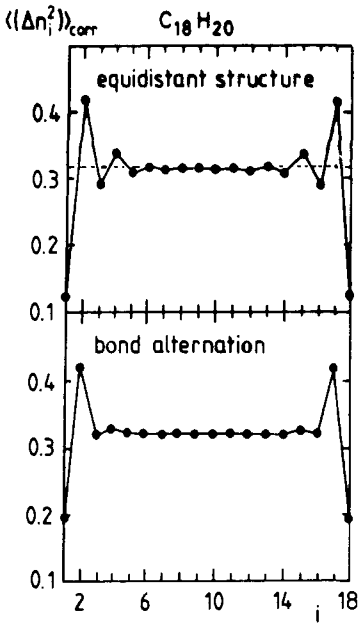

Figure 9. Charge fluctuations $\langle(\Delta n_i^2)\rangle_{corr}$ at the π centers in the nonalternating ($\delta = 0$) and alternating ($\delta = 8$ pm) $C_{18}H_{20}$ polyene. The dotted horizontal line in the upper diagram indicates the charge fluctuations in 18 annulene. We have used the standard enumeration of the π centers.

5. Bond Length Alternation in Cyclic and Linear Alternant Hydrocarbons

A large part in the subsequent discussion is reserved for the analysis of the π electron localization parameters $\langle(\Delta n_i^2)\rangle_{corr}$ and $\Delta_i = \Sigma_i$ as a function of the bond length alternation δ in linear and cyclic alternant hydrocarbons. The energetics of this process in the SCF/independent-particle picture has been studied in detail in the past three decades.[10,55,56] For cyclic systems simple analytic formulas can be given. With an increasing number n of π centers the monocycles become unstable with respect to bond alternation, i.e., dimerization in the language of solid-state theory. For the orbitally nondegenerate $4n + 2$ Hückel rings the SCF energy goes as $4f(n)\delta^2$ with $f(n)$ denoting a size-dependent prefactor increasing logarithmically with n; $f(n)$ diverges with $n \rightarrow \infty$. For the Jahn–Teller distortive $4n$ anti-Hückel rings an energy reduction per π center following a $f'(n)|\delta|$ law is observed. In contrast to the Hückel rings $f'(n)$ is a decreasing function of the ring dimension. With increasing n the fundamental instability of the monocycles is attenuated. On the basis of these independent-particle results we may also expect that the δ dependence of the many-body results is determined by the ring size, and orbital degeneracy = gap behavior.

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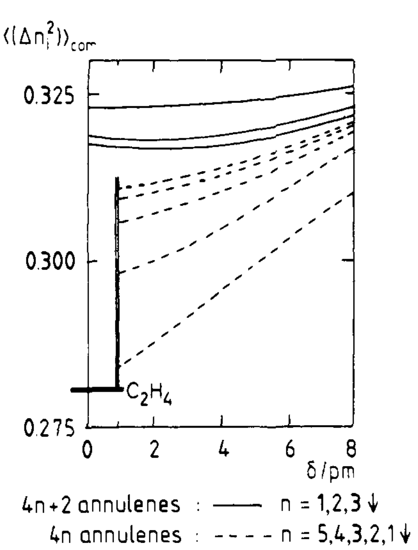

Figure 10. Charge fluctuations $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ in $4n + 2$ Hückel and $4n$ anti-Hückel annulenes as a function of the bond length alternation δ. With increasing δ all curves converge to a roughly common value. For the orbitally degenerate $4n$ rings we have adopted $\delta = 1$ pm as a starting point to open a gap between occupied and unoccupied π orbitals. On the lower left we have indicated the charge fluctuations realized at the π centers of a localized CC π bond; internuclear separation 140 pm.

Before analyzing cyclic π systems with only one degree of freedom we discuss the charge fluctuations in the equidistant and alternating structure of the $C_{18}H_{20}$ polyene. The atomic fluctuations $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ are shown schematically in Figure 9. The adopted bond length alternation in the lower diagram amounts to 8 pm. It is seen that alternating CC bonds cause an enhancement of the π atomic electron density delocalization. Bond length alternation in the $C_{18}H_{20}$ polyene attenuates the oscillations in the $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ spectrum. Figure 9 demonstrates that the largest response in the $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ numbers as a function of bond alternation is found at the end atoms where the width in the $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ distribution is sizeably reduced. At the inner C atoms bond alternation leads throughout to an enhancement of the fluctuations; see below. This analysis demonstrates that bond alternation renders the possibility to enhance the charge fluctuations of the π electrons. This is found in any of the studied alternant materials.

In the model calculations on the π monocycles we have always assumed D_{nh} and $D_{nh/2}$ geometries for the nonalternating and alternating forms. Of course these structures are not realized in larger ring systems. For the present analysis the simplification is, however, sufficient as the considered many-particle indices are prevailingly topologic quantities, which are largely independent on finer details of the molecular geometry.

In Figure 10 we have displayed the variation of the π charge fluctuations $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ in monocyclic hydrocarbons as a function of the bond length alternation δ. We have considered $4n + 2$ as well as $4n$ rings in the numerical simulation. The associated Δ_i curves for both classes of compounds are portrayed in Figure 11 where we have also given the Δ_i elements calculated for polyenes. The $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ variations in Figure 10 indicate the following: bond length alternation in π monocycles leads throughout to enlarged π electron delocalization. For the $4n + 2$ Hückel rings this effect is less pronounced than in the $4n$ anti-Hückel frames. In the considered δ interval of 8 pm the $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ curves of the $4n + 2$ systems have a minimum at ca. 4 pm corresponding to maximum atomic electron density localization. For $\delta > 4$ pm the fluctuations increase again. The magnitude of $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ in the $4n + 2$ annulenes is reduced with increasing ring size; i.e., the π electrons in benzene are more delocalized than the π electrons in larger rings. This information is of course already feasible in the independent-particle picture, average kinetic energy argument.

In the neighborhood of the equidistant D_{nh} structure the π electrons of cyclobutadiene show localization properties that resemble closely the one of ethylene (CC bond length of 140 pm assumed). Bond alternation in not only C_4H_4, but also other $4n$ annulenes, causes rather strong enhancements in the $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ numbers. Figure 10 demonstrates that the δ-dependent enhancement of $\langle(\Delta n_i^2)\rangle_{\text{corr}}$/reduction of Δ_i is simply related to size and orbital gap of the corresponding π rings. Reduction of the gap between occupied and virtual MOs leads to a stronger atomic localization of the π electrons and thus also to stronger electronic correlations. Note that the $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ and Δ_i curves for all considered molecules saturate roughly to common boundary values. With increasing n the latter limits are approached from different directions in the case of the $4n + 2$ and $4n$ monocycles. The $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ boundary is reached from above in the $4n + 2$ series and from below in the $4n$ one (increasing n); vice versa for the correlation-strength parameter Δ_i.

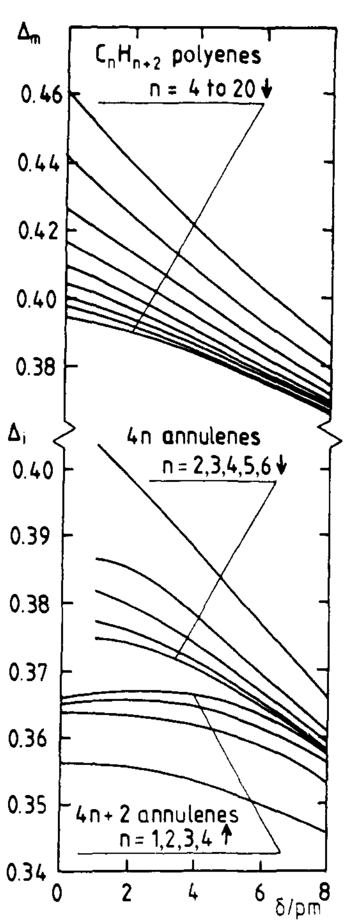

Figure 11. Correlation-strength parameter Δ_i in $4n + 2$ and $4n$ hydrocarbon monocycles as a function of the bond alternation δ (bottom diagram); see legend Figure 10. In the upper half we have given the mean value of the correlation-strength parameter Δ_m in linear C_nH_{n+2} polyenes as a function of δ. Alternation is here coupled to a net length reduction in the molecule, which is attenuated with increasing chain length. The number of carbon centers in the three families of π systems is always indicated. n increases from top to bottom in the polyenes and anti-Hückel rings; vice versa in the Hückel monocycles.

The $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ curves in Figure 10 demonstrate immediately that a bond length alternation up to 8 pm in annulenes does not support any electronic localization in the π frame. The resulting fluctuations are sizeably larger than those realized in a localized isolated double bond. The Δ_i curves collected in Figure 11 complete the information from Figure 10. The two diagrams show the simple mirror symmetry between fluctuations and the correlation-strength parameters Δ_i in alternant materials. This symmetry is violated in nonalternant hydrocarbons.

The δ dependence of the correlation-strength parameter Δ_m in polyenes is given on the top of Figure 11; m stands for the corresponding mean value averaged over all π centers. In contrast to the annulenes, bond alternation in polyenes is coupled to a net length reduction. Again we find that bond alternation allows for increasing fluctuations, i.e., decreasing electronic correlations. The

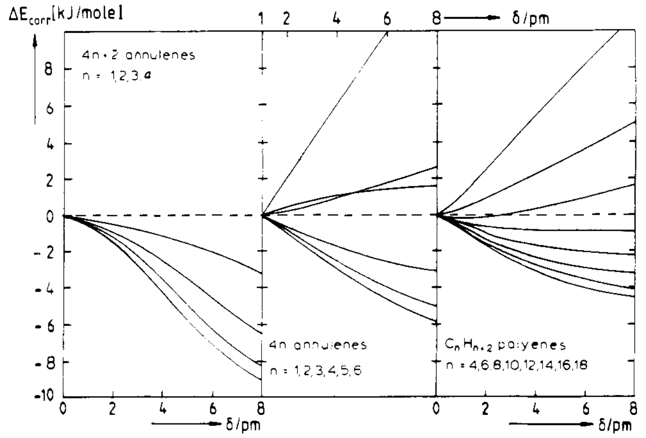

Figure 12. Modulation of the π correlation energy ΔE_{corr} in the $4n + 2$ and $4n$ monocycles and C_nH_{n+2} polyenes as a function of the bond length alternation δ; from left to right. Normalization always refers to one electron pair. The polyene data correspond to a mean value averaged over all π electrons. In the Hückel rings and polyenes the equidistant conformation has been employed to fix the reference energy. For the $4n$ perimeters $\delta = 1$ pm has been selected as a reference point. The topmost curve in each diagram corresponds always to the smallest n value, which is enlarged from top to bottom.

gradient of the Δ_i curves is even steeper than in the $4n$ annulenes. To a large part this behavior can traced back to the net length reduction accompanying the bond alternation.

Guided by some traditional pictures in quantum chemistry one might expect that the magnitude of the π correlation energy $|E_{corr}|$ in the above families of alternant hydrocarbons is reduced with increasing bond alternation. This expectation has the following origin. As emphasized in section 2, correlations are frequently equated with increasing localization of the bonding electrons at the atomic sites. Therefore one may expect that increasing charge fluctuations implies decreasing $|E_{corr}|$ numbers. However, this 1:1 correspondence is strictly valid in two-center bonds, where increasing intermolecular separation is indeed coupled to a suppression of the fluctuations and an increasing weight of doubly excited Slater determinants in the correlated ground state $|\psi_0\rangle$. Under these conditions the correlation energy is indeed enhanced. The nonvalidity of this extrapolation in larger molecules becomes clear by analyzing Figure 12. Here we have displayed the normalized π correlation energy ΔE_{corr} of the $4n + 2$ annulenes, $4n$ rings, and C_nH_{n+2} polyenes (from left to right) as a function of the bond alternation δ. Normalization refers always to one pair of π electrons.

$|E_{corr}|$ is an increasing function of δ in all $4n + 2$ Hückel rings. The gradient of the $|\Delta E_{corr}|$ curves becomes steeper with increasing dimension of the π perimeter. Interatomic π correlations are one driving force for the bond alternation in the corresponding systems. The correlation influence on the alternation properties of $4n$ rings and linear polyenes depends on the number of carbon atoms. For smaller n the electronic correlations suppress the alternation of the π bonds. The gradient of the $|\Delta E_{corr}|$ curves changes sign after $n = 3$ in the anti-Hückel networks and $n = 4$ in the linear π compounds. The Jahn–Teller distortion in the orbitally degenerate $4n$ perimeters with $n = 1$, 2, or 3 is therefore attenuated by the many-particle π interactions. Figure 13 also demonstrates a comparable gain in E_{corr} as a response to the spatial dimerization in the series $C_6H_6 \rightarrow C_{16}H_{16}$ and $C_{14}H_{16}$. The "finite-size" effects discriminating the three classes of π compounds in the limit of smaller molecular dimensions are more and more reduced with increasing n.

The above model calculations allow for the formulation of several general rules. (i) The π electronic delocalization in monocyclic hydrocarbons and linear polyenes is enhanced as a function of increasing distortion amplitudes δ. (ii) For larger ring and chain dimensions, increasing charge fluctuations as a response to bond alternation are nevertheless compatible with a gain in the interatomic π correlation energy. (iii) The correlation energy $|E_{corr}|$ increases with increasing dimension of the π systems in the $4n + 2$ annulenes and polyenes. This is a result of the reduced gap between occupied and empty π orbitals. (iv) The two observed δ-dependent combinations of $\langle(\Delta n_i^2)\rangle_{corr}$ and $|E_{corr}|$ (i.e., both quantities are enhanced; $\langle(\Delta n_i^2)\rangle_{corr}$ is enhanced/$|E_{corr}|$ reduced) are possible due to a rather sensitive competition between the δ variation of the two-electron repulsion (i.e., residual interaction) and the kinetic hopping. E_{corr} depends on the interaction squared divided by the one-electron energy and $\langle(\Delta n_i^2)\rangle_{corr}$ on the ratio between two- and one-electron elements. This difference is often sufficient to influence $|E_{corr}|$ and $\langle(\Delta n_i^2)\rangle_{corr}$ into directions not expected a priori. We believe that the above analysis leads to some microscopic insight into not only many-particle effects accompanying the bond alternation in π systems, but also the metal–insulator transition of the Peierls-type in quasi one-dimensional synthetic metals. Previous work of one of us has indicated[50,51] that the Peierls transition in strongly correlated solids is sizeably influenced by many-particle interactions. Finally it should become intelligible that the distortive character of π frames is stronger in the presence of sizeable π correlations. Until now we have studied alternant π compounds, where local electronic localization at end atoms could be attenuated when increasing the dimension of the systems. At the end of this section we present some many-particle results derived for π topologies, where the number of terminal sites increases with the size of the system. Two examples are displayed in Figure 13. The $C_{12}H_{14}$ polymethylidene (=dendralene) is shown on the top and the $C_{12}H_{12}$ radialene on the bottom. Dendralene derivatives have become feasible only in the very recent past.[57] Spectroscopic investigation has shown the strong localization of the π electrons in these systems. This is in line with our computational findings, which have been summarized in Table III. We have collected the π electron locali-

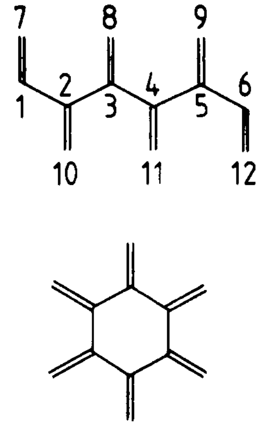

Figure 13. Schematic representation of the $C_{12}H_{14}$ polymethylidene = dendralene together with the employed atomic numbering scheme and the $C_{12}H_{12}$ radialene.

Table III. Correlation-Strength Parameter Δ_i in $C_{12}H_{14}$ Dendralene and $C_{12}H_{12}$ Radialene[a]

compd	π center i	Δ_i	Δ_m
$C_{12}H_{14}$	$C_1 = C_6$	0.185	
	$C_2 = C_5$	0.166	
	$C_3 = C_4$	0.162	
	$C_7 = C_{12}$	0.714	
	$C_8 = C_{11}$	0.782	
	$C_9 = C_{10}$	0.777	
			0.464
$C_{12}H_{12}$	C_{inner}	0.151	
	C_{outer}	0.756	
			0.454
C_2H_4		0.438	0.438

[a] For the atomic numbering scheme see Figure 13. Structures with equidistant CC bonds of 140 pm have been assumed. Δ_i of ethylene at a bond length of 140 pm is given in the bottom line.

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(57) Loerzer, T.; Gerke, R.; Lüttke, W. *Angew. Chem.* **1986**, *98*, 560.

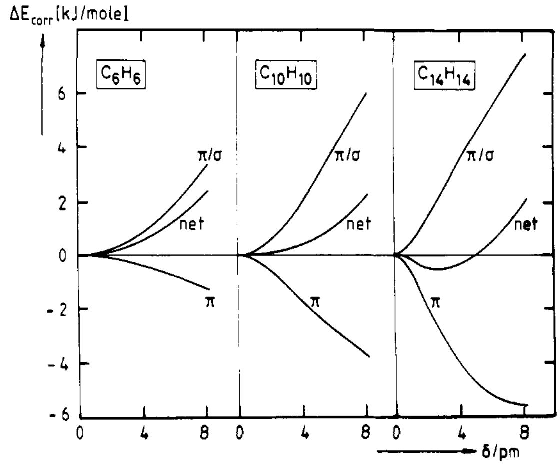

Figure 14. Modification of the interatomic π correlation energy as well as the mutual π/σ coupling in $4n + 2$ annulenes as a function of the bond alternation δ. The "net" curves contain π and σ correlations as well as the π/σ coupling. All ΔE_{corr} numbers have been normalized with respect to two π electrons.

zation parameter Δ_i together with the corresponding mean value Δ_m for the two systems. The Δ_m numbers in $C_{12}H_{14}$ and $C_{12}H_{12}$ (=0.464, 0.454) are larger than the Δ_i element in ethylene (=0.438) and indicate strong π localization. The atomic Δ_i elements in Table III suggest, however, a convenient subdivision of the π systems in both hydrocarbons into two subsets, the terminal functions with strong density localization and the inner π centers with sizeable charge fluctuations. Enhancement in the number of C_2H_2 fragments does not allow for increasing fluctuations. We predict even the opposite trend. In the dendralenes C_nH_{n+2} with n = 6 and 12, Δ_m is slightly enhanced from 0.457 to 0.464; see Table III. π systems derived from structures shown in Figure 13 are highly unstable. By adopting the instability number γ_{in} suggested in the last section this observation is easy to explain.

6. π/σ Coupling in Annulenes

In the latter sections we have only studied the π subspace of the considered hydrocarbons. In the course of our work we have demonstrated that π correlations are a driving force toward bond alternation in all $4n + 2$ annulenes. In the above context it has been emphasized that there exists a direct relation between the strength of the π correlations and their tendency to support bond alternation. In this section we describe the interplay between pure π correlations and π/σ coupling on the latter process. As our ab initio model Hamiltonian has been designed only for π interactions we have to select another computational procedure covering also the σ orbitals. To convey the philosophy of the present ZDO approach, we decided to adopt a semiempirical Hamiltonian of an improved INDO (intermediate neglect of differential overlap) type.[58] The method had been developed to reproduce the results of elaborate ab initio calculations. The combination of the INDO formalism of ref 58 with the LA led to the evaluation of trustworthy many-body results. See refs 8, 21, and 49 for recent model calculations on hydrocarbon π compounds. In the many-body step both the π and σ correlations are taken into account. To improve the quality of the subsequent results we have added interorbital excitations in the determination of $|\psi_0\rangle$. This leads to a renormalization of the π correlations.

In Figure 14 we have plotted the variation of the π correlation energy, the π/σ coupling, and the total interatomic many-particle interaction in $4n + 2$ (n = 1, 2, or 3) annulenes as a function of the bond alternation δ. As concerns the π correlations the results derived in the last section are reproduced in their general trend. For the two small-ring systems C_6H_6 and $C_{10}H_{10}$ the π correlations are, however, overcompensated by the mutual π/σ coupling which stabilizes the nonalternant structure. Already in $C_{14}H_{14}$ the π correlations dominate over the π/σ coupling. An energetic minimum in the sum curve is predicted here at ca. 3 pm. We have thus an interesting competition between π and σ electronic correlations on the bond length alternation in annulenes. Transition of a critical dimension is necessary to force a dominance of the π correlations over the σ ones and the π/σ coupling. The discussion in the last section suggests that this mutual competition should be less strong in $4n$ annulenes or polyenes, as the π interactions are of larger strength here. Finally we want to emphasize that we have only studied the many-particle nature of π electron bonding. Not mentioned are SCF/independent-particle contributions to the bond alternation. We end with the following comment: adoption of the LA in combination with simplified models guarantees that the evaluation of reliable many-body data is much easier than deriving quantitative SCF results such as electronic energies, equilibrium structures, etc.

7. Conclusions

The localization properties of π electrons in hydrocarbon compounds and the associated many-particle character of π bonding have been studied by the method of the local approach. As a quantitatively defined localization measure we have used the mean-square deviations of the π charge around the respective mean value $\langle n_i \rangle$. Evaluation of $\langle(\Delta n_i^2)\rangle$ elements requires the adoption of the correlated ground state. On the other side, reliable electronic energies and charge distributions are already feasible by any single-determinantal procedure. This difference has the following origin: The latter wave functions and energies are valid up to first-order in perturbation; corrections due to electronic correlations occur at first in second-order of perturbation. This is not true for the charge fluctuations, where correlation effects are already first-order corrections.

We feel that it is most convenient for the reader to summarize the principal results of the last sections in the form of a catchword-like collection. (i) The π electrons in hydrocarbons are sizeably localized/correlated and, with sparse exceptions, far from the one-determinantal limit. (ii) The degree of localization and the many-particle interactions cover a sizeable width. The $\langle(\Delta n_i^2)\rangle_{corr}$ and Δ_i and Σ_i numbers for the π electrons in hydrocarbons map an array that coincides with the one encountered in many element combinations and types (i.e., σ,π interactions) of bonds. (iii) The accessible $\langle(\Delta n_i^2)\rangle_{corr}$ and Δ_i intervals in nonalternant systems are narrower than in alternant molecules. Fluctuations for weaker correlated electrons are attenuated in the former systems, but are strengthened when approaching strong correlations. (iv) The strength of covalent bonding is an increasing/decreasing function of $\langle(\Delta n_i^2)\rangle_{corr}/\Delta_i$, which measure interatomic sharing. (v) The local nature of correlation processes guarantees that the considered many-particle indices $\langle(\Delta n_i^2)\rangle_{corr}$, Δ_i, and Σ_i are highly site-specific and local probes characterizing the topology of the considered center. They are therefore transferable from one compound to the other. (vi) We believe that topic v does not become transparent when using most of the conventional methods of quantum chemistry. Topic v provides furthermore a microscopic explanation for the remarkable success of graph theory approaches in the field of hydrocarbon compounds. (vii) Bond alternation in π systems allows for an enhancement of the corresponding charge fluctuations. The enhancement is an increasing function of the strength of π electronic correlations and is of maximum size in orbitally degenerate (monocyclic) systems. (viii) Molecular size effects in $4n + 2$ and $4n$ monocycles act in opposite directions. In Hückel rings the strength of the correlations is an increasing function of the ring size and vice versa in $4n$ annulenes. (ix) Bond alternation is always affected by a competition between σ and π electronic effects, both in the SCF level and correlated ground state. Equidistant structures are forced by the σ frame. Bond alternation is caused by a dominance of π electron interactions in the limit of strong correlations. (x) For monocycles and linear polyenes we have detected two possible combinations of how charge fluctuations and π correlation energy can change as a function of the bond alternation δ. Only the combination of $\langle(\Delta n_i^2)\rangle_{corr}$ enhancement and $|E_{corr}|$ reduction seems to be in line with traditional chemical assumptions. But

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[58] Böhm, M. C.; Gleiter, R. *Theor. Chim. Acta* **1981**, *59*, 127, 153.

also for this couple $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ enhancement with increasing δ is not excepted a priori. In the present work we have rationalized the electronic origin for the in-phase combination of $\langle(\Delta n_i^2)\rangle_{\text{corr}}$ and $|E_{\text{corr}}|$ as a function of δ. (xi) It has been shown that the charge fluctuations in several highly unstable nonalternant molecules are roughly comparable with the ones encountered in systems like, e.g., C_6H_6 which are frequently adopted as an example for highly delocalized π electrons. The π delocalization in nonalternant networks is supported by bond alternation and violation of the alternancy symmetry $(\langle n_i\rangle \neq 1.0)$. (xii) Increasing the size of π systems in combination with an increasing number of terminal carbon centers leads to increasing atomic electron density localization and thus to decreasing stability. Studied examples are dendralenes and radialenes.

Finally we have touched the instability/stability of many nonalternant π systems; the instability of the orbitally degenerate alternant hydrocarbons needs no further comments. Theoretical investigations of the nonalternant compounds by one-electron Hamiltonians in the 1950s and 1960s have shown the occurrence of sizeable π energies.[3] This is reproduced by the present numerical results and advanced ab initio methods. We believe that our analysis sheds some light on the nonvalidity of theoretical approaches, which are restricted to the single-particle level. Furthermore we believe, that also stability concepts based on resonance/delocalization energies are not very helpful to explain instabilities of (nonalternant) hydrocarbons. Even if cyclic arrangements would not be accompanied by an additional stabilization in comparison to the linear reference structure, the high reactivities of the cyclic systems are not evident. The corresponding compounds should resemble in their behavior the linear pendants. As a first step to define an instability index by using information from the exact/correlated ground state, we have suggested the sum of the mean value of the localization parameter Δ_m and the associated mean-square deviation. The first term measures the net localization properties of the (π) electrons and the second one the influence of π centers with strong localization. These sites should cause the high reactivity/instability of the corresponding systems. The utility of our suggestion has been demonstrated for a series of nonalternant systems. Additional work is nevertheless necessary. Generally we expect that reactivities (=stabilities) of π compounds should be controlled by the dynamics (=charge fluctuations) of the electronic system. This is intuitively accepted by the experimental community and found its usage in labels like "tautomeric resonance structures", etc. The present contribution should be accepted as an attempt to transform this into a quantitative basis.

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Appendix

Subsequently we concisely summarize the matrix elements occurring in the π electronic calculations of the present work. As already mentioned we have used a local correlation approach to observe the correlated ground state $|\psi_0\rangle$. It is the conceptual advantage of this technique that the local nature of the correlation hole is explicitly taken into account.[28] In the employed model the total π correlation energy can be given as a sum of pair elements

$$E_{\text{corr}} = \sum_i E_{\text{corr},i} = -\sum_i \eta_i C_i \tag{A.1}$$

with variational parameters η_i measuring the weight of doubly excited Slater determinants in the correlated ground state. In the present π implementation we have taken into account only the leading intraorbital excitations. C_i in A.1 measures the π electron interaction that cannot be described by any single-determinantal wave function $|\psi_{\text{SCF}}\rangle$. In eq A.2 we relate the variational parameters η_i and the matrix elements C_i to a second set of parameters K_{ij} entering the evaluation of the correlated π electronic ground state. The parameters K_{ij} measure the stiffness of the ground-state wave function. Pictorially they can be described as virtual "kinetic" excitations from the occupied π orbitals to the unoccupied ones. Note that A.2 is used to evaluate the

$$\sum_i K_{ij}\eta_i = C_j \tag{A.2}$$

variational parameters η_i. Expression A.2 is based on a linearized approximation for $|\psi_0\rangle$ which corresponds to the conventional CEPA-0 formulation.[45] To summarize: In the derivation of the π electronic ground state we have accepted several approximations. (i) Restriction to two-electron excitations of the intraorbital type which allow for density–density π electronic correlations. (ii) Linearization in the formulation of $|\psi_0\rangle$. Both simplifications prevent the calculation of quantitative many-body parameters. For the intended general discussion they can however by justified.[21,25,26,46]

The matrix elements C_i and K_{ij} formulated in terms of the π electron bond-order matrices per spin direction P_{ij}, matrix elements $D_{ij} = \delta_{ij} - P_{ij}$, two-electron repulsion integrals V_{mn}, and Hartree–Fock matrix elements F_{mn} are expressed in eqs A.3, A.4, and A.5. We have

$$C_i = 2\sum_{m\leq n} V_{mn}P_{in}D_{in}P_{im}D_{im} \tag{A.3}$$

$$K_{ij} = 4P_{ij}D_{ij}\sum_{mn} F_{mn}(P_{ij}D_{jn}D_{mi} - P_{im}P_{nj}D_{ij}) \tag{A.4}$$

$$F_{mn} = t_{mn} - 0.5P_{mn}V_{mn} \tag{A.5}$$

The numerical calculation of the hopping (kinetic energy) integrals t_{mn} and the π repulsions V_{mn} has been explained in section 2.

Next we express the charge fluctuations in the one-determinantal scheme $|\psi_{\text{SCF}}\rangle$ and correlated ground state $|\psi_0\rangle$ in terms of the matrix elements P_{ii} and D_{ii} and variational parameters η_i.

$$\langle(\Delta n_i^2)\rangle_{\text{SCF}} = 2P_{ii}D_{ii} \tag{A.6}$$

$$\langle(\Delta n_i^2)\rangle_{\text{corr}} = 2P_{ii}D_{ii}(1 - 4\eta_i P_{ii}D_{ii}) \tag{A.7}$$

Expression (A.7) corresponds to an approximation, in which we have neglected the mutual coupling between the different π correlation processes.

Finally we have to explain the simple setup of the adopted $|\psi_{\text{SCF}}\rangle$ model. The employed one-electron operator is exclusively defined by Hückel-type resonance integrals t_{ij} which are formulated in the conventional nearest-neighbor tight-binding approximation. This degree of sophistication has also been used to define the so-called Hartree–Fock hopping matrix elements F_{mn} in eq A.5. Detailed descriptions of the present many-body model have been given in previous work.[24-26] The allvalence calculations of section 6 intended to treat π and σ correlation effects have been explained in refs 8, 41, and 42.