Clar’s Sextet Rule Is a Consequence of the σ-Electron Framework

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A number of condensed PAHs are examined to identify the underlying reasons governing empirical Clar’s rule taking benzene as a limiting case. It is found that the so-called Clar’s structures are the only minima on the MP2(fc) potential energy hypersurfaces, meaning that other conceivable valence isomers are nonexistent. The influence of the electron correlation energies to the stability of Clar’s structures is substantial with predominating influence of the σ-electrons. However, the contributions arising from the σ- and π-electron correlation energies are approximately the same, if Clar’s structures are compared with some artificial π-electron localized or graphite-like delocalized planar systems. Analysis of the Hartree−Fock (HF) energies provides a compelling evidence that the origin of stability of Clar’s structures lies in a decrease of the positive T, V_{ee} and V_{nn} energy terms relative to some characteristic virtual “delocalized” or “localized” model geometries. Partitioning of the mixed $V_{\mathrm{ee}}^{\sigma\pi}$ and $V_{\mathrm{nn}}^{\sigma\pi}$ terms in the σ- and π-type contributions, by using the stockholder (SHR), equipartitioning (EQP) and standard π (SPI) schemes, unequivocally shows that the driving force leading to Clar’s structures are more favorable σ-type interactions. All these conclusions hold for the archetypal benzene too, which could be considered as a limiting Clar system. Finally, the boundaries of Clar’s hypothesis and some common misconceptions are briefly discussed. Perusal of the geometric parameters and π-bond orders reveals that there are no benzene rings completely “vacant” or “fully occupied” by the π-electrons, envisaged by Clar in his picture of condensed benzenoid compounds. Instead, there are six-membered rings with higher and lower total π-electron density. The bond length anisotropy of the former rings is smaller. It is concluded that Clar’s proposition is a useful rule of thumb providing qualitative information on the stability of the PAH systems, which in turn should not be overinterpreted.

1. Introduction

Aromaticity is one of the cornerstones of (organic) chemistry and yet—paradoxically as it is—it is impossible to define its notion in a unique way. Despite a number of criteria developed to quantify aromaticity,[1−17] ranging from the thermodynamic and geometric assessments to the molecular response magnetic properties, it remains as elusive as ever.[18] The extraordinary high stability of the planar rings possessing $(4n + 2)\pi$ electrons was postulated by Hückel[19,20] on the basis of his simple single particle π-electron theory based on the effective Hamiltonian. A perfect example illustrating Hückel’s rule is benzene, which has high D_{6h} symmetry. However, it turned out later that in larger monocycles involving $(4n + 2)\pi$ electrons the Hückel theory of aromaticity faced serious difficulties due to inherent angular strain leading to nonplanar structures, which hampered efficient π-electron conjugation. Nevertheless, there is a clear tendency of the $(4n + 2)\pi$ electrons to delocalize and to equalize bond distances as much as possible in systems other than benzene like, e.g., in the cyclopentadienyl anion, which assumes D_{5h} symmetry, or in the case of benzo[1,2:4,5]icyclobutadiene, where the π-electrons are delocalized over the perimeter of the tricyclic system, thus forming a quasi[10] annulene.[21] High symmetries and perfect delocalization are, however, more exceptions than a rule. Speaking of exceptions, it is noteworthy that Hückel’s simple theory does not necessarily apply to polycyclic aromatic hydrocarbons (PAHs). These very interesting systems are given by condensed benzenoid compounds containing benzene rings coalesced by one or several CC bonds. Instead of Hückel’s $(4n + 2)\pi$ electron count rule, their stability is governed by Clar’s empirical finding,[22,23] which indicates that the most stable structure of annelated benzenes is the one possessing the maximal number of the aromatic sextets separated by the entirely “empty” six-membered rings. To put it another way, the π-electrons of the latter are considered to be spin-coupled in the nearest neighbor rings, thus belonging to their moieties and consequently forming their sextet substructures. Thus the π-electrons tend to be “semilocalized” in disjoint π-sextets, which form isolated aromatic islands surrounded by the π-electron “empty” rings (i.e., the gaps). Let us consider phenanthrene **I** and triphenylene **II** as the simplest characteristic examples (Chart 1). The former has a central ring with a “perfectly localized” π-double bond, whereas the latter possesses a central, “completely vacant”, ring according to a common understanding of Clar’s rule.

The fact of the matter is that the optimized electronic and spatial structures, yielding minima on the Born−Oppenheimer (BO) potential energy hypersurfaces, resemble those given by the maximum possible number of the isolated aromatic sextets as depicted in Chart 1, but only in a very broad sense. In spite

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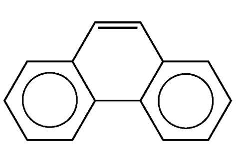
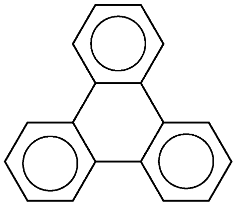
CHART 1

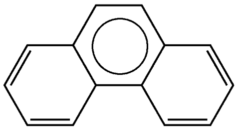


I

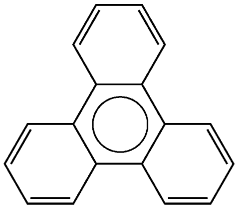


II

CHART 2



I_a



II_a

of that, we shall conditionally term the optimized geometries as Clar's structures in what follows. On the other hand, the minimal aromatic sextet representation of the same molecules, given by the electron spin coupling schemes $\mathbf{I}_a$ and $\mathbf{II}_a$ (Chart 2), are of higher total energy and do not correspond to local minima on the ground-state BO hypersurfaces. Consequently, $\mathbf{I}_a$ and $\mathbf{II}_a$ are not the valence (or bond-stretch) isomers of phenanthrene and triphenylene, respectively.

Rather, each of them represents a combination of two Kekulé resonance structures describing the central benzene ring, which participate (albeit with low weighting factors) in forming the total VB wave function of the corresponding ground states. The same holds for any other conceivable combination of "localized" π-bonds and "semilocalized" aromatic sextets.

The origin of Clar's rule was much discussed, but the final conclusion was not reached. We shall disregard considerations based on the π-electron only theories of chemical bonding, because the σ-framework seems to be very important in discussing aromaticity,[24−29] and focus on indices based on the total electron densities instead, if not stated otherwise. Recently, Solá et al.[30] examined Clar's aromatic sextet rule in a number of polycyclic aromatic hydrocarbons (PAHs) by using three criteria. The first was based on a simplified DFT form of para-delocalization indices (PDI) introduced by Bader, Streitwieser, and co-workers,[31] rooted in the atoms in molecules (AIM) picture of chemical bonding.[32] It heavily hinges on the assumption that the aromatic stabilization of a six-membered ring is proportional to a sum of all two-atom delocalization indices, which are placed at para positions. The second criterion was a structural harmonic oscillator model (HOMA) introduced by Kruszewski and Krygowski.[33,34] It reflects the electronic structure of aromatic molecules via BO hypersurfaces through the spatial structures corresponding to the true minima. Finally, Schleyer's nuclear independent chemical shifts (NICS)[35] were employed. All three criteria indicated that the six-membered rings corresponding to benzene-like fragments in Clar's structures should be more aromatic than the other ones. Some discrepancies between PDI and HOMA indices on one side, and NICS values on the other, were noted. Ponec and co-workers[36] pointed out that the PDI indices have some inherent imperfections. They discussed Clar's PAHs by the six-center bond indices derived from the generalized population analysis. They were invariably larger in "semilocalized" sextets. However, indices mentioned above cannot say anything about the underlying interactions leading to PAH structures conforming to Clar's rule. It is the aim of the present analysis to provide the physical basis of this important empirical rule of thumb focusing on the interplay between the σ- and π-electrons on one hand and charges placed on the atoms on the other. For this purpose a number of PAHs will be considered together with the archetypal aromatic molecule benzene, taken as a limiting case of condensed benzenoid systems. Anticipating forthcoming results, one can say that the driving force leading to Clar's spatial structures is provided by the more favorable kinetic energy, electron−electron and nuclear−nuclear repulsions compared to idealized model geometries, and that the preponderant effect is exerted by the σ-part of the molecular framework.

2. Methodology

The structural parameters are optimized at the Møller−Plesset[37] second-order perturbation MP2(fc) method employing Dunning's cc-pVDZ basis set.[38] It will be denoted thereafter as MP2(fc). The total molecular energies will be analyzed in terms of the Hartree−Fock HF//cc-pVDZ//MP2(fc)/cc-pVDZ model, whereas the correlation energy corrections will be estimated at the MP2(fc) level. The former are going to be examined by three energy partitioning schemes thoroughly discussed in our previous work.[28,29] Briefly, the total HF energy is given by

$$E_{\mathrm{HF}} = E(T)_{\mathrm{HF}} + V_{\mathrm{HF}} \tag{1}$$

where $E(T)_{\mathrm{HF}}$ is kinetic energy and V_{HF} is potential energy:

$$V_{\mathrm{HF}} = V_{\mathrm{ne}} + V_{\mathrm{ee}} + V_{\mathrm{nn}} \tag{2}$$

where components have the usual meaning. The electron and nuclear repulsions V_{ee} and V_{nn}, respectively, cannot be unequivocally decomposed into σ- and π-parts, because they involve pairwise interactions. For instance, the electron repulsion,

$$V_{\mathrm{ee}} = V_{\mathrm{ee}}^{\sigma\sigma} + V_{\mathrm{ee}}^{\pi\pi} + V_{\mathrm{ee}}^{\sigma\pi} \tag{3}$$

includes the $V_{\mathrm{ee}}^{\sigma\pi}$ term, which couples the σ- and π-electrons. We suggested stockholder (shareholder) partitioning SHR where

$$V_{\mathrm{ee}}^{\sigma} = V_{\mathrm{ee}}^{\sigma\sigma} + (n_\sigma/N)V_{\mathrm{ee}}^{\sigma\pi} \tag{4}$$

and

$$V_{\mathrm{ee}}^{\pi} = V_{\mathrm{ee}}^{\pi\pi} + (n_\pi/N)V_{\mathrm{ee}}^{\sigma\pi} \tag{5}$$

which yield the σ- and π-contributions to the total repulsion V_{ee}. Here, n_σ and n_π denote the number of the σ- and π-electrons, respectively, whereas $N = n_\sigma + n_\pi$. Equipartitioning of the mixed term $V_{\mathrm{ee}}^{\sigma\pi}$ leads to the EQP scheme advocated by Jug and Köster,[39] where $V_{\mathrm{ee}}^{\sigma} = V_{\mathrm{ee}}^{\sigma\sigma} + (1/2)V_{\mathrm{ee}}^{\sigma\pi}$ and $V_{\mathrm{ee}}^{\pi} = V_{\mathrm{ee}}^{\pi\pi} + (1/2)V_{\mathrm{ee}}^{\sigma\pi}$. Finally, the whole $V_{\mathrm{ee}}^{\sigma\pi}$ term could be ascribed to the π-network as in the standard π-electron theories,[40] giving rise to the standard π-partitioning (SPI). Analogously, a one-to-one correspondence between protons in the nuclei and the σ/π-electrons is established, which means in the present case $Z(\mathrm{C})^{\sigma} = 5$, $Z(\mathrm{C})^{\pi} = 1$, $Z(\mathrm{H})^{\sigma} = 1$ and $Z(\mathrm{H})^{\pi} = 0$. The $V_{\mathrm{nn}}^{\sigma\pi}$ term is partitioned according to the stockholder principle in the SHR scheme. The same is retained in the EQP scheme, which is the point of departure from the full Jug−Köster equipartitioning recipe,[39] because the latter employs 50:50 decomposition even for the repulsion of the nuclear charges. Finally, the whole nuclear repulsion V_{nn} including the $V_{nn}^{\sigma\pi}$ contribution is attributed to the σ-framework in the SPI decomposition scheme, which is quite arbitrary.

The MP2 correlation energies were calculated by

$$E(\mathrm{MP2})_{\mathrm{corr}} = E[\mathrm{HF/cc-pVDZ//MP2(fc)/cc-pVDZ}] - E[\mathrm{MP2(fc)/cc-pVDZ}] \quad (6)$$

where we define the correlation energy as a positive quantity for convenience. However, in some cases we found it necessary to consider separately the nondynamical and dynamical components of the total correlation energy. We shall consider then the nondynamical correlation of the π-electrons $E(\mathrm{ND})^{\pi}$ by using multiconfiguration self-consistent field MCSCF method, taking into account the complete active space of the π-MOs (CASSCF$^{\pi}$) according to the formalism developed by Ruedenberg et al.[41] and Roos.[42] The nondynamical correlation energy is given by

$$E(\mathrm{ND})^{\pi} = E(\mathrm{HF}) - E(\mathrm{CASSCF})^{\pi} \quad (7)$$

To be consistent with the theoretical framework adopted here, we used geometries optimized at the MP2(fc)/cc-pVDZ level. The dynamical correlation is treated by the CASPT2 method,[43,44] which utilizes the CASSCF$^{\pi}$ function as a starting point for perturbational treatment. Two types of the CASPT2 calculations were carried out. The first involves only the dynamical correlation of the π-electrons and it is referred to as (CASPT2)$^{\pi}$. The second includes dynamical correlation of all valence electrons (keeping only the σ-core electrons frozen) and consequently it allows for an active participation of the σ-valence electrons too. It is denoted by (CASPT2)$^{(\pi)+\sigma}$.[45,46] The calculations have been carried out by using GAUSSIAN,[47] MOLCAS[48] and MOLPRO[49] suites of programs. The HF energy partitioning has been obtained by the COLUMBUS code.[50]

3. Results and Discussion

3.1. Hartree−Fock Energies. Compounds **1**−**10** examined here are depicted in Figure 1. The optimized structures are given in Clar's representation,[22] which has its advantages and shortcomings. In addition to the optimized structures, which correspond to true minima on the BO potential energy hypersurfaces, we consider some idealized geometries belonging to two conceivable, but diametrically opposite situations. The first includes ideal benzene rings with equivalent CC bond lengths of 1.406 Å and all CCC angles equal to 120°. These idealized "graphite-like" structures are denoted by $\mathbf{1}_a$−$\mathbf{10}_a$ (Figure 1). They will be conditionally termed "delocalized" geometries. It should be mentioned that the CC bond length 1.406 Å corresponds to the MP2(fc) optimized geometry of benzene. It is very close to the most accurate experimental value of 1.398 Å.[51] The second conceived case involves virtual systems possessing "fully localized" C=C double bonds, thus yielding particular Kekulé resonance structures. The alternating C−C single and C=C double bond distances were fixed at 1.460 and 1.339 Å, respectively, corresponding to the MP2(fc) bond lengths in 1,3-butadiene. An alternative electron diffraction geometry determination of Kveseth et al.[52] gave $d(\mathrm{C-C}) = 1.467$ Å and $d(\mathrm{C=C}) = 1.349$ Å, thus corresponding to a structure more delocalized than the employed one. However, these modest differences in geometry cannot affect the final results. The rest of the structural parameters have been optimized. These systems are signified by $\mathbf{1}_b$−$\mathbf{10}_b$. Some additional Kekulé pairing schemes $\mathbf{1}_c$−$\mathbf{3}_c$ are studied for the first three simplest compounds too to illustrate the fact that the final conclusion is independent of a particular choice of the Kekulé structures. Our task is to ascertain the underlying reasons, which offer an explanation why Clar's structures correspond to the energy minima, whereas others do not. The decrease in stability $\Delta E(\mathbf{n}_{\omega})$ on going from the stable Clar geometries **n** to conceived virtual structures ($\mathbf{n}_{\omega}$) is given by

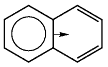
$$E(\mathbf{n}) = E(\mathbf{n}_{\omega}) + \Delta E(\mathbf{n}_{\omega}) \quad (8)$$

where ω stands for a, b or c in compounds $\mathbf{n} = \mathbf{1} - \mathbf{10}$. The $\Delta E(\mathbf{n}_{\omega})$ values give the intrinsic aromaticity[28] of condensed benzenoid systems, because the topology of the π-electron AOs is not changed in the deformation process. It should be noticed that a set of equations (8) corresponds to homodesmotic[3−6] reactions, because the hybridization of the carbon atoms is conserved on the average during the deformation process. They could be characterized more precisely as homostructural reactions as suggested recently,[29] because their structures are similar, but by no means equivalent due to a redistribution of the π-bond orders (π-electron density) and hybrids' s-characters (local σ-density polarization) within the CC bonds emanating from the same carbon. Because benzene can be considered as a limiting case of Clar's structures consisting of a single six-membered ring, we shall consider it separately. The corresponding isostructural reaction[29] reads

$$\text{benzene} = \text{cyclohexatriene} + \Delta E(\mathrm{iase})_{\mathbf{B}} \quad (9)$$

where ΔE (iase)$_{\mathbf{B}}$ denotes intrinsic aromatic stabilization of benzene.

Survey of the results given in Table 1 shows that stability of the optimized structures **n** increases, relative to the idealized ones $\mathbf{n}_a$ and $\mathbf{n}_b$, with the number of benzene rings as a rule, but there are also some notable exceptions. For example, $|\Delta E(\mathbf{n}_a)|$ increases in a series $\mathbf{n} = \mathbf{1}$, **2**, **3**, and **7** assuming 2.6, 7.1, 11.1 and 14.4 kcal/mol, respectively, as intuitively expected. Their building blocks are 2 (1), 3 (2), 4 (3) and 6 (4) six-membered rings, respectively, where the number of benzene-like rings is given within parentheses. Kekulene (superbenzene) **8** possessing 12 six-membered and a subset of 6 benzene-like rings is strongly stabilized relative to the perfectly delocalized structure $\mathbf{8}_a$ by 37 kcal/mol, which is the largest difference found here. However, hexabenzocoronene **10** with 13 six-membered and among them 7 benzene-like rings has the energy difference $|\Delta E(\mathbf{10}_a)|$ of "only" 19.9 kcal/mol. It appears that stabilization energy is not a linear function of the number of either six-membered rings or a subset of the benzene-like rings. There are more examples such as that (Table 1). Thus, the difference in HF energies does depend also on the shape of a compound as might be expected on intuitive grounds. A similar conclusion holds for the $|\Delta E(\mathbf{n}_b)|$ energies. A useful byproduct of the present analysis is a finding that the valence bond structures possessing annelated localized π-double bonds $\mathbf{n}_b$ are of lower energy than their $\mathbf{n}_c$ counterparts for $\mathbf{n} = \mathbf{1}$, **2**, **3**. In fact, the difference in energy is significant being roughly 10 kcal/mol. It should be pointed out that the difference in stability is persistent and that it is little changed by an explicit account of the correlation energy (see later). This result is in accordance with the Mills−Nixon (MN) hypothesis,[53] which was confirmed in a number of theoretical studies.[54−56] To be more precise, this particular form of the double bond localization corresponds to the anti-MN effect.[55,56] It follows that the double bond fixation electron spin pairing schemes, given by $\mathbf{n}_b$ ($\mathbf{n} = \mathbf{1}, \mathbf{2}, \mathbf{3}$) patterns, should be slightly preferred in true compounds over $\mathbf{n}_c$ ones. Another interesting observation is that **2** is more stable than **4**



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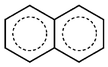
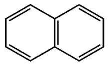
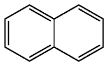


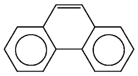
1$_a$



1$_b$



1$_c$



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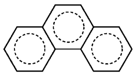

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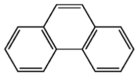

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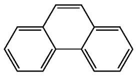

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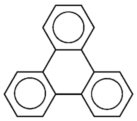

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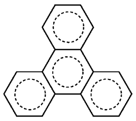

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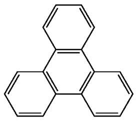

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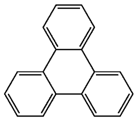

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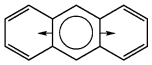

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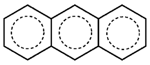

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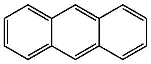

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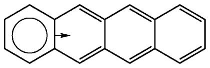

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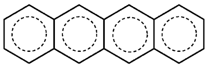

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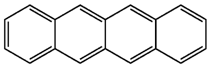

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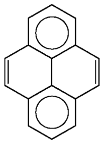

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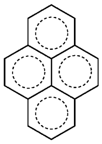

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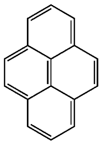

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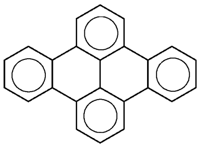

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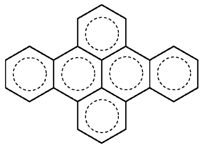

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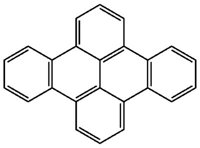

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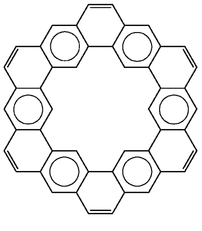
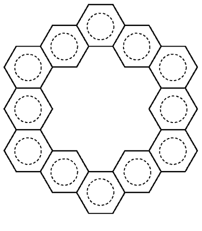
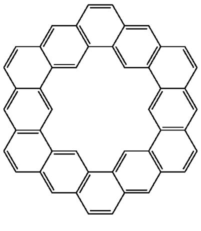


8



8$_a$



8$_b$

Figure 1. Continued

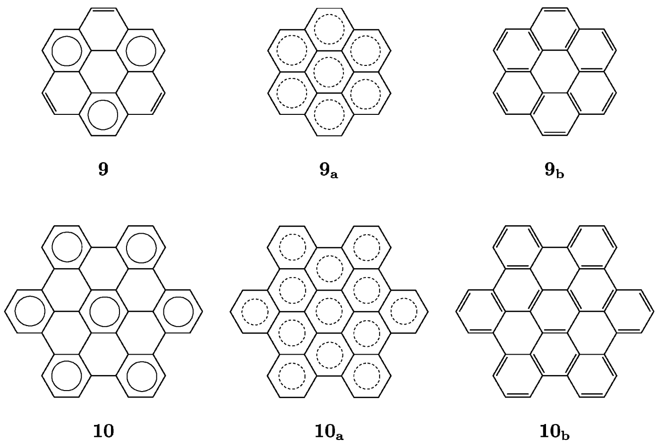


Figure 1. Schematic representation of three types of the examined structures: (1) optimized **n**, (2) graphite-like $\mathbf{n}_a$ and (3) localized ones corresponding to the VB resonance structures $\mathbf{n}_b$ (or $\mathbf{n}_c$). The "travelling" aromatic sextets in linear acenes are denoted by an arrow.

TABLE 1: Kinetic and Potential Energy Components of Differences in Total Energies ΔE^{tot} between the Optimized and Deformed Structures Given by Homostructural Reaction 8 As Obtained by the HF/cc-pVDZ//MP2(fc)/cc-pVDZ Model (in kcal/mol)

molecule	ΔT	ΔV_{ne}	ΔV_{ee}	ΔV_{nn}	ΔE^{tot}
$\mathbf{1}_a$	−152.6	4134.4	−1984.4	−2000.1	−2.6
$\mathbf{1}_b$	−280.7	4047.1	−1893.8	−1876.4	−3.8
$\mathbf{1}_c$	−275.1	3949.1	−1837.9	−1846.1	−10.0
$\mathbf{2}_a$	−318.7	11996.9	−5829.9	−5855.4	−7.1
$\mathbf{2}_b$	−449.7	9518.3	−4551.0	−4524.9	−7.3
$\mathbf{2}_c$	−429.9	8584.7	−4075.3	−4097.3	−17.9
$\mathbf{3}_a$	−509.3	22868.6	−11168.5	−11201.9	−11.1
$\mathbf{3}_b$	−648.5	17046.9	−8214.4	−8195.1	−11.2
$\mathbf{3}_c$	−637.3	14148.3	−6780.6	−6753.2	−22.7
$\mathbf{4}_a$	−315.0	9708.1	−4687.0	−4711.9	−5.7
$\mathbf{4}_b$	−431.1	7184.1	−3384.2	−3373.5	−4.8
$\mathbf{5}_a$	−484.7	16238.0	−7866.3	−7895.1	−8.2
$\mathbf{5}_b$	−596.1	11715.2	−5563.3	−5571.0	−15.3
$\mathbf{6}_a$	−431.6	13727.8	−6632.6	−6669.1	−5.3
$\mathbf{6}_b$	−509.5	9533.6	−4526.1	−4506.6	−8.7
$\mathbf{7}_a$	−809.8	39024.8	−19091.0	−19138.3	−14.4
$\mathbf{7}_b$	−893.6	24198.4	−11669.8	−11652.0	−17.0
$\mathbf{8}_a$	−1918.9	122701.9	−60410.2	−60409.9	−37.1
$\mathbf{8}_b$	−1829.7	55683.3	−26974.7	−26907.7	−28.7
$\mathbf{9}_a$	−834.5	31098.0	−15113.2	−15156.4	−5.9
$\mathbf{9}_b$	−832.1	19028.4	−9148.7	−9057.8	−10.2
$\mathbf{10}_a$	−1818.9	101083.8	−49598.2	−49686.6	−19.9
$\mathbf{10}_b$	−1720.9	60652.6	−29548.2	−29417.6	−34.2
B	0	0	0	0	0
CHT	−131.1	1265.7	−569.2	−570.2	−4.8

by 7.4 and 6.4 kcal/mol by the HF and MP2 models, respectively (Table S1 of the Supporting Information). This is a rather nice illustration of the fact that "diluted" benzene in linear acenes is less stable than the "localized" benzenes in the corresponding zigzag acenes as conjectured by Clar. The present result is in accordance with an earlier finding of Schulman et al.[57] They found inter alia that **2** is lower in energy than **4** by 6.9 kcal/mol and that chrysene is more stable than tetracene by twice as much (14 kcal/mol), as estimated by the HF/6-31G* model. A similar conclusion was reached by Krygowski et al.[58] by using their HOMA aromaticity index.

Last but not least, it should be mentioned that the equilibrium D_{6h} structure of benzene (**B**) is more stable than the artificial cyclohexatriene (**CHT**) by 4.8 kcal/mol.

To reveal the origin of the increased stability of Clar's structures, let us consider the breakdown of the differences in total HF energies $\Delta E(\mathbf{n}_a)$, $\Delta E(\mathbf{n}_b)$ and $\Delta E(\mathbf{n}_c)$ into ΔT, ΔV_{ne}, ΔV_{ee} and ΔV_{nn} energy components without the σ/π partitioning of the last two terms. Perusal of the data in Table 1 convincingly shows that all optimized structures **n** and benzene **B** are stable compounds due to more advantageous kinetic energy ΔT, electron−electron repulsion ΔV_{ee} and nuclear repulsion ΔV_{nn} terms relative to both conceived delocalized $\mathbf{n}_a$ and localized $\mathbf{n}_b$ (or $\mathbf{n}_c$) virtual structures. In contrast, the nuclear−electron attraction is less favorable, but the aforementioned energy terms prevail. Hence, the first important conclusion to be drawn is that empirical Clar's rule is a consequence of the fact that the destabilizing kinetic energy T as well as V_{ee} and V_{nn} repulsion energies are lower in true minimum energy geometries. This is the reason behind the experimental evidence that the condensed benzenoid compounds are constructed neither from ideal benzene building blocks nor from the six-membered rings moieties exhibiting highly pronounced localized π-electron patterns. Instead, the true picture is provided by a particular combination of these two extremes, being not so distant from Clar's postulate. There are, however, no hypothetized "π-electron empty" and "π-electron full" six-membered rings in reality, implying that Clar's idea should be taken cum grano salis (see later). It should be noted that the largest decrease in destabilizing interactions occurring in the optimized (Clar's) structures is found in the V_{ee} and V_{nn} terms. The corresponding ΔV_{ee} and ΔV_{nn} values are large and roughly comparable. On the other hand, ΔT values are considerably smaller (in the absolute sense), being, in spite of that, very important.

The second interesting conclusion is obtained by considering the σ- and π-electron energies as offered by various energy partitioning schemes:

$$\Delta E^{\sigma} = \Delta T^{\sigma} + \Delta V^{\sigma}_{ne} + \Delta V^{\sigma}_{ee} + \Delta V^{\sigma}_{nn} \qquad (10)$$

and

$$\Delta E^{\pi} = \Delta T^{\pi} + \Delta V^{\pi}_{ne} + \Delta V^{\pi}_{ee} + \Delta V^{\pi}_{nn} \qquad (11)$$

Perusal of the results given in Table 2 shows that the optimized structures **n** are more stable than the virtual structures $\mathbf{n}_a$, $\mathbf{n}_b$ and $\mathbf{n}_c$ due to more favorable σ-type interactions, which is an important finding. Second, this corollary is independent of the way the decomposition of the $V^{\sigma\pi}_{ee}$ and $V^{\sigma\pi}_{nn}$ mixed terms is carried out. Consequently, it is safe to conclude that Clar's rule is rooted in the properties of the σ-framework of condensed benzenoid compounds. To put it another way, the π-type interactions are more advantageous in the virtual model systems $\mathbf{n}_a$ and $\mathbf{n}_b$ (and some alternative spin-schemes $\mathbf{n}_c$), but the σ-type interactions prevail, leading to stable compounds **n** (**n = 1−10**). It is worth reiterating that the driving force leading to the stable

TABLE 2: σ/π Partitioning of the HF Energy Differences Defined by Homostructural and Isostructural Equations (8) and (9), Obtained at the HF/cc-pVDZ//MP2(fc)/cc-pVDZ Level (in kcal/mol)[a]

molecule/(σ/π)	ΔT^{σ}	ΔT^{π}	ΔV_{ne}^{σ}	ΔV_{ne}^{π}	ΔV_{ee}^{σ}	ΔV_{ee}^{π}	ΔV_{nn}^{σ}	ΔV_{nn}^{π}	ΔE^{σ}	ΔE^{π}	ΔE^{tot}
1$_a$	−144.0	−8.6	3561.1	573.3							
SHR					−1873.4	−111.0	−1872.9	−127.2	−329.2	326.6	−2.6
EQP					−1704.5	−279.9	−1872.9	−127.2	−160.3	157.7	−2.6
SPI					−1465.2	−519.1	−2000.1		−48.2	45.6	−2.6
1$_b$	−204.9	−75.8	3281.9	765.2							
SHR					−1769.8	−124.0	−1754.8	−121.6	−447.6	443.8	−3.8
EQP					−1568.3	−325.4	−1754.8	−121.6	−246.2	242.3	−3.8
SPI					−1283.0	−610.7	−1876.4		−82.5	78.6	−3.8
1$_c$	−203.5	−71.6	3256.2	692.9							
SHR					−1727.4	−110.5	−1729.2	−116.9	−403.8	393.8	−10.0
EQP					−1543.6	−294.4	−1729.2	−116.9	−220.0	210.0	−10.0
SPI					−1283.2	−554.8	−1846.1		−76.5	66.5	−10.0
2$_a$	−298.5	−20.2	10299.6	1697.3							
SHR					−5496.7	−333.2	−5484.7	−370.6	−980.4	973.3	−7.1
EQP					−4996.8	−833.1	−5484.7	−370.6	−480.5	473.4	−7.1
SPI					−4284.9	−1545.0	−5855.4		−139.2	132.1	−7.1
2$_b$	−343.5	−106.2	7902.0	1616.3							
SHR					−4266.5	−284.5	−4234.5	−290.3	−942.5	935.2	−7.3
EQP					−3822.9	−728.1	−4234.5	−290.3	−498.9	491.6	−7.3
SPI					−3191.2	−1359.9	−4524.9		−157.5	150.2	−7.3
2$_c$	−333.4	−96.5	7194.0	1390.7							
SHR					−3832.8	−242.5	−3834.0	−263.3	−806.3	788.4	−17.9
EQP					−3450.0	−625.3	−3834.0	−263.3	−423.4	405.5	−17.9
SPI					−2904.7	−1170.6	−4097.3		−141.4	123.5	−17.9
3$_a$	−470.8	−38.5	19567.9	3300.7							
SHR					−10516.1	−652.4	−10486.5	−715.4	−1905.4	1894.4	−11.1
EQP					−9547.8	−1620.7	−10486.5	−715.4	−937.2	926.1	−11.1
SPI					−8164.6	−3003.9	−11201.9		−269.4	258.3	−11.1
3$_b$	−512.5	−135.9	14297.5	2749.4							
SHR					−7712.1	−502.3	−7667.2	−527.9	−1594.4	1583.2	−11.2
EQP					−6943.2	−1271.3	−7667.2	−527.9	−825.5	814.3	−11.2
SPI					−5844.8	−2369.7	−8195.1		−255.0	243.8	−11.2
3$_c$	−486.6	−150.7	11793.3	2355.0							
SHR					−6356.3	−424.3	−6322.5	−430.7	−1372.0	1349.3	−22.7
EQP					−5706.6	−1073.9	−6322.5	−430.7	−722.4	699.6	−22.7
SPI					−4778.6	−2002.0	−6753.2		−225.0	202.6	−22.7
4$_a$	−297.3	−17.7	8348.2	1359.9							
SHR					−4419.9	−267.1	−4409.5	−302.4	−778.5	772.8	−5.7
EQP					−4020.1	−666.9	−4409.5	−302.4	−378.7	373.0	−5.7
SPI					−3450.7	−1236.3	−4711.9		−111.7	105.9	−5.7
4$_b$	−320.9	−110.2	5905.1	1279.0							
SHR					−3170.2	−214.0	−3155.7	−217.8	−741.8	737.0	−4.8
EQP					−2828.6	−555.6	−3155.7	−217.8	−400.2	395.4	−4.8
SPI					−2342.0	−1042.2	−3373.5		−131.4	126.6	−4.8
5$_a$	−455.4	−29.4	13937.9	2300.1							
SHR					−7411.7	−454.6	−7386.1	−509.0	−1315.3	1307.1	−8.2
EQP					−6737.4	−1129.0	−7386.1	−509.0	−640.9	632.7	−8.2
SPI					−5773.9	−2092.4	−7895.1		−186.5	178.3	−8.2
5$_b$	−448.2	−147.9	9760.4	1954.8							
SHR					−5226.6	−336.7	−5213.8	−357.2	−1128.3	1112.9	−15.3
EQP					−4694.0	−869.3	−5213.8	−357.2	−595.6	580.3	−15.3
SPI					−3933.1	−1630.2	−5571.0		−192.0	176.6	−15.3
6$_a$	−402.8	−28.8	11742.3	1985.5							
SHR					−6239.3	−393.3	−6231.4	−437.7	−1131.2	1125.9	−5.3
EQP					−5662.9	−969.7	−6231.4	−437.7	−554.8	549.5	−5.3
SPI					−4837.3	−1795.3	−6669.1		−167.0	161.7	−5.3
6$_b$	−380.7	−128.8	7859.6	1674.0							
SHR					−4235.4	−290.7	−4211.8	−294.8	−968.3	959.7	−8.7
EQP					−3785.2	−740.9	−4211.8	−294.8	−518.2	509.5	−8.7
SPI					−3140.3	−1385.7	−4506.6		−168.1	159.4	−8.7
7$_a$	−747.3	−62.5	33303.0	5721.8							
SHR					−17946.5	−1144.5	−17893.3	−1245.0	−3284.1	3269.7	−14.4
EQP					−16279.2	−2811.8	−17893.3	−1245.0	−1616.8	1602.4	−14.4
SPI					−13884.4	−5206.7	−19138.3		−467.0	452.6	−14.4
7$_b$	−705.2	−188.4	20254.2	3944.2							
SHR					−10937.3	−732.5	−10886.5	−765.5	−2274.7	2257.7	−17.0
EQP					−9840.1	−1829.7	−10886.5	−765.5	−1177.5	1160.6	−17.0
SPI					−8264.2	−3405.6	−11652.0		−367.1	350.1	−17.0

TABLE 2: (Continued)

molecule/(σ/π)	ΔT^{σ}	ΔT^{π}	ΔV^{σ}_{ne}	ΔV^{π}_{ne}	ΔV^{σ}_{ee}	ΔV^{π}_{ee}	ΔV^{σ}_{nn}	ΔV^{π}_{nn}	ΔE^{σ}	ΔE^{π}	ΔE^{tot}
8$_a$	−1794.3	−124.6	104508.6	18193.3							
SHR					−56696.2	−3714.0	−56460.7	−3949.3	−10442.5	10405.4	−37.1
EQP					−51398.1	−9012.1	−56460.7	−3949.3	−5144.4	5107.4	−37.1
SPI					−43745.3	−16664.9	−60409.9		−1440.9	1403.8	−37.1
8$_b$	−1440.2	−389.5	46615.4	9067.9							
SHR					−25255.4	−1719.3	−25136.2	−1771.5	−5216.4	5187.6	−28.7
EQP					−22732.3	−4242.4	−25136.2	−1771.5	−2693.2	2664.5	−28.7
SPI					−19087.7	−7887.0	−26907.7		−820.2	791.5	−28.7
9$_a$	−769.7	−64.8	26461.0	4637.0							
SHR					−14179.5	−933.7	−14140.1	−1016.3	−2628.2	2622.3	−5.9
EQP					−12846.7	−2266.4	−14140.1	−1016.3	−1295.5	1289.6	−5.9
SPI					−10921.6	−4191.5	−15156.4		−386.7	380.8	−5.9
9$_b$	−626.1	−206.0	15679.1	3349.4							
SHR					−8532.4	−616.3	−8451.4	−606.3	−1930.9	1920.7	−10.2
EQP					−7625.5	−1523.2	−8451.4	−606.3	−1023.9	1013.7	−10.2
SPI					−6315.4	−2833.3	−9057.8		−320.2	310.0	−10.2
10$_a$	−1667.3	−151.6	85811.9	15271.9							
SHR					−46474.1	−3124.1	−46336.3	−3350.4	−8665.8	8645.8	−19.9
EQP					−42083.4	−7514.9	−46336.3	−3350.4	−4275.0	4255.1	−19.9
SPI					−35709.7	−13888.5	−49686.6		−1251.7	1231.8	−19.9
10$_b$	−1357.2	−363.7	50715.2	9937.4							
SHR					−27611.7	−1936.5	−27431.2	−1986.4	−5685.0	5650.8	−34.2
EQP					−24843.7	−4704.6	−27431.2	−1986.4	−2917.0	2882.8	−34.2
SPI					−20825.7	−8722.6	−29417.6		−885.2	851.1	−34.2
CHT	−89.7	−41.4	1002.1	263.6							
SHR					−533.3	−35.9	−534.8	−35.4	−155.7	150.8	−4.8
EQP					−467.7	−101.6	−534.8	−35.4	−90.0	85.2	−4.8
SPI					−375.7	−193.5	−570.2		−33.5	28.6	−4.8

[a] Stability of benzene (**B**) relative to cyclohexatriene (**CHT**) is determined by eq 9.

Clar's spatial structures is provided by a decrease in the positive (destabilizing) contributions of the T, V_{ee} and V_{nn} terms to the total HF energy. Perusal of the data in Table 2 shows that benzene attains D_{6h} equilibrium structure due to a more favorable σ-type intramolecular interactions in harmony with detailed analyses of Shaik, Hibberty and co-workers[24,25] and Jug and Schaefer and co-workers.[26,27] The question arises whether these conclusions hold beyond the HF model. The influence of the correlation energy is addressed in the next section.

3.2. Correlation Energy Effect. There is a widely accepted opinion that the correlation energy should be explicitly taken into account in considering the electronic structure of planar systems. On the other hand, some evidence strongly indicates that its influence on the aromaticity is not significant. To shed some more light on this important problem with an emphasis on Clar's rule, we shall first discuss two formulas describing the aromatic stabilization of the archetypal benzene. Let us commence with homodesmotic reaction[3−6] based on linear open chain polyenes, which was thoroughly discussed recently:[28,29]

$$\text{benzene} + 3[\text{ethylene}] = 3[trans-1,3-\text{butadiene}] + E(\text{ease})_{\mathbf{B}} \quad (12)$$

where $E(\text{ease})_{\mathbf{B}}$ denotes the extrinsic aromatic stabilization. It was found that the impact of electron correlation energy on $E(\text{ease})_{\mathbf{B}}$ was small and that it was practically canceled by the zero point vibrational energy (ZPVE) effect.[28] This finding was in line with the earlier MP4 calculations by Haddon and Raghavachari,[59] being also compatible with general considerations, based on the atomic additivity of the correlation energy.[61] The latter strongly indicates that the correlation energy effect in homodesmic reactions is negligible in the first approximation, whereas it is very important in isodesmic reactions. A careful analysis has shown that the nondynamical correlation energy of the π-electrons $E(\text{ND})^{\pi}$ was lower in benzene compared to zigzag polyene (as, e.g., in eq 12), which was compensated by the $E(\text{D})^{(\pi)+\sigma}$ dynamical correlation of all valence electrons. A similar conclusion holds for homostructural reaction 13:

$$\text{benzene} + 3[\text{cyclohexene}] = 3[\text{cyclohexadiene}] + \text{cyclohexane} + E(\text{ease})'_{\mathbf{B}} \quad (13)$$

where all model compounds are considered to be planar as far as the carbon nuclei are concerned. It turned out that the MP2-(fc)/cc-pVDZ//HF/cc-pVDZ calculation increased aromaticity $E(\text{ease})'_{\mathbf{B}}$ by 3.7 kcal/mol in absolute value compared to the HF result.[29] Although the correlation contribution is obviously not decisive in determining extrinsic aromaticity by homodesmotic or homostructural reactions,[28,29] this is not necessarily so a priori in the case of eqs 8 and 9, which describe deformations of the Clar's equilibrium structures. The striking difference is that eqs 8 and 9 are related to intrinsic aromatic stabilization. Hence, the correlation energy effect should be meticuluosly examined before a final conclusion on Clar's rule could be drawn. The calculated MP2(fc)/cc-pVDZ correlation energies E_{corr} are summarized in Table 3. Let us commence with benzene. It turns out that the correlation energy stabilizes the D_{6h} structure by 3.6 kcal/mol. Even if it were the result of the π-electrons only, it would mean that the σ-framework prevails in the HF energy by a very small, but conceptually significant, amount of 1.2 kcal/mol. We shall come back to this point later. As to the condensed PAHs, a survey of the results reveals that a similarity between $E(\mathbf{n})_{corr}$ and $E(\mathbf{n}_a)_{corr}$ values is outstanding. The difference Δ(opt-deloc) is negligible with two notable exceptions. The MP2(fc) correlation energy is larger in the optimized geometries of coronene and hexabenzocoronene by 4.4 and 7.5 kcal/mol, respectively. This is, however, smaller than the

TABLE 3: Correlation Energies of Optimized, Delocalized and Localized Molecular Structures of Benzene and Condensed Benzenoid Systems (Figure 1)[a]

molecule	E(MP2)$_{\text{corr}}$ optimized (**n**)	delocalized (**n**$_a$)	localized (**n**$_b$)	Δ(opt-deloc)	Δ(opt-loc)
benzene	493.6		490.0		3.6
naphthalene	816.7	816.7	808.6 [810.5]	0.0	8.1 [6.2]
phenanthrene	1140.5	1140.8	1129.2 [1133.2]	−0.3	11.3 [7.3]
triphenylene	1466.2	1466.3	1451.6 [1454.9]	−0.1	14.6 [11.3]
anthracene	1141.5	1141.0	1129.1	0.5	12.4
tetracene	1467.8	1467.1	1452.8	0.7	15.0
pyrene	1298.9	1298.0	1284.7	0.9	14.2
dibenzopyrene	1949.9	1948.8	1929.7	1.1	20.2
kekulene	3893.3	3895.4	3851.6	−2.1	41.7
coronene	1940.3	1935.9	1916.0	4.4	24.3
hexabenzocoronene	3395.9	3388.4	3355.9	7.5	40.0

[a] $E(MP2)_{\text{corr}}$ is taken as a difference between the HF and MP2 total energies obtained by the MP2(fc)/cc-pVDZ method (in kcal/mol). Values given within squared parentheses correspond to the resonance structure **n**$_c$.

TABLE 4: Nondynamical and Dynamical Components of the Correlation Energy of Naphthalene 1 and Phenanthrene 2, Calculated at the CASSCF $(n, n)^{\pi}$/cc-pVDZ//MP2(fc)/cc-pVDZ, CASPT2 $(n, n)^{\pi}$/cc-pVDZ//MP2(fc)/cc-pVDZ and CASPT2 $(n, n)^{(\pi)+\sigma}$/cc-pVDZ //MP2(fc)/cc-pVDZ Level of Theory, along with Additivity Values[46] (in kcal/mol)[a]

	naphthalene				phenanthrene			
	1 optimized	**1**$_a$ delocalized	**1**$_b$ localized	additivity[b]	**2** optimized	**2**$_a$ delocalized	**2**$_b$ localized	additivity[a]
$E(\text{ND})^{\pi}$	78.0	78.0	76.5	83.0	108.8	108.6	105.0	115.9
$E(\text{D})^{\pi}$	33.4	33.8	32.7	29.2	48.2	49.0	47.3	42.0
$E(\text{D})^{(\pi)+\sigma}$	736.7	736.6	732.8	729.6	1027.2	1027.5	1020.6	1015.9
$E(\text{ND})^{\pi} + E(\text{D})^{\pi}$	111.4	111.8	109.2	112.2	157.0	157.6	152.3	157.9
$E(\text{ND})^{\pi} + E(\text{D})^{(\pi)+\sigma}$	814.7	814.6	809.3	812.6	1136.0	1136.1	1125.6	1131.8
$E(\text{MP2})_{\text{corr}}$	816.7	816.7	808.6		1140.5	1140.8	1129.2	

[a] MP2 correlation energies are given for comparison. [b] Additivity: $E(\text{ND})^{\pi} = 8.10n_{\text{C}} + 0.25n_{\text{H}}$, $E(\text{D})^{(\pi)+\sigma} = 69.27n_{\text{C}} + 4.61n_{\text{H}}$ and $E(\text{D})^{\pi} = 3.62n_{\text{C}} - 0.87n_{\text{H}}$.[46]

corresponding decrease in the $|\Delta E(\text{HF})_{\text{tot}}|$ values of 5.9 and 19.9 kcal/mol (Table 1) meaning that the σ-framework prevails in any case irrespective of the individual contributions of the σ- and π-electron subsets to the differential correlation energy. Nevertheless, the origin of the correlation effect deserves due attention, particularly if the artificial localized structures are considered. Consequently, the main body of the forthcoming discussion will be dedicated to localized geometries. The correlation energies of the idealized localized structures $E(\mathbf{n}_b)_{\text{corr}}$ are invariably and appreciably smaller than those found in the true optimized structures **n**. The differences under the heading Δ(opt-loc) in Table 3 yield the correlation contributions to the stability of the optimized equilibrium structures of the studied benzenoid molecules. They are sometimes as large as 41.7 and 40.0 (in kcal/mol) like in kekulene and hexabenzocoronene, respectively. It appears that the correlation energy affects the stability of Clar's structures more than the HF energy as a rule (viz. Tables 1 and 3) on going from "localized" structures **n**$_b$ to the optimal ones **n**. Hence, the question arises, whether it is possible to partition the correlation energy contributions into σ- and π-parts, as was done with the HF energies. Strictly speaking, this is impossible,[40] but a simple and intuitively appealing qualitative answer can be provided by considering separately the nondynamical and dynamical correlation energies. Let us focus on naphthalene **1** and phenanthrene **2** taken as representative examples, which are prone to a detailed analysis due to a small size. We shall try to delineate the role of the σ- and π-electrons in determining the total electron correlation energy by considering the nondynamical and dynamical components. The $E(\text{ND})^{\pi}$, $E(\text{D})^{\pi}$, $E(\text{D})^{(\pi)+\sigma}$ and $E(\text{MP2})_{\text{corr}}$ correlation energies are given in Table 4. They refer to values obtained by the CASSCF $(n, n)^{\pi}$/cc-pVDZ//MP2(fc)/cc-pVDZ, CASPT2 $(n, n)^{\pi}$/cc-pVDZ//MP2(fc)/cc-pVDZ, CASPT2 $(n, n)^{(\pi)+\sigma}$/cc-pVDZ//MP2(fc)/cc-pVDZ and MP2(fc)/cc-pVDZ methods, respectively. Here, (n, n) denotes the number of active electrons and orbitals correspondingly. It should be noticed that optimized MP2(fc)/cc-pVDZ geometries are used for the equilibrium structures (true minima on the BO hypersurfaces), whereas model structures are employed where appropriate as specified earlier. Keeping in mind that definition of the nondynamical and dynamical components of the valence electrons correlation energies is somewhat arbitrary, one can write

$$E(\mathbf{n})_{\text{corr}} = E(\mathbf{n})^{\pi}_{\text{corr}} + E(\mathbf{n})^{\sigma}_{\text{corr}} \tag{14}$$

where $E(\mathbf{n})^{\pi}_{\text{corr}} = E(\text{ND})^{\pi}_{\mathbf{n}} + E(\text{D})^{\pi}_{\mathbf{n}}$ and $E(\mathbf{n}_{\text{corr}})^{\sigma} = E(\text{D})^{(\pi)+\sigma}_{\mathbf{n}} - E(\text{D})^{\pi}_{\mathbf{n}}$ implying that the σ-electrons contribute only to the dynamical correlation. Perusal of the results presented in Table 4 reveals that the π-electron correlation energy in **1** is $E(\mathbf{1})^{\pi}_{\text{corr}} = 111.4$ kcal/mol. It is considerably lower than the $E(\mathbf{1})^{\sigma}_{\text{corr}}$ energy of 703.3 kcal/mol. The total correlation energy $E(\mathbf{1})_{\text{corr}} = 814.7$ kcal/mol is in good accordance with the $\mathbf{E(1)}^{\text{MP2}}_{\text{corr}}$ value of 816.7 kcal/mol, as it was observed in a number of other molecules earlier.[46] It is important to realize that a lion's share in stabilizaion of **1** due to the electron correlation effect arises from the valence σ-electrons. Obviously, the same holds for for the "delocalized" structure **1**$_a$, because the correlation energy components in **1** and **1**$_a$ are virtually the same (Table 4). The pivotal point is analysis of a difference in the correlation energy between the structures **1** and **1**$_b$. It appears that $E(\mathbf{1})_{\text{corr}} - E(\mathbf{1}_b)_{\text{corr}} = \Delta E^{\pi}_{\text{corr}} + \Delta E^{\sigma}_{\text{corr}} = 5.4$ kcal/mol, where $\Delta E^{\pi}_{\text{corr}}$ and $\Delta E^{\sigma}_{\text{corr}}$ assume 2.2 and 3.2 kcal/mol, respectively, implying that the contribution of the σ-electrons is larger by 1 kcal/mol. Similar results are obtained for phenanthrene **2**. The σ-correlation energy has an overwhelming influence on the stability of **2** ($E(\mathbf{2})^{\sigma}_{\text{corr}} = 979.0$ kcal/mol) compared to the π-electron contribution ($E(\mathbf{2})^{\pi}_{\text{corr}} = 157.0$ kcal/mol). Further,

TABLE 5: Nondynamical and Dynamical Components of the Correlation Energy in Benzene (in kcal/mol)

	optimized B	localized CHT	additivity[a]
$E(\mathrm{ND})^{\pi}$	46.1	45.1	50.1
$E(\mathrm{D})^{\pi}$	18.8	18.3	16.5
$E(\mathrm{D})^{(\pi)+\sigma}$	447.1	444.8	443.3
$E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{\pi}$	64.9	63.4	66.6
$E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma}$	493.2	489.9	493.4
$E(\mathrm{MP2})_{\mathrm{corr}}$	493.6	490.0	−

[a] Additivity: $E(\mathrm{ND})^{\pi} = 8.10n_{\mathrm{C}} + 0.25n_{\mathrm{H}}$, $E(\mathrm{D})^{(\pi)+\sigma} = 69.27n_{\mathrm{C}} + 4.61n_{\mathrm{H}}$ and $E(\mathrm{D})^{\pi} = 3.62n_{\mathrm{C}} - 0.87n_{\mathrm{H}}$.[46]

the difference $E(\mathbf{2})_{\mathrm{corr}} - E(\mathbf{2}_{\mathrm{b}})_{\mathrm{corr}} = 10.4$ kcal/mol can be broken down to the σ- and π-electron contributions $\Delta E^{\sigma}_{\mathrm{corr}}$ and $\Delta E^{\pi}_{\mathrm{corr}}$ being 5.7 and 4.7 kcal/mol, respectively. Because the difference between correlation energy components between **2** and **2**$_{\mathrm{a}}$ is negligible, it is fair to conclude that the π- and σ-electron contributions to the stability of Clar's structures in systems **1** and **2** are approximately the same. It is also plausible to assume that this corollary holds for all systems studied here. Namely, the more abundant σ-electrons populate lower MOs, thus being less susceptible to excitations necessary in describing the electron correlation. In contrast, the π-electrons are less numerous, but they are placed in the MOs possessing higher orbital energies, thus implying easier excitations. These two opposing effects are roughly balanced in planar molecules. Hence, the difference in stability between Clar's and virtual structures can be reduced to the difference in their HF energies. It is worth noting that the $E(\mathbf{2})^{\mathrm{MP2}}_{\mathrm{corr}}$ value is again comparable to the total electron correlation $E(\mathbf{2})_{\mathrm{corr}} = E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma}$. Consequently, we shall use the MP2 estimates of the correlation energy in large systems.

It is well documented by now that various components of the correlation energy exhibit the atomic additivity property.[28,45,46,62] We shall employ the additivity formulas for planar systems, which were extensively discussed in our earlier paper,[46] and compare the correlation energy estimated by the additivity rules with the results of the actual calculations employing methods mentioned above. It turned out that the nondynamical correlation energy $E(\mathrm{ND})^{\pi}$ of the π-electrons in true equilibrium geometries of **1** and **2** was lower than that predicted by the additivity rule, as expected for the aromatic compounds (Table 4). It was namely found that the $E(\mathrm{ND})^{\pi}$ values are higher in linear open chain polyenes and nonaromatic π-molecules compared to the aromatic ones.[45,63] This decrease in stability is to some extent remedied by the dynamical correlation $E(\mathrm{D})^{\pi}$ of the π-electrons (Table 4), but the total $E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{\pi}$ energy in naphthalene is still smaller than the additivity estimate albeit by only 0.8 kcal/mol. A turnover is a consequence of the dynamical correlation of the σ-electrons reflected in the $E(\mathrm{D})^{(\pi)+\sigma}$ value, which is larger in the optimized Clar's structure by 7.1 kcal/mol than the additivity result. The bottom line is that the total correlation energy $E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma}$ is larger in true equilibrium structure of **1** by 2.1 kcal/mol than the additivity value (Table 4). It follows that the σ-electrons contribute to the correlation energy of **1** by 2.9 kcal/mol more than the π-electrons.

This is compatible with previous conclusion based on the computed $E(\mathrm{ND})^{\pi}$, $E(\mathrm{D})^{\pi}$, $E(\mathrm{D})^{(\pi)+\sigma}$ components. The same results and conclusions are obtained for phenanthrene, as evidenced by the data in Table 4.

The prototypal limiting case benzene deserves a separate comment, although the pattern is the same (Table 5). It appears that the σ- and π-electrons contribute to the equilibrium D_{6h} structure 1.8 and 1.5 kcal/mol, respectively, due to the correlation energy effects. Hence, we are in position to state that the perfectly symmetric benzene structure is beyond doubt a consequence of the σ-framework. It is noteworthy that the total correlation energies $E(\mathrm{ND})^{\pi} + E(\mathrm{D})^{(\pi)+\sigma}$ are once more in good agreement with MP2 estimates. They are 493.2 (493.6) and 489.9 (490.0) kcal/mol in **B** and **CHT**, respectively, where the MP2 results are given within parentheses.

To epitomize, Clar's structures are more stable than any other conceivable geometries due to predominant σ-effects reflected in the HF energies. This inference is based on the following chain of arguments: (1) the differences between $E(\mathrm{MP2})^{\mathrm{opt}}_{\mathrm{corr}}$ and $E(\mathrm{MP2})^{\mathrm{deloc}}_{\mathrm{corr}}$ are insignificant. The $E(\mathrm{ND})^{\pi}$, $E(\mathrm{D})^{\pi}$ and $E(\mathrm{D})^{\sigma}$ correlation energies obtained by the CASSCF and CASPT2 calculations for **1** and **2** strongly indicate that influence of the σ-electrons is overwhelming. (2) $E(\mathrm{MP2})^{\mathrm{opt}}_{\mathrm{corr}}$ is appreciably larger than $E(\mathrm{MP2})^{\mathrm{loc}}_{\mathrm{corr}}$, but (3) the deviations $E(\mathrm{MP2})^{\mathrm{opt}}_{\mathrm{corr}} - E(\mathrm{MP2})^{\mathrm{loc}}_{\mathrm{corr}}$ can be apportioned to the σ- and π-electrons in approximately equal amounts, as revealed by the analysis of the E^{π}_{corr} and $E^{\sigma}_{\mathrm{corr}}$ contributions. Therefore, it is safe to conclude that Clar's structures are stable due to the dominant features of the σ-framework mirrored in the HF energies.

As a footnote, let us mention that the differences in the MP2(fc) energies between the resonance structures $\mathbf{n}_{\mathrm{b}} - \mathbf{n}_{\mathrm{c}}$ ($\mathbf{n} = \mathbf{1}$, **2**, **3**) are −4.1, −6.6 and −8.3 kcal/mol, respectively, implying that the $\mathbf{n}_{\mathrm{b}}$ resonance structure satisfying the (anti)-Mills−Nixon rule[55,56] are more stable, thus corroborating conclusion drawn earlier by considering the HF energies.

3.3. Structural Characteristics. We shall briefly discuss the structural features of the optimized geometries. Let us recall for this purpose that the gauge values are distances $d(\mathrm{CC}) = 1.406$ Å in benzene, $d(\mathrm{C{=}C}) = 1.460$ Å and $d(\mathrm{C{-}C}) = 1.339$ Å in 1,3-butadiene, respectively, as calculated by the MP2(fc) method. The computed MP2(fc) geometries of compounds **n** are given in Figure 2. We shall distinguish two types of the six-membered rings in Clar's structures: the benzene-like denoted by **A** and the rings signified as **B**, possessing either a "localized" π-bonds as in **2**, or an "empty" cyclic perimeter like in **3** (viz. Figure 1). Two parameters characterizing these rings are pivotal. The first is the average CC bond distance $d(\mathrm{CC})_{\mathrm{av}} = (1/6)\sum_{i=1}^{6} d(\mathrm{CC})_i$ and the anisotropy of the bond distances $\Delta(\mathrm{CC}) = \sum_{i=1}^{6}|d(\mathrm{CC})_i - d(\mathrm{CC})_{\mathrm{av}}|$. Perusal of the average bond distances reveals that all rings are blown up relative to benzene. It comes as no surprise that rings of the type **B** are more enlarged than those of the type **A**. The arithmetic means over compounds **n** (**n** = **2**, **3**, **6**, **7**, **8**, **9**, **10**) for rings **A** and **B** are 1.416 and 1.437 Å, respectively. It is noteworthy that the difference is 0.02 Å, which is not a dramatic change, although it is significant. Another interesting piece of information is that variations around these arithmetic means are small, as evidenced by the average absolute deviations of 0.003 and 0.007 Å, respectively. It follows that the size of the rings **A** and **B** is not grossly different between counterparts in compounds **2**, **3**, **6**, **7**, **8**, **9** and **10**. Let us turn to the anisotropies starting with systems **2** and **3**. The Δ(CC) values for the rings **A** and **B** in the former compound are 0.08 and 0.11 Å, respectively. Analogously, the corresponding data in compound **3** are 0.07 and 0.12 Å, respectively. It is remarkable that the anisotropies of the rings possessing a "localized" π-double bonds (in **2**) and an "empty perimeter" (in **3**) are almost the same. The average anisotropy values for compounds **2**, **3**, **6**, **7**, **8**, **9** and **10** obtained for the rings **A** and **B** are 0.06 and 0.10 Å, respectively. It appears that anisotropy of the latter rings is not so large in general as it might be expected according to a simplified picture put forward by Clar, which is an important

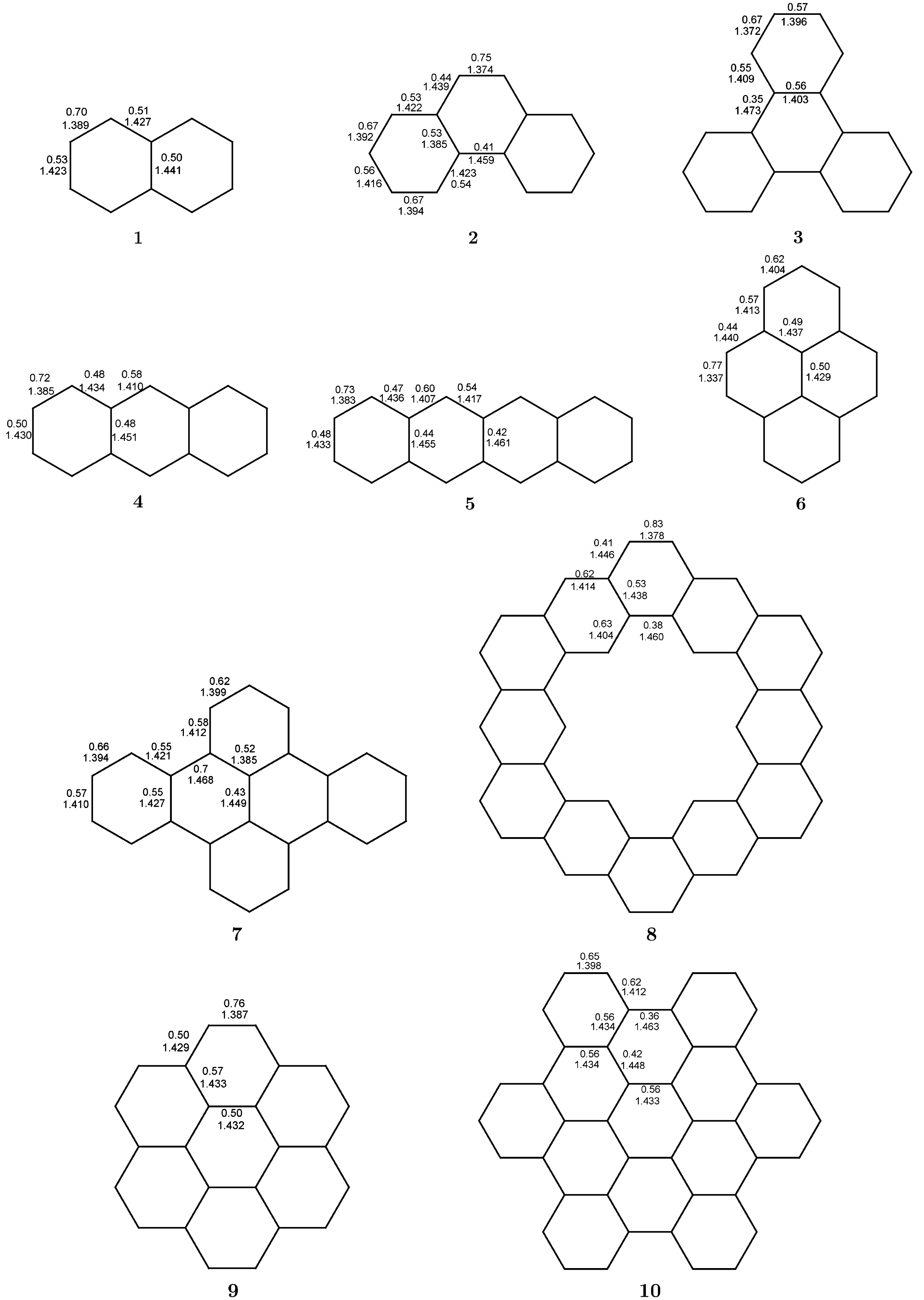
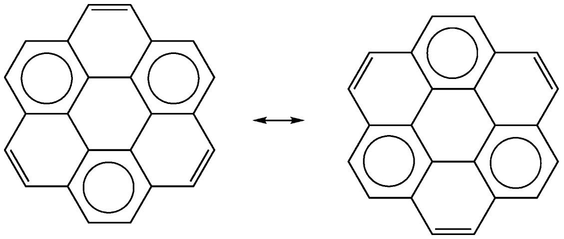


Figure 2. CC bond distances (in Å) and π-bond orders of all molecules.

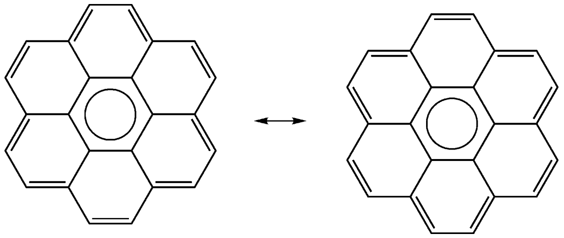
observation. Analysis of the π-electron density distributions given by the π-bond orders corroborates this conjecture (vide infra). A noteworthy anomaly is found in **10**, where the central benzene-like ring is embedded in a corona of the "empty" benzenes. The latter exhibit a lower anisotropy $\Delta(CC) = 0.06$ Å, than the outermost "full benzenes", which have $\Delta(CC) = 0.09$ Å. Finally, a few words on linear acenes **1**, **4** and **5** are in place here. Their rings do not differ much in size as revealed by the $d(CC)_{av(p)}$ and $d(CC)_{av(c)}$ distances, where "p" and "c" denote peripheral and central rings, respectively. Let us give diads [$d(CC)_{av(p)}$; $d(CC)_{av(c)}$] for acenes **1**, **4** and **5**. The corresponding values read (in Å) [1.416; 1.416], [1.420; 1.424] and [1.421; 1.427], thus proving the point and indicating that benzene moieties are enlarged. Actually, the average CC distances increase with the size of the system. The idea of Clar that the benzene ring is "diluted" in linear acenes is fitting. If an acene is odd like **4**, then the asymmetry of the central ring is considerably lower, as evidenced by $\Delta(CC)_c = 0.06$ Å as compared to $\Delta(CC)_p = 0.14$ Å.

The π-electron bond orders (π-bo) calculated by using Löwdin's[60] symmetric orthogonalization procedure are given within parentheses in Figure 2. We shall discuss just a few characteristic compounds as illustrative examples, because the rest of the data speak for themselves. Let us commence with **2**, where a localized π-double bond in the central ring has π-bo 0.75, which should be compared with that found in ethylene (0.94) and 1,3-butadiene (0.88). It is remarkable that other CC bonds have π-bo 0.41 (0.44), unless they are coalesced with benzene rings (0.53), which is comparable to the central C−C bond in 1,3-butadiene (0.34). In the case of two peripheral rings the π-bo are spread between 0.5 and 0.7, which is fairly close to that in benzene (0.62). Analysis of these data shows that there is a small, but significant degree of delocalization within the central ring and a weak localization within the peripheral rings. It appears that there is a π-electron "communication" between the peripheral rings and a "localized" π-double bond, and between the peripheral rings themselves. The same conclusion holds for compounds **3** and **6**, as expected. Let us consider the system **3** in some more detail. The peripheral rings possess again a fairly even distribution of the π-electron density reflected in the π-bos spread between 0.56 and 0.67. On the other hand, the central ring has alternating π-bo of 0.56 and 0.35. It should be stressed that it is by no means a π-electron empty ring. There is a significant "communication" between the peripheral rings via π-electrons across the central ring evidenced by the π-bo 0.35. Obviously, there are no completely "isolated aromatic sextets" and entirely "π-electron empty" six-membered rings. Taking this fact into account, the structure of triphenylene **3** is best understood as a system of three coalesced naphthalenes.[56] It follows that the real picture is much more subtle than Clar's idea symbolically denoted by the embedded circles, because of the delocalized nature of electrons in general and of the π-electrons in particular. A realistic description requires more resonance structures than implied by Clar's rule. Nevertheless, Clar's picture is a good starting point, which should be subsequently refined. This conclusion holds for all congested systems studied here but linear acenes, which in turn form a special subset for obvious reasons. One of the special cases deserving a comment is coronene **9**, where at least two equivalent structures are necessary to describe the symmetry of the system (Scheme 1).

SCHEME 1



SCHEME 2



Consequently, a use of a single Clar's structure would be highly misleading, thus illustrating the point expounded above. Moreover, the central ring has a perfect D_{6h} symmetry, implying equal bond lengths and uniform π-bo distribution. It is very interesting to mention that all π-bos are 0.5, meaning that they are lower by only 0.1 compared to free benzene. Hence, the contribution of the aromatic central ring to the stability of coronene should be significant (Scheme 2). Another point of interest is that there is a pronounced alternation of the π-bos over the outer perimeter, which does not form an aromatic ribbon despite 18π-electrons. This is a rather nice illustration of the fact that Hückel's $(4n + 2)\pi$ rule does not work in condensed systems. We note parenthetically that the π-bos of the CC bonds between the outer perimeter and inner six-membered ring are very high, being 0.57, thus providing conclusive evidence that **9** is not a simple superposition of an aromatic sextet embedded in an 18π-electron aromatic perimeter.

Similarly, the central ring in hexabenzocoronene **10** has D_{6h} symmetry too, like its counterpart in **9**, but the π-bond order is even higher (0.56), approaching the value for benzene. The π-bond orders of the CC bonds emanating from the central ring are 0.42, which means that the latter quite intensively interacts with the peripheral parts of the system via mobile π-electrons. Despite that, it is customary to characterize the central ring as a benzene moiety annelated to the six-membered rings characterized as the "π-electron deserted area" (Figure 1). Obviously, such representation should be taken with an utmost care.

As a final comment, let us briefly consider the total sums of the π-bos of particular six-membered rings denoted by SPBO (Figure 2). The π-electron "full" benzene-like rings have typical SPBO values between 3.50 (**2**) and 3.66 (**10**). On the other hand, the characteristic SPBO values for "vacant" rings are 2.73 (**3**), 2.74 (**7**), 2.86 (**10**) and 3.00 (**9**). It is plausible to suppose that rings with higher SPBO values contribute more to the stability of a compound than the lower ones, which would be in harmony with Clar's hypothesis. This is perfectly acceptable at the π-electron level of the theoretical description of condensed benzenoid systems. However, we would like to issue a caveat emptor that the decisive contribution to the stability of Clar's structures comes from the σ-framework as conclusively shown in this paper. It is also important to bear in mind that the rings with inscribed circles may markedly differ in their properties and energetic contents within the same molecule or between different systems. For instance, the central and outermost benzene-like rings in **10** possess SPBOs of 3.36 and 3.66, respectively. Naturally, the latter stabilize **10** more than the former ring. At the same time, the outer rings exhibit appreciable bond length anistropy (Δ(CC) = 0.09 Å), whereas the anisotropy of the central ring is nil. This is in sharp contradiction with the principle that lower bond alternation implies higher aromaticity, which casts doubts on the use of nonthermodynamic indices in discussing stability of the planar π-systems. As to the difference of the benzene rings between various condensed benzenoids, it is quite clear that the outermost ring in **10** is widely different from its counterpart, e.g., in **6**. It is therefore fair to conclude that Clar's circles in benzenoid planar systems imply only that the π-electron sextet spin coupling in appropriate six-memebered rings, represent a spin pairing scheme in the VB structure possessing large weight in the final wave function. However, the actual weighting coefficients strongly depend on the global electronic structure of a system under scrutiny. The bottom line is that Clar's hypothesis offers a useful rule of thumb in interpreting the thermodynamic stability of condensed benzenoid systems, but nothing more than that. Quantitative information should be sought and found by ab initio computations.

4. Concluding Remarks

We have shown that: (1) The so-called Clar's structures are the only minima on the MP2(fc) BO potential energy hypersurfaces, implying that their presumed valence isomers are nonexistent. (2) The influence of the electron correlation energy on the stability of Clar's structures is very large with the overwhelming contribution of the σ-electrons. However, the electron correlation contributions of the σ- and π-electrons are approximately the same, when Clar's structures are compared with artificial π-electron localized or graphit-like delocalized model systems. (3) As to the HF energies, a careful analysis provides compelling evidence that stability of Clar's structures originates in a substantial decrease in the T, V_{ee} and V_{nn} terms relative to both "delocalized" and "localized" model geometries. (4) Partitioning of the mixed $V_{\mathrm{ee}}^{\sigma\pi}$ and $V_{\mathrm{nn}}^{\sigma\pi}$ terms into the σ- and π-type contributions, by using widely different SHR, EQP and SPI decomposition schemes, convincingly shows that the driving force leading to stable Clar's structures are favorable σ-type interactions. This result is independent of the partitioning scheme used. (5) All these conclusions hold for benzene, which can be considered as the simplest possible Clar's structure. (6) Analysis of the structural parameters and π-bond orders convincingly shows that there are no the π-electron "vacant" and "fully occupied" benzene rings. The fact of the matter is that the MP2(fc) geometries and distribution of the π-electron densities do exhibit some similarity with those of idealized structures envisaged by Clar, but the true picture is much more subtle. (7) An interesting byproduct of the present analysis is that the Kekulé resonance structures conforming to (anti)-Mills−Nixon bond fixation are more stable than their counterparts, which do not satisfy the (anti)-MN rule.

To summarize in two sentences: Clar's hypothesis represents a useful rule of thumb in determining the thermodynamic stability of condensed PAHs in qualitative terms. Quantitative information on the structural and energetic properties of these systems can be obtained only by careful analysis of the experimental and ab initio computational data.

Acknowledgment. This paper is dedicated to Professor Rolf Gleiter on the occasion of his 70th birthday.

Supporting Information Available: Table of energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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