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Analysis of MO Ground States of Benzenoid Hydrocarbons in Terms of BORT Resonance Structures

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In order to determine the most important resonance structures in the description of benzenoid hydrocarbons, Hückel and Pariser-Parr-Pople ground states of all such hydrocarbons with up to five benzene rings were analyzed in terms of BORT resonance structures. Due to the exponential increase of the number of resonance structures with the size of a benzenoid molecule, we used an approximate optimization procedure based on the greedy algorithm. The analysis of cumulative contributions of various sequences of resonance structures to the MO ground states of the considered benzenoids reveals that, besides the Kekulé structures, Claus structures are also very important in the description of these systems. The relative importance of Claus structures can be attributed to the local benzene-like character of these π-electron systems, and to the fact that benzene ground state is exactly represented as a linear combination of the two Kekulé and one Claus structures. The relative importance of other types of structures is generally much smaller. The real contribution of these other structures is somewhat obscured due to their large number and nonorthogonality.

INTRODUCTION

Many aspects of chemistry of benzenoid hydrocarbons (BHs) are commonly interpreted in terms of resonance among various π-electron bonding schemes. It is a well-known property of the valence-bond (VB) quantum-chemical methods that a number of resonance structures increases exponentially with the number of π-electrons. Accordingly, the ability to obtain the

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exact solution of the corresponding eigenvalue problem decreases rapidly with the size of the chemical system.[1–3] Hence, for practical success of these methods it is crucial to have fast convergent expansions in terms of resonance structures.

It has been shown that within the bond-orbital-resonance-theory (BORT) approach the benzene π-electron self-consistent field (SCF) ground state can be represented as a linear combination of only three resonance structures shown in Figure 1: two Kekulé structures, **1** and **2**, and one Claus structure, **3**.[4] For comparison, in order to describe the same ground state within the traditional VB approach, one has to include the three Dewar structures and a number of ionic structures in addition to the two Kekulé structures. It has also been shown that the contribution of the ionic structures is very significant.[5,6] In the usual VB calculations the Claus structure is not considered mainly due to Rumer's non-crossing rule.[7]

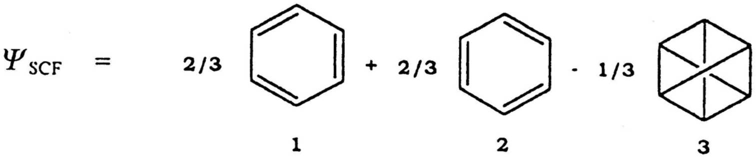

Figure 1. Expansion of the benzene SCF ground state in terms of three BORT resonance structures: Kekulé structures **1** and **2**, and Claus structure **3**. Structure **3** was first introduced by Adolf Claus in 1867. He suggested this completely crossed bonding scheme in order to explain the fact that the ortho-disubstituted derivatives of benzene exist in only one isomeric form.

The remarkably simple BORT representation of the benzene SCF ground state suggests that in addition to the Kekulé structures, Claus structures may also be important in the description of ground states of other BHs.[8] In order to test this assumption we performed systematic computations on all cata- and peri-condensed benzenoids with, at most, five fused benzene rings, shown in Figure 2. A single-determinantal molecular orbital (MO), Hückel or Parriser-Parr-Pople (PPP),[9] ground-state wave function of each BH was analyzed in terms of BORT resonance structures in such a way as to maximize its projection onto a space of these bonding schemes. Because of the huge number of resonance structures, an approximate optimization procedure based on a greedy algorithm was used.

In the BORT approach the π-electron wave function is represented as a linear combination of the so-called regular resonance structures. These resonance structures are defined in the next section. In Section 3 the optimization procedure is briefly described. The results are presented and discussed in Section 4, and the concluding remarks are given in the last section.

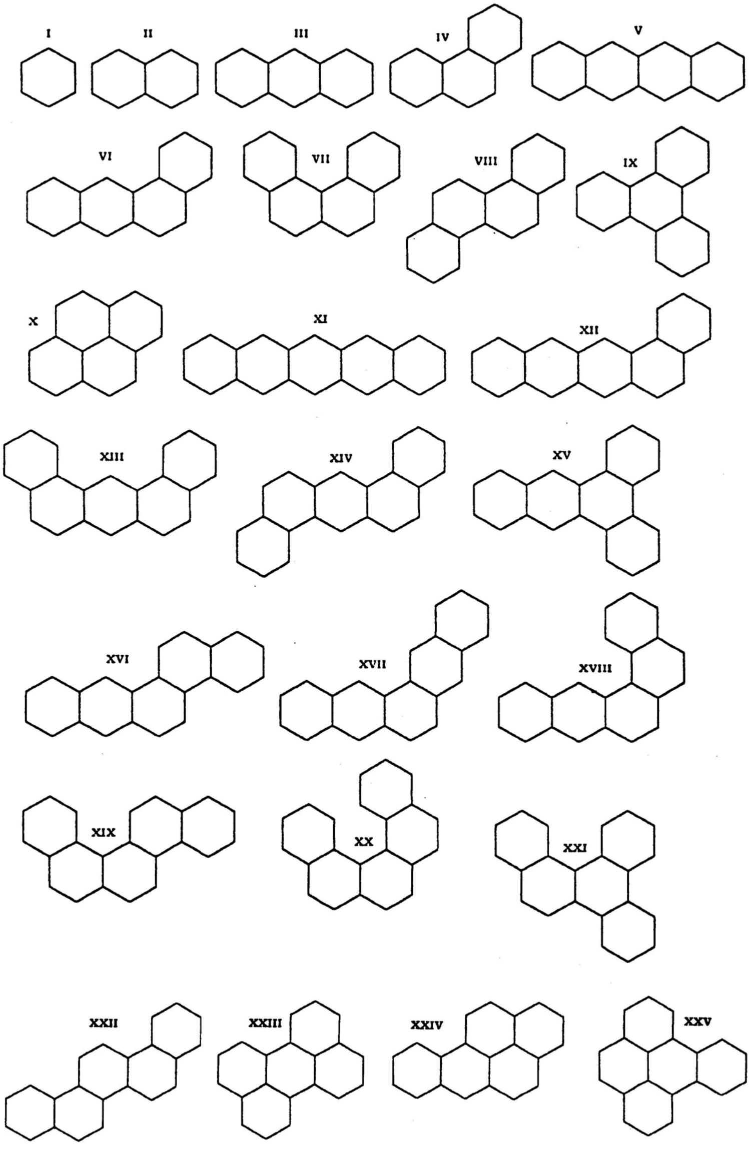

Figure 2. Benzenoid hydrocarbons containing up to five benzene rings.

REGULAR RESONANCE STRUCTURES

Regular resonance structures (RRSs) are defined in the following way:[10–13]

(i) Partition set B containing $2n$ orthonormalized orbitals χ_i into subsets B° and B^* containing n source and n sink orbitals, respectively. In the case of conjugated alternant hydrocarbons, such as BHs, this partition may coincide with the partition on starred and unstarred atoms, while orbitals χ_i may correspond to carbon $2p_z$ atomic orbitals.

(ii) Form nonexcited and excited bond orbitals

$$\phi_{ij} = 2^{-1/2} (\chi_i + \chi_j) \quad \text{nonexcited bond orbital}$$

$$\phi_{ij}{}^* = 2^{-1/2} (\chi_i - \chi_j) \quad \text{excited bond orbital} \tag{1a}$$

satisfying the condition:

$$\chi_i \in B^\circ, \quad \chi_j \in B^* \tag{1b}$$

that is, each bond orbital connects one source and one sink orbital.

(iii) Each Slater determinant containing n mutually disconnected nonexcited and/or excited bond orbitals satisfying condition (1b) is an n-electron regular resonance structure.

The set of all n-electron RRSs spans the configuration interaction (CI) space X_n generated by n electrons moving over $2n$ atomic orbitals.

In the graphic representation of RRS, atomic orbitals are displayed as vertices, while nonexcited and excited bond orbitals are shown as nonoriented and oriented bonds, respectively. Although there is a formal graphic similarity between BORT and VB resonance structures, these structures are fundamentally different and they represent physically completely different functions.[10–13]

In this work we used a simplified BORT approach in which spin-α and spin-β electrons are treated separately. Within this approximation, a closed-shell ground state Ψ of a $2n$-electron molecule is written in a spin-separated form as

$$\Psi = |{}^\alpha\Phi \, {}^\beta\Phi > \tag{2}$$

where ${}^\alpha\Phi$ and ${}^\beta\Phi$ are spin-α and spin-β n-electron substates, respectively. This approximation is not as good as full CI, but it is better than the SCF approach since each single-determinantal MO ground state can be always represented in the spin-separated form of Eq. (2). In the case of closed-shell systems, states ${}^\alpha\Phi$ and ${}^\beta\Phi$ are equivalent up to the spin, and it is sufficient to consider only one of them, *e.g.* ${}^\alpha\Phi$. For the sake of simplicity we shall use the symbol Φ instead of ${}^\alpha\Phi$ in the remaining part of the article, and we shall refer to this state as a ground state. The state Φ is an n-electron state and it can be expanded in terms of n-electron RRSs:

$$\Phi = \Sigma_i \lambda_i S_i \tag{3}$$

where λ_i are coefficients of linear expansion and S_i are RRSs.

The set of all RRSs is overcomplete. This set can be partitioned into two subsets containing »positive« and »negative« structures, respectively. In the case of alternant systems these subsets do not interact with each other, and ground states of alternant systems contain only RRSs of the same parity[13]. Without losing generality, we can choose these structures to be positive. There is a simple graphic way of determining the relative parity of two RRSs.[13] First, one forms the superposition G_{ij} of two structures S_i and S_j by superimposing their graphical representations. Superposition G_{ij} consists of disconnected even cycles C_μ. Each cycle is characterized by two numbers, n_μ and m_μ, where $2n_\mu$ is the number of bonds in C_μ, while m_μ is the number of oriented bonds in C_μ. Cycle C_μ is called »passive« if $(n_\mu + m_\mu)$ is even, and »active« if $(n_\mu + m_\mu)$ is odd. If the superposition G_{ij} contains an even number of passive cycles, the structures S_i and S_j are of the same parity. Otherwise, they are of the opposite parity. Terms »passive« and »active« are justified by the fact that in the case of alternant systems structures S_i and S_j do not interact with each other if their superposition G_{ij} contains at least one passive cycle.

The partition on positive and negative structures decreases twice the number of structures to be considered. Moreover, it can be shown that each RRS containing two or more excited bond orbitals can be expressed as a linear combination of RRSs containing at most one excited bond orbital.[12] Accordingly, there is no need to consider numerous structures with more than one excited bond orbital.

The number of RRSs which need to be considered is thus greatly reduced, but it is still larger than the dimension of the corresponding CI space X_n.[12] The redundancy of the basis set is not necessarily a disadvantage. It offers a wide flexibility in the choice of RRSs since the same ground state can be represented in many different ways as a linear combination of various RRSs. Since fast convergent expansion is desirable, it is important to find out which sequences of resonance structures have optimal convergence properties with respect to the ground state, and which thus determine the most important resonance structures for the description of ground-state properties.

Since the number of positive RRSs with, at most, one excited bond orbital still increases exponentially with the number of π-electrons, it is practically impossible to verify all possible sequences. One is therefore forced to use some plausible criterion to select optimum structures. Usually, the energy criterion is applied. According to this criterion, the familiar Kekulé structures are considered first because they have the lowest energy among all types of bonding schemes. Next, structures are considered which are energetically closest to the Kekulé structures, and so on. Concerning the energy criterion, two points should be emphasized. First, the sequence of resonance structures is not uniquely defined by this criterion since all structures which have the same energy can be permuted in an arbitrary order. Second, the Claus structures, which are expected to be quite important in the description of BHs' ground states, are very unfavourable according to the energy criterion.[8] According to the estimation using the simple Hückel Hamiltonian, the Claus structures lie 3β (β is a Hückel resonance integral) above the Kekulé structures. Hence, they should be considered after all energetically singly- (or 1β-) and doubly- (or 2β-) excited resonance structures are taken into account.

In order to assess the relative importance of various RRSs, particularly Kekulé and Claus RRSs, we have applied the following optimization approach.

OUTLINE OF THE APPROACH

Assuming the spin-separation approximation (Eq. (2)), the spin-α substate Φ of the full $2n$-electron reference ground state is analyzed in terms of positive n-electron RRSs, possessing at most one excited bond orbital. Due to the huge number of such RRSs, it is usually impossible to take them all into account. Hence, one has to consider some subset of all these structures, and this subset has to contain the most important structures.

Efficient identification of the most important structures requires the solution of the following numerical problem. Given the set $\mathcal{S} = \{S_i \mid i = 1,...,k\}$ containing k resonance structures, and assuming that one can take into account only r structures, consider all possible subsets $\mathcal{S}_r$ containing only r structures, and find an optimum subset $\mathcal{S}_r^{\circ}$. In order to find this optimum subset, one has to construct for each subset $\mathcal{S}_r$ the state Φ_r, a linear combination of structures $S_i \in \mathcal{S}_r$, which approximates the ground state Φ in the best way. Next, one has to compare all such states Φ_r in order to find the optimum state Φ_r°, which then determines the optimum subset $\mathcal{S}_r^{\circ}$.

In order to solve this problem in a general way, it is necessary to consider all possible subsets $\mathcal{S}_r$ containing r RRSs, to compare their efficiencies, and to choose the best one. However, the number of all such subsets is $k!/r!(k-r)!$, which increases exponentially with k and r. This is computationally not feasible even for relatively small values of k and r. Therefore, one has to devise an approximate approach. We have chosen to use an approach based on the greedy algorithm. Such an approach produces an *optimum sequence* of the RRSs, thus providing an efficient tool for picking out the most important bonding schemes. The approach works as follows.

Given the set $\mathcal{S} = \{S_i \mid i = 1,...,k\}$ of k RRSs, one first chooses the structure $S_p \in \mathcal{S}$ which best approximates the ground state Φ. This choice determines the optimum subset $\mathcal{S}_1{}^\circ$ containing only one RRS. Next, one considers all subsets $\mathcal{S}_2$ that contain the already chosen structure S_p and any other structure $S_i \in \mathcal{S}$. Among all such subsets, one chooses the optimum one. Next, one considers all subsets $\mathcal{S}_3$ containing the two structures already selected, and as the third structure any remaining structures $S_i \in \mathcal{S}$. Among all subsets $\mathcal{S}_3$, one again chooses the optimum one. This process is repeated iterativelly with each subsequent subset $\mathcal{S}_r$. In the r-th step $(r-1)$ structures are already selected, and hence there are only $(k-r+1)$ remaining structures $S_i \in \mathcal{S}$ to be considered.

This approach is numerically much more efficient than the general method. In each step one has to consider only $(k-r+1)$ instead of $k!/r!(k-r)!$ subsets $\mathcal{S}_r$. Of course, one pays the price of not obtaining the true optimum subset. However, the obtained subset $\mathcal{S}_r{}^\circ$ is the best one for each step in the sense that, provided the $(r-1)$ already selected structures are retained, the one which maximally improves approximate ground state is chosen as the r-th structure. Although the subset $\mathcal{S}_r{}^\circ$ obtained in this way is not necessarily optimal, it is likely to be very close to the real optimum subset. This slight disadvantage is highly offset by the extreme improvement in the efficiency of the algorithm. Accordingly, the sequence of RRSs obtained in this way is optimal in the sense that in each step the next structure to be included maximally improves the approximate ground state, and thus it provides a natural way of recognizing and picking out the most important structures.

It remains to be specified in which sense state Φ_r is an optimum approximation of the ground state Φ. Different criteria are possible, and we have chosen to minimize the mean-square deviation of an approximate ground state Φ_r from the reference, Hückel or PPP, ground-state wave function Φ. This is equivalent to the maximization of a square of overlap between Φ_r and Φ

$$W_r = | < \Phi_r \mid \Phi > |^2. \tag{4}$$

W_r is the probability of finding the approximate state Φ_r in the reference state Φ. It gives the cumulative contribution of the r RRSs contained in set $\mathcal{S}_r{}^\circ$ to the ground state Φ. The sequence $\{W_r \mid r = 1, 2,...k\}$ approaches unity as r increases, and the rate of this approach to unity serves as an indicator of the quality of this sequence.

To the above method for obtaining an optimum sequence, one can impose various additional conditions. In this way one can produce various optimum sequences. In order to obtain a better insight into the relative importance of different RRSs, we have considered two types of optimum sequences. If no condition for the construction of the optimum sequence is imposed, one obtains a so-called unrestricted sequence. In general, the most important structures appear at the beginning of the unrestricted sequence, while less important structures appear at the end of this sequence. Another type of optimum sequence is obtained by imposing the energy criterion. This so-called energy sequence is obtained by first partitioning the set $\mathcal{S} = \{ S_i \mid i = 1,...,k\}$ into different subsets which are ordered according to the energy criterion. In the simple Hückel scheme the first subset thus contains all Kekulé RRSs, the second subset contains all singly-excited RRSs which are energetically 1β above the Kekulé structures, *etc.* Optimum sequence is now constructed in such way as to obey this energy condition. In other words, Kekulé structures are optimized first, and next all singly-excited RRSs are optimized, *etc.*

The above approach can be directly applied only to relatively small BHs. Due to the huge number of RRSs, one cannot carry out complete calculations for larger BHs. Therefore, we have slightly modified this approach, and in search for a subset of RRSs that produces an optimum sequence we have employed the following heuristic procedure. First, a series of truncated optimization calculations were performed for naphthalene, **II**, anthracene, **III**, and phenanthrene, **IV** (see Figure 2) which have comparatively small π-electron systems. In these calculations, we have employed the sets of all energetically singly- and doubly-excited RRSs. In addition, we have also examined the relative importance of some Claus-like types of triply-excited RRSs (see next section). Energy and unrestricted sequences for different subsets of Kekulé structures, singly- and doubly-excited structures, Claus and Claus-like structures have been generated and analyzed for these π-electron systems. In this way we have made a preliminary selection of relatively more important types of RRSs, and at the same time we have developed a systematic procedure for producing the optimum, that is, nearly optimum unrestricted sequence for a benzenoid molecule.

In the next stage of this heuristic procedure, optimum sequences are formed for all larger BHs shown in Figure 2. The unrestricted sequence for each BH is obtained by projecting the reference ground-state wave function onto a space of selected efficient types of RRSs in a systematic way: sets of RRSs of different types are optimized separately. The first few most important structures of all unrestricted sequences thus obtained are then combined into a new set. It is assumed that unrestricted optimization of this combined set produces the most convergent, that is, optimum sequence for a given BH. Accordingly, the leading structures of this sequence are assumed to correspond to the most important bonding schemes in the representation of the single-determinantal MO ground-state wave function of a particular benzenoid molecule.

RESULTS AND DISCUSSION

Using the optimization procedure described above we have calculated and analysed BORT ground-state sequences for a series of BHs having up to five fused benzene rings. In the case of relatively small molecules, such as naphthalene **II**, anthracene **III**, and phenanthrene **IV** (see Figure 2), all singly- and doubly-excited RRSs were considered.

Let us consider the phenanthrene molecule **IV** as a typical example. Figure 3 shows cumulative contributions $W_1, W_2, \ldots W_{55}$, for the three optimum sequences which approximate the phenanthrene PPP ground state. The lowest line corresponds to the energy sequence, the medium line corresponds to the unrestricted sequence built from all Kekulé, singly-excited and Claus structures, while the uppermost line corresponds to the unrestricted sequence which, in addition, contains Claus-like structures.

The first five values of cumulative contributions W_1–W_5 are equal for all three sequences, and they correspond to the five Kekulé structures. The cu-

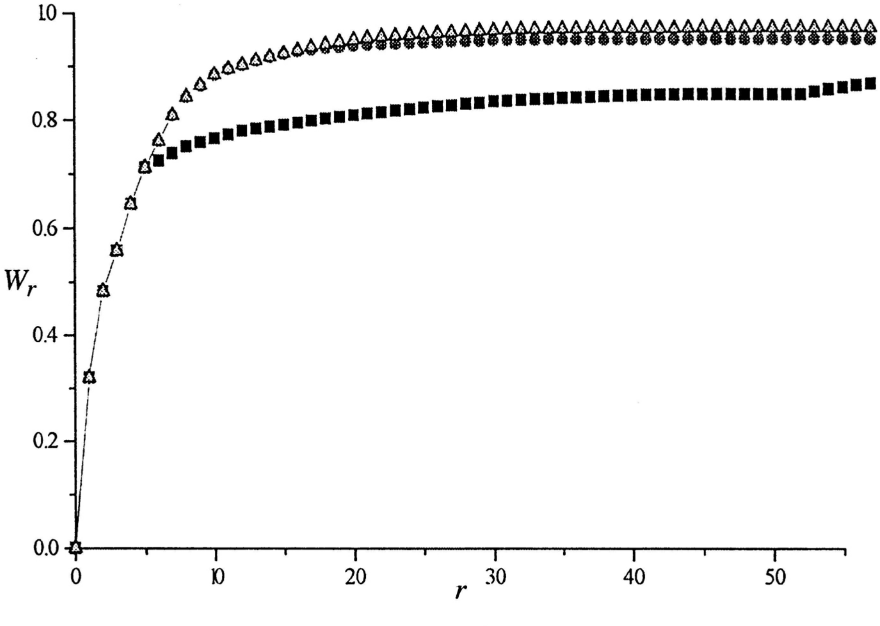

Figure 3. A comparison of cumulative contributions $W_1, W_2, \ldots W_{55}$ for three different optimum sequences approximating the PPP ground state of phenanthrene, **IV**. The lowest line corresponds to the energy sequence, the medium line corresponds to the unrestricted sequence built from all Kekulé, singly-excited and Claus structures (see Figure 4), while the uppermost line corresponds to the unrestricted sequence which contains, in addition, Claus-like structures (see Figure 5).

mulative contribution of all 5 Kekulé structures to the PPP ground state is W_5^P = 71.09%, while this contribution to the Hückel ground state is W_5^H = 66.36% (see Table I). Note that the Kekulé RRSs better approximate the more sophisticated PPP ground state than Hückel ground state. Moreover, the BORT representation of the PPP ground state remains better than the representation of the Hückel ground state if one further includes any other type of RRSs in the optimization procedure.

In the case of the energy sequence (the lowest line in Figure 3) one has to consider all 47 singly-excited RRSs after the Kekulé structures have been exhausted. After the singly-excited RRSs are exhausted, one has to start including doubly-excited structures. Cumulative contribution of the set of all 5 Kekulé and all 47 singly-excited RRSs to the phenanthrene PPP ground state is W_{52}^P = 84.38%, while this contribution to the Hückel ground state is W_{52}^H = 83.89% (see Table II). None of the several types of singly-excited RRSs is as important as the triply-excited Claus structures, and the convergence of the energy sequence is relatively slow (see Figure 3). The choice of RRSs in subsequent steps is fairly irregular and the contributions of the last few singly-excited RRSs are negligible. The inflection at point W_{52}, corresponding to the last singly-excited structure suggests that better convergence properties should be obtained if selection of efficient doubly-excited RRSs starts before all singly-excited RRSs have been used up.

The unrestricted PPP and Hückel sequences obtained for the set of all Kekulé, singly-excited and Claus RRSs have much better convergence properties than the corresponding energy sequences. The first 30 structures, S_1, S_2,...,S_{30}, of the PPP unrestricted sequence are displayed in Figure 4. The corresponding cumulative contributions are shown by the medium line in Figure 3. The cumulative contribution of the first 10 structures, 5 Kekulé structures followed by 5 Claus structures, is W_{10}^P = 88.43%. If instead of a singly-excited structure one further includes a bi-Claus structure as the 11th term of a sequence, 89.19% of the phenanthrene PPP ground state is recovered (see Table I). In order to achieve this value of cumulative contribution in the energy sequence, one needs to consider, in addition to 5 Kekulé and 47 singly-excited RRSs, also 31 most important doubly-excited RRSs. In the Hückel case, the corresponding contribution of 5 Kekulé and 6 Claus RRSs is W(K+C) = 83.28%. In the energy sequence this value is reached by inclusion of all Kekulé structures and 39 most efficient singly-excited RRSs.

The 14th structure of the unrestricted phenanthrene PPP sequence containing Kekulé, singly-excited and Claus RRSs, is the bi-Claus RRS (see Figure 4). In the simple Hückel estimation, this structure lies 6β above the Kekulé structures, and it is noteworthy that this energetically very unfavourable structure is selected before most singly-excited RRSs. In the corresponding sequence for the Hückel ground state, the bi-Claus RRS is selected as the 16th structure.

In the above unrestricted phenanthrene sequence, as well as in the corresponding unrestricted sequences for other BHs, singly-excited structures with »long bond« connecting nonadjacent π-centers of different rings are usually more significant than the Dewar-type structures with a »long bond« connecting *para* π-centers within the same benzene ring. This feature is, how-

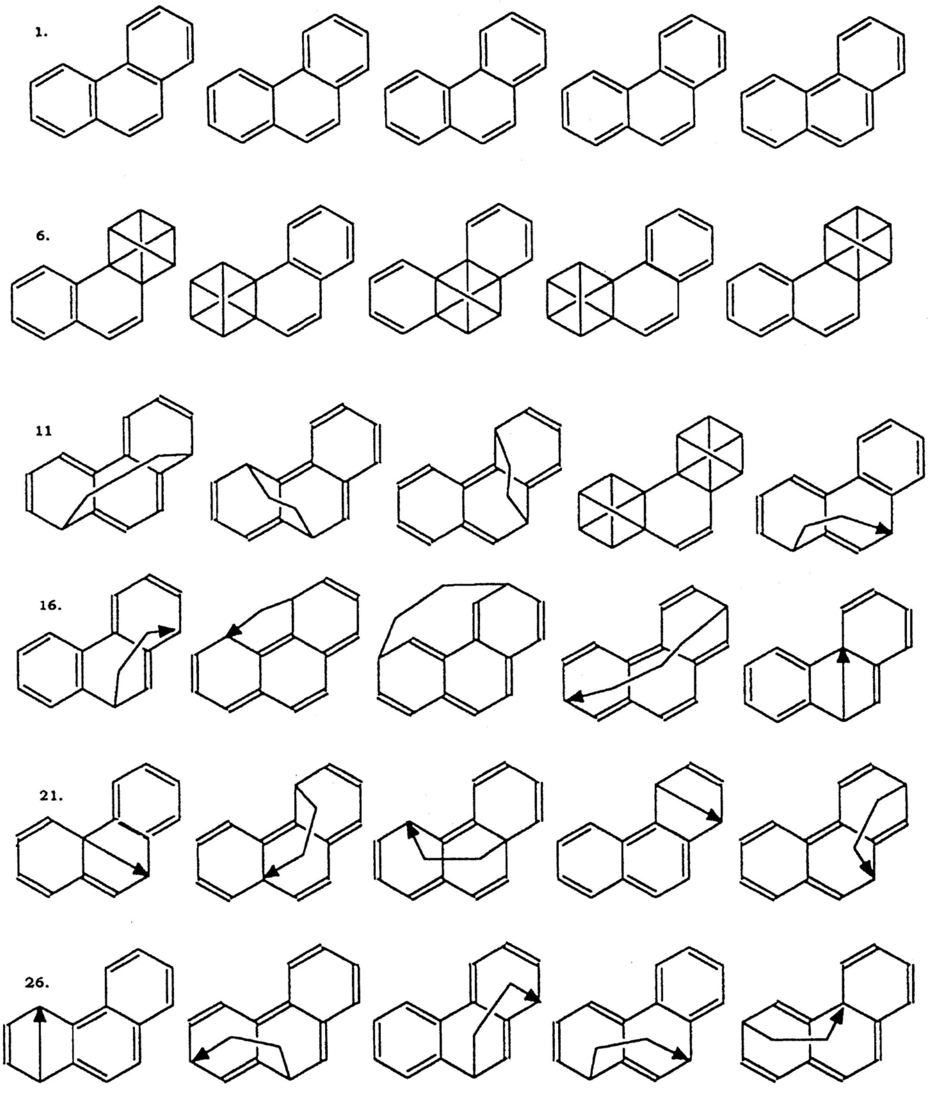

Figure 4. First 30 RRSs of the unrestricted sequence approximating the PPP ground state of phenanthrene, **IV**. The sequence is obtained by optimizing a set of all Kekulé, singly-excited and Claus RRSs without any constraint of the energy criterion.

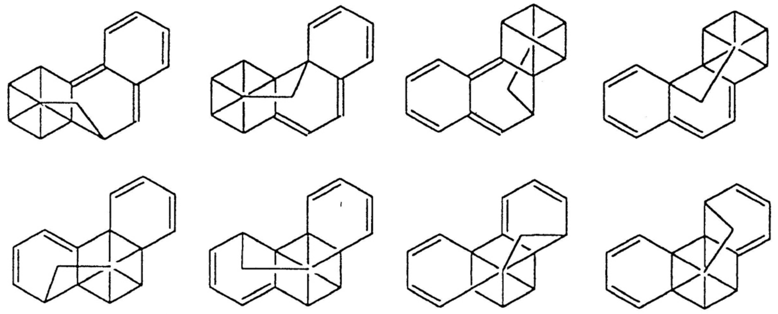

Figure 5. Eight so-called Claus-like structures for the phenanthrene molecule **IV**.

ever, not so much pronounced, and no particularly important type of singly-excited RRSs was found.

The uppermost line in Figure 3 shows cumulative contributions of the unrestricted PPP sequence which in addition to Kekulé, singly-excited and Claus RRSs of BH **IV** contains its 8 so-called Claus-like structures depicted in Figure 5. It was found that these Claus-like structures improve the contribution *W*(K+C) slightly better than any other RRSs considered for BH **IV**.

Similar results were obtained for BHs **II** and **III**. In Table I are shown cumulative contributions *W*(K), *W*(C) and *W*(K+C) which correspond to the set of all Kekulé structures, the set of all Claus structures, and the combined set of all Kekulé and all Claus RRSs, respectively. The values are given for both the Hückel and PPP ground states. As expected, the Kekulé RRSs provide the dominant contribution to the ground states for all these BHs. The analysis of various unrestricted sequences of RRSs shows that the Kekulé structures are always selected as leading structures. A linear com-

TABLE I

Cumulative contributions of the sets of all Kekulé structures *W*(K), all Claus structures *W*(C), and all Kekulé and Claus structures *W*(K+C), to the Hückel (HÜCK) and Parriser-Parr-Pople (PPP) ground states of small BHs. *N*(K) and *N*(C) denote the number of all Kekulé and all Claus structures, respectively.

BH	*N*(K)	*W*(K)		*N*(C)	*W*(C)		*W*(K+C)	
		HÜCK	PPP		HÜCK	PPP	HÜCK	PPP
I	2	0.9000	0.9000	1	0	0	1	1
II	3	0.7606	0.7953	2	1.8 × 10–6	1.1×10^{-4}	0.8867	0.9261
III	4	0.6023	0.6784	3	2.2×10^{-6}	2.7×10^{-4}	0.7210	0.8123
IV	5	0.6636	0.7109	6[a]	2.6×10^{-6}	2.6×10^{-4}	0.8328	0.8919

[a] The bi-Claus structure is also included.

bination of Kekulé structures generally provides a very good zeroth-order approximate ground-state wave function, and all the generated sequences include them, along with other types of RRSs.

In addition to the Kekulé structures, the important contributors to the BHs' ground states are the Claus structures. A subset of Kekulé and Claus structures provides the most convergent sequence of BORT resonance structures. However, the Claus RRSs alone provide a very poor representation of BHs' ground states (see Table I). This can be explained as follows. In the case of benzene **I**, a simple Claus structure is exactly orthogonal to its ground state. Polycyclic BHs can be considered to consist of mutually interacting benzene-like rings,[11] and negligible contributions of Claus structures alone can now be interpreted as an indication of weak interactions between the component benzene-like rings.

TABLE II

Cumulative contributions for the set of all Kekulé and singly-excited RRSs *W*(K+S), the set of all Kekulé, singly-excited and Claus RRSs *W*(K+S+C), and the set which also includes all so-called Claus-like structures *W*(K+S+C+Cl). *N*(S) is the number of all singly-excited RRSs.

BH	*N*(S)	*W*(K+S)		*W*(K+S+C)		*W*(K+S+C+Cl)	
		HÜCK	PPP	HÜCK	PPP	HÜCK	PPP
I	3	0.9444	0.9444	1	1	1	1
II	16	0.8893	0.8982	0.9593	0.9709	0.9867	0.9897
III	48	0.8281	0.8486	0.8940	0.9230	0.9518	0.9650
IV	47	0.8338	0.8489	0.9308	0.9527	0.9610	0.9741

Table II gives cumulative contributions for the set of all Kekulé and singly-excited structures, *W*(K+S), the set of all Kekulé, singly-excited and Claus RRSs, *W*(K+S+C), and the set which additionally contains Claus-like structures, *W*(K+S+C+Cl).

In the case of the PPP ground state of BH **II**, a linear combination of its 3 Kekulé and 2 Claus structures has the contribution *W*(K+C) = 92.61%, that is, it is in error only by 7.39%. This is 2.8 times better than the contribution obtained by the Kekulé structures alone, and 1.4 times better than the contribution of 3 Kekulé and all 16 singly-excited RRSs, *W*(K+S) = 89.82% (see Tables I and II). In order to achieve the value *W*(K+C) = 92.61%, one needs to include 13 most efficient doubly-excited RRSs into the energy sequence, in addition to all Kekulé and all singly-excited RRSs. In the Hückel case, the corresponding value *W*(K+C) = 88.67% is obtained by including all Kekulé and 14 most efficient singly-excited structures into the corresponding energy sequence.

The optimum PPP and Hückel sequences containing Kekulé, singly-excited and Claus RRSs for BH **II** generally exhibit similar properties to the corresponding sequences for BH **IV**. However, in the case of BH **III**, RRSs show relatively different behaviour. **III** is a member of polyacene series, the class of linearly fused BHs whose properties are quite different from those of angular BHs.[15] The number of Kekulé and Claus structures for this series does not grow exponentially but linearly with the number of 6-membered rings. Therefore, a representation of the π-electron ground state of these BHs in terms of Kekulé and Claus structures is not reliable enough. This is also justified by our numerical results. The cumulative contribution *W*(K+C) = 81.23% of 4 Kekulé and 3 Claus structures to the anthracene PPP ground state, is exceeded by the energy sequence of all Kekulé and only 14 most significant singly-excited RRSs. In the case of the Hückel energy sequence, one achieves the value W(K+C) = 72.1% by selection of all Kekulé and only 5 most significant singly-excited RRSs. Although 4 Kekulé structures come first and 3 Claus structures are selected as the next important ones in the anthracene unrestricted sequence containing Kekulé, singly-excited and Claus RRSs, their cumulative contribution is not so significant as for systems **II** and **IV**. Instead, the singly-excited RRSs with a »long bond« connecting π-centres of different, adjacent or nonadjacent, benzene rings account for the larger part of the ground states. Such behaviour is characteristic of all linear polyacenes. It was found that the approximation of ground states of linear polyacenes in terms of the Kekulé and Claus structures is even less reliable for larger π-systems, such as naphthacene **V** and pentacene **XI**.

TABLE III

The same as Table II, except that all singly-excited RRSs are replaced with an equal number of most important doubly-excited RRSs.

BH	*W*(K+D)		*W*(K+D+C)		*W*(K+D+C+Cl)	
	HÜCK	PPP	HÜCK	PPP	HÜCK	PPP
II	0.8465	0.8603	0.9440	0.9647	0.9641	0.9762
III	0.8311	0.8505	0.8970	0.9258	0.9509	0.9659
IV	0.8376	0.8469	0.9432	0.9615	0.9635	0.9761

Table III shows some cumulative contributions for the optimum sequences of BHs **II**, **III** and **IV**, which include doubly-excited RRSs instead of singly-excited RRSs. The number of doubly-excited RRSs is significantly larger than the number of singly-excited RRSs. In order to estimate the relative importance of singly- and doubly-excited RRSs, we show cumulative contributions *W*(K+D), *W*(K+D+C) and *W*(K+D+C+Cl) for as many doubly-excited RRSs as there are singly-excited RRS. *W*(K+D) is a cumulative contribution of all Kekulé and as many of the most efficient doubly-excited structures as there are singly-excited RRSs. *W*(K+D+C) and *W*(K+D+C+Cl) refer to the corresponding cumulative contributions of unrestricted sequences which additionally contain Claus and Claus-like structures. Cumulative contributions *W*(K+D), *W*(K+D+C) and *W*(K+D+C+Cl) are only marginally better than the corresponding contributions of sequences with singly-excited structures. This slight advantage of doubly-excited structures over singly-excited structures is highly offset by the fact that there are many more doubly- than singly-excited structures, and by the requirement that one has to determine which among the very numerous doubly-excited structures are the most important. There is, however, no simple way to do this. In comparison with Claus structures, the doubly-excited structures are better contributors only in the case of **III**. This is in agreement with the above results obtained with singly-excited RRSs. In order to exceed the cumulative contributions *W*(K+C) of the set of 4 Kekulé and 3 Claus RRSs to the anthracene Hückel and PPP ground states, one has to admix 7 and 21 most efficient doubly-excited RRSs to the set of 4 Kekulé structures, respectively. However, in the case of **II**, the set of all Kekulé and all 41 doubly-excited RRSs has a smaller cumulative contribution than the set of only 2 Kekulé and 3 Claus structures. In the case of the PPP ground state for BH **IV**, in order to achieve the cumulative contribution *W*(K+C) obtained by the set of all Kekulé and Claus structures, one needs to select over 100 most efficient doubly-excited RRSs in addition to the Kekulé structures. In the case of the Hückel ground state the corresponding value *W*(K+C) is achieved by the sequence of all Kekulé structures and 41 most efficient doubly-excited RRSs.

We have observed some regularities in selecting the singly- and doubly-excited RRSs.[16] However, among all singly- and doubly-excited structure types, no type is as efficient in representing BHs' ground states as the triply-excited Claus structures: the number of structures of any type is, in general, significantly larger than the number of Claus structures, and symmetrically nonequivalent structures of a given type usually have quite different contributions.

Besides the Claus structures, some other triply-excited RRSs were also examined. None of the considered types of very numerous triply-excited RRSs show such high efficiency as the Claus structures. The only significant exception are the so-called Claus-like structures, which are for BH **IV** depicted in Figure 5. It has been found that these Claus-like structures, in combination with Kekulé and Claus structures, generally improve the contribution to the π-electron ground state somewhat better than any other type of the RRSs considered. Further, in unrestricted sequences comprising the Kekulé, Claus, Claus-like and singly- or doubly-excited structures, most of the Claus-like RRSs come immediately after Kekulé and Claus structures, that is, prior to many singly- and doubly-excited RRSs. In order to assess their relative importance, we give several cumulative contributions of sequences including the Claus-like structures in the rightmost columns of Tables II and III.

TABLE IV

Cumulative contributions for BHs having four fused benzene rings. *W*(K) and *W*(K+C) are cumulative contributions of the set of all Kekulé structures and of the set of all Kekulé and Claus structures, respectively. *W*(K+mS) and *W*(K+S) are cumulative contributions of the set of all Kekulé and m[a] most important singly-excited RRSs, and of the set of all Kekulé and all singly-excited RRSs, respectively. *N*(K), *N*(C) and *N*(S) are the numbers of Kekulé, Claus and singly-excited RRSs, respectively.

BH	*N*(K)	*W*(K)		*N*(C)[b]	*W*(K+C)		*N*(S)	*W*(K+mS)		*W*(K+S)	
		HÜCK	PPP		HÜCK	PPP		HÜCK	PPP	HÜCK	PPP
V	5	0.4541	0.5620	4	0.5526	0.6852	110	0.5711	0.6345	0.7581	0.7935
VI	7	0.5390	0.6155	10	0.7029	0.8036	112	0.6525	0.7000	0.7710	0.7993
VII	8	0.5703	0.6297	13	0.7611	0.8388	116	0.6742	0.7136	0.7764	0.7999
VIII	8	0.5683	0.6291	13	0.7584	0.8380	117	0.6741	0.7143	0.7765	0.7998
IX	9	0.5956	0.6400	20	0.8194	0.8814	117	0.7005	0.7240	0.7825	0.7991
X	6	0.5661	0.6374	7	0.7172	0.8108	87	0.6714	0.7091	0.7929	0.8153

[a] m equals to the number of Claus RRSs *N*(C).
[b] Bi- and tri-Claus structures are also included.

TABLE V

Cumulative contributions for BHs having five fused benzene rings. This Table is analogous to Table IV, except that column *W*(K+S) is not included here.

BH	*N*(K)	*W*(K)		*N*(C)[b]	*W*(K+C)		*W*(K+mS)	
		HÜCK	PPP		HÜCK	PPP	HÜCK	PPP
XI	6	0.3302	0.4545	5	0.4062	0.5610	0.4460	0.5256
XII	9	0.4150	0.5165	14	0.5534	0.6911	0.5477	0.6101
XIII	12	0.4770	0.5540	27	0.6731	0.7833	0.6025	0.6509
XIV	12	0.4764	0.5538	27	0.6723	0.7831	0.6064	0.6553
XV	13	0.4925	0.5588	34	0.7085	0.8053	0.6262	0.6627
XVI	11	0.4569	0.5399	20	0.6303	0.7444	0.5776	0.6385
XVII	10	0.4424	0.5383	17	0.6020	0.7339	0.5637	0.6304
XVIII	11	0.4588	0.5405	20	0.6330	0.7452	0.5804	0.6384
XIX	13	0.4917	0.5600	30	0.7016	0.7976	0.6184	0.6597
XX	13	0.4923	0.5602	30	0.7025	0.7978	0.6156	0.6579
XXI	14	0.5050	0.5634	37	0.7333	0.8172	0.6277	0.6625
XXII	13	0.4898	0.5596	30	0.6989	0.7970	0.6161	0.6600
XXIII	9	0.4613	0.5567	16	0.6269	0.7564	0.5844	0.6427
XXIV	9	0.4658	0.5545	14	0.6221	0.7427	0.5852	0.6441
XXV	11	0.5161	0.5787	23	0.7109	0.8035	0.6374	0.6721

[a,b] See comments for Table IV.

The results for larger BHs, having four and five rings, are summarized in Tables IV and V, respectively. These results are in good agreement with the results obtained for smaller BHs **II**, **III** and **IV**. The findings for BHs **II**, **III** and **IV** generally hold for all other polycyclic cata- and peri-condensed benzenoid molecules considered in the present study.

The columns *W*(K) of Tables IV and V show that Kekulé RRSs generally make the dominant contribution to both Hückel and PPP ground states. This result is in agreement with the classical chemical picture of BHs and the generally acknowledged importance of Kekulé resonance structures. In addition, Kekulé BORT resonance structures better describe the more sophisticated PPP ground state than the Hückel ground state, and the relative importance per Kekulé structure increases as the π-system becomes larger.

The best improvement of the cumulative contribution of the set of Kekulé structures is commonly produced by selection of the set of Claus RRSs. The cumulative contributions of the sets of all Kekulé and all Claus RRSs for BHs with four and five benzene rings are shown in columns *W*(K+C) of Tables IV and V, respectively. The unrestricted optimization procedure shows that the choice of Claus structures is usually preferable to the choice of any other type of RRSs. Improving effect of the Claus RRSs with respect to convergence properties of various sequences is more pronounced for the PPP ground state than for the Hückel ground state. It should be pointed out that the Claus structures alone make a negligible contribution to the π-electron ground states, and this can be attributed to the fact that BHs to a great extent retain a benzene-like character.[16]

The obtained results are generally consistent with Clar's empirically based model of these molecular systems.[15] For example, the best description of the π-electron ground state in terms of Kekulé and Claus structures is obtained for the so-called fully benzenoid systems in which benzene rings are either denoted by isolated π-sextets or are shown as »empty«.[15] On the other hand, the worst description of the π-electron ground state in terms of these structures is obtained for linear polyacenes. According to Clar, in the case of linear polyacenes a single mobile aromatic sextet is shared among all rings regardless of the π-system size.[15] The results further show that besides (mono-) Claus structures, bi-Claus RRSs are also quite important in the description of ground states of angular BHs. Likewise, a tri-Claus structure of the triphenylene molecule **IX** is selected before most singly-excited structures in the corresponding unrestricted sequence. The systematically better representation of PPP than Hückel ground states in terms of Kekulé and Claus RRSs may also be interpreted in terms of the more pronounced local benzene properties of PPP ground states. The common efficiency of the Claus-like RRSs additionally points out the pronounced local benzene character of 6-membered rings of BHs and suggests that short range interactions between adjacent rings may be next important factor for successful description of the ground states of benzenoid systems.

In order to compare the relative merits of various sequences with and without Claus RRSs, Tables IV and V show values of cumulative contributions of Kekulé structures and as many most efficient singly-excited structures as there are Claus structures. From these Tables one can deduce, contrary to expectations based on the energy criterion, that Claus structures make a larger contribution to the single-determinantal MO ground-state wave function than the equal number of the most efficient singly-excited RRSs. The larger efficiency of Claus structures, as compared with singly-excited structures, is more emphasized in the case of the PPP ground state. The Claus RRSs are more favourable for angular BHs, while linear acenes, naphthacene **V** and pentacene **XI** exhibit a similar behaviour to anthracene, **III**. Although some regularities in the choice of singly-excited RRSs were found, there are no common singly-excited RRSs which contribute so considerably to the ground state as Claus structures. Various choices of singly-excited RRSs cause relatively small variations of cumulative contributions. In addition, due to the large number of these resonance structures and their nonorthogonality, the optimum choice is somewhat obscured.

A similar analysis of variationally determined optimum sequences further confirms important role of the set of Kekulé and Claus RRSs in the description of ground-state properties of all BHs having up to five benzene rings.[16]

CONCLUDING REMARKS

The obtained results demonstrate the relative importance of the Kekulé and Claus structures in the BORT description of Hückel or PPP ground states for all the cata- and peri-condensed BHs considered.

As expected, Kekulé structures have a dominant contribution to the ground states of these π-systems, and their linear combination generally provides a very good zeroth-order description.

Besides Kekulé structures, Claus resonance structures also provide a significant contribution to the ground states of the considered BHs. This finding is quite counter-intuitive since Claus RRSs are energetically very unfavourable, and according to the energy criterion they should be considered after all singly- and doubly-excited structures have been exhausted. The relative importance of Claus structures can be attributed to the local benzene-like character of BHs.[16]

Although some regularities in selecting BORT resonance structures of other types are observed, the contribution of these RRSs to a ground state is not significant. Furthermore, the large number and nonorthogonality of these structures conceal their true contribution to a ground state.

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SAŽETAK

Analiza MO osnovnih stanja benzenoidnih ugljikovodika pomoću rezonantnih struktura pristupa BORT

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Kako bi se odredile najvažnije rezonantne strukture u opisu benzenoidnih ugljikovodika, Hückelova i Pariser-Parr-Popleova osnovna stanja svih benzenoida s najviše pet benzenskih prstenova analizirana su s pomoću rezonantnih struktura (pristup BORT). Zbog eksponencijalnog porasta broja rezonantnih struktura s veličinom benzenoidne molekule, upotrijebljen je aproksimativni optimizacijski postupak utemeljen na tzv. pohlepnom algoritmu. Za promatrane benzenoide analiza kumulativnih doprinosa različitih nizova rezonantnih struktura osnovnim stanjima MO-tipa pokazuje da su, uz Kekuléove strukture, i Clausove strukture također vrlo važne za opis tih sustava. Relativna važnost Clausovih struktura se može pripisati lokalnim benzenskim svojstvima tih π-elektronskih sustava te činjenici da je osnovno stanje benzena prikazano točno kao linearna kombinacija dviju Kekuléovih i jedne Clausove strukture. Relativna važnost ostalih tipova struktura općenito je znatno manja. Stvarni doprinos drugih struktura dosta je nejasan zbog njihova velikog broja i međusobne neortogonalnosti.