

Ground-state properties of benzenoid hydrocarbons by simple bond orbital resonance theory approach

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π -electron energies and bond orders of benzenoid hydrocarbons with up to five fused hexagons have been considered by the simple Bond Orbital Resonance Theory (BORT) approach. The corresponding ground states were determined according to four BORT models. In the first three models a diagonalisation of the Hückel-type Hamiltonian was performed in the bases of Kekulé, of Kekulé and mono-Claus and of Kekulé and Claus resonance structures, respectively. In the fourth model a simple BORT ansatz was used. According to this ansatz, the ground state is a linear combination of the positive Kekulé structures, all with equal coefficients. It was shown that π -electron energies and bond orders obtained by these models correlate much better with the PPP energies and bond orders than with the Hückel energies and bond orders. This indicates that a simple BORT approach is quite reliable in predicting the more sophisticated PPP results. Concerning the relative performance of the four BORT models, the best results were obtained with the BORT ansatz. The performance deteriorates with the expansion of the basis set. This is attributed to the fact that in these models the improvement of the basis set is not accompanied with the corresponding improvement of the Hamiltonian. Comparing the BORT-ansatz bond orders with the Pauling bond orders, it was shown that BORT-ansatz bond orders correlate much better with the PPP bond orders.

1. Introduction

Bond Orbital Resonance Theory (BORT) is a semi-empirical resonance model of an electronic structure of molecules. It considers an electronic state as a linear combination of the so-called Regular Resonance Structures (RRSs) [16]. Each RRS corresponds to a Slater determinant made up of mutually disjunct bond orbitals. Bond orbitals are assumed to be built of orthonormal atomic orbitals and are shown graphically as formal bonds [16]. For instance, within the σ - π approximation a π -electron system of a conjugated molecule may be described in terms of RRSs whose bond orbitals are composed of orthonormal $2p_z$ atomic orbitals of conjugated atoms.

Recently, the extensive sequential optimization of RRSs describing π -electron ground states of Benzenoid Hydrocarbons (BHs) with up to five fused hexagonal rings (figure 1) was performed. As expected, it was shown that the most efficient RRSs in

the description of π -electron ground states of these molecules are Kekulé structures [7]. The importance of Kekulé structures is consistent with the widespread use of the energy criterion in selecting the most important basis functions. However, it was found that besides Kekulé structures, the next important RRSs are energetically very unfavourable Claus structures [7,13]. A Claus RRS possesses one or more rings with the three “long” diagonal *para*-bond orbitals, while the remaining part of the structure is of the Kekulé type. With respect to the number of Claus rings, we distinguish mono-Claus RRSs, bi-Claus RRSs and so on. The relative importance of Claus RRSs can be ascribed to the pronounced local benzene-like properties of BHs and the fact that the benzene ground state is exactly (within the independent-particle model) represented by the linear combination of its two Kekulé and one Claus RRSs [13]. Other types of relatively very numerous RRSs generally have quite negligible and obscure importance and can be discarded in the first approximation [7].

The purpose of this work is to investigate the effect of extending the basis of Kekulé RRSs by other RRSs. We extended the Kekulé basis by Claus RRSs since these structures were found to be the most important among all excited RRSs. In this article we consider four different BORT models and use them to determine some π -electron ground-state properties of BHs, such as energy and bond orders. The four models differ in the choice of a basis set, which includes either Kekulé RRSs alone, or some combination of Kekulé and Claus RRSs, and in the way how the π -electron ground state is approximated.

All four models utilise the spin-separation approximation [11,16]. Within this approximation the $2n$ -electron closed-shell ground state of a BH is given as $|\Psi\rangle = |\Phi \bar{\Phi}\rangle$, where the normalized n -electron α -spin Φ and β -spin $\bar{\Phi}$ substates are identical up to the spin. Hence, the expectation value of a one-particle spin-independent operator O in the state $|\Psi\rangle = |\Phi \bar{\Phi}\rangle$ is given by

$$\langle O \rangle = 2\langle \Phi | O | \Phi \rangle / \langle \Phi | \Phi \rangle. \quad (1)$$

Within BORT the substate Φ is represented as a linear combination of n -particle RRSs $\{S_a\}$:

$$\Phi = \sum_a a_a S_a, \quad (2)$$

and, hence,

$$\langle O \rangle = 2 \sum_{a,b} a_a a_b \langle S_a | O | S_b \rangle / \sum_{a,b} a_a a_b \langle S_a | S_b \rangle. \quad (3)$$

Models considered differ in the way how the coefficients $\{a_a\}$ of the linear expansion (2) were determined. In models **(I)**, **(II)** and **(III)** these coefficients were determined by a diagonalization of the Hückel Hamiltonian in the bases of only Kekulé RRSs (K), of Kekulé and mono-Claus RRSs (K+mC), and of Kekulé and all Claus RRSs (K+C), respectively. In model **(IV)**, a simple BORT-ansatz approximation was used. According to this approximation, to the ground state of an alternant hydrocarbon

contribute only Kekulé RRSs which are all of the same parity, and the contribution of each such Kekulé structure is the same [15,16]. The requirement that Kekulé structure of only one parity should be included in the ground state follows from the fact that in the case of alternant hydrocarbons all matrix elements of the Hamiltonian operator between RRSs of the opposite parity vanish [12,16]. However, in the case of benzenoid systems such as considered here, all Kekulé structures are of the same parity, and, hence, in this special case, the BORT ansatz reduces to the well-known VB ansatz [12,15,16]. Thus, in model (IV), the expression (3) simplifies to

$$\langle \mathcal{O} \rangle = 2 \sum_{a,b} \langle S_a | \mathcal{O} | S_b \rangle / \sum_{a,b} \langle S_a | S_b \rangle, \quad (4)$$

where summation is performed only over Kekulé RRSs.

All matrix elements $\langle S_a | \mathcal{O} | S_b \rangle$ in relations (3) and (4) can be calculated by the simple graphical algorithms [12]. While models (I)–(III) require a diagonalization of the Hamiltonian matrix in order to determine coefficients $\{a_a\}$, in model (IV) no diagonalization is required. The determination of energy and bond orders in model (IV) is thus reduced to the straightforward summation over contributions of different superposition diagrams.

In order to estimate relative performance of models (I)–(IV), the calculated energies and bond orders were compared with the corresponding values calculated by the Hückel and Pariser–Parr–Pople (PPP) MO methods. The BORT bond orders were also compared with the Pauling bond orders. We used a variant of the PPP method with Dewar parameters [2]. For the sake of simplicity, a hexagonal geometry of six-membered rings with the fixed carbon–carbon distance (1.397 Å) was assumed and all Coulomb interactions between atoms which are more than three bonds apart were ignored.

2. Results and discussion

2.1. Energy

The total π -electron energies were calculated with the models (I)–(IV), that is by using the wave functions whose coefficients $\{a_a\}$ (equation (2)) are determined by the diagonalization of the Hückel-type Hamiltonian in the bases of only Kekulé RRSs ($E_\pi(\text{K})$), of Kekulé and mono-Claus RRSs ($E_\pi(\text{K+mC})$), and of Kekulé and all Claus RRSs ($E_\pi(\text{K+C})$), and the BORT-ansatz wave functions ($E_\pi(\text{A})$). The values $E_\pi(\text{K})$, $E_\pi(\text{K+mC})$, $E_\pi(\text{K+C})$ and $E_\pi(\text{A})$ are listed in table 1 for all BHs in figure 1. In the last two columns of this table energies calculated by the Hückel ($E_\pi(\text{H})$) and PPP ($E_\pi(\text{P})$) MO methods are also given. These energies provide a reference for a comparison and estimation of the relative performance of the four BORT models. The BORT and Hückel energies are expressed in units of the Hückel resonance integral β , while the PPP energies are given in eV. The coefficients of correlation r^{P} and r^{H} of

Table 1
 π -electron energies for BHs I–XXV in figure 1.

BH	$E_{\pi}(\text{K})$	$E_{\pi}(\text{K+mC})$	$E_{\pi}(\text{K+C})$	$E_{\pi}(\text{A})$	$E_{\pi}(\text{H})$	$E_{\pi}(\text{P})$
I	7.2000	8.0000	8.0000	7.2000	8.0000	12.8273
II	11.8271	12.9425	12.9425	11.8182	13.6832	21.9003
III	16.200	17.4710	17.4710	16.1730	19.3137	30.7401
IV	16.6997	18.2766	18.38599	16.6848	19.4483	31.2730
V	20.4399	21.7979	21.7979	20.3924	24.9308	39.4583
VI	21.1970	22.9899	23.1449	21.1681	25.1012	40.2187
VII	21.4586	23.3824	23.5693	21.4359	25.1875	40.5333
VIII	21.4586	23.3824	23.5693	21.4359	25.1922	40.5358
IX	21.7423	23.8307	24.1580	21.7284	25.2745	40.8012
X	18.9302	20.5816	20.6786	18.9016	22.5055	36.1593
XI	24.6034	26.0141	26.0141	24.5376	30.5440	48.1182
XII	25.5060	27.4144	27.5913	25.4581	30.7256	48.9919
XIII	26.1313	28.3591	28.6870	26.0987	30.8795	49.6479
XIV	26.1313	28.3591	28.6870	26.0987	30.8805	49.6484
XV	26.3076	28.6241	29.0255	26.2839	30.9418	49.8107
XVI	25.9027	27.9985	28.2213	25.8649	30.8390	49.4379
XVII	25.7486	27.7783	27.9887	25.7080	30.7627	49.2144
XVIII	25.9027	27.9985	28.2213	25.8649	30.8338	49.4353
XIX	26.2682	28.5536	28.8817	26.2384	30.9386	49.8376
XX	26.2682	28.5536	28.8817	26.2384	30.9362	49.8366
XXI	26.4313	28.7983	29.1963	26.4067	30.9990	50.0011
XXII	26.2682	28.5536	28.8817	26.2384	30.9432	49.8397
XXIII	23.6542	25.6624	25.8849	23.6364	28.2453	45.3317
XXIV	23.5698	25.5158	25.6911	23.5283	28.2220	45.3055
XXV	24.0087	26.1395	26.4256	23.9816	28.3361	45.7153

Table 2
 Coefficients of correlations of energies calculated with the four BORT models with energies calculated by the PPP and Hückel MO methods for BHs I–XXV.

Coef. corr.	$E_{\pi}(\text{K})$	$E_{\pi}(\text{K+mC})$	$E_{\pi}(\text{K+C})$	$E_{\pi}(\text{A})$
$E_{\pi}(\text{P})$	0.9992	0.9972	0.9960	0.9991
$E_{\pi}(\text{H})$	0.9978	0.9949	0.9934	0.9977

the BORT energies with the corresponding PPP and Hückel energies, respectively, are listed in table 2.

In all considered cases the correlation is very good. This shows that the Hückel and PPP energies are both very well represented by all four BORT models. In addition, in all cases one obtains significantly better correlation of the BORT energies with the PPP energies than with the Hückel energies. This finding agrees with the outcome of the ground-state optimization: for each considered BH, the PPP reference state is represented better than the Hückel reference state, provided one approximates these states as linear combinations of either only Kekulé RRSs or Kekulé and Claus RRSs [7].

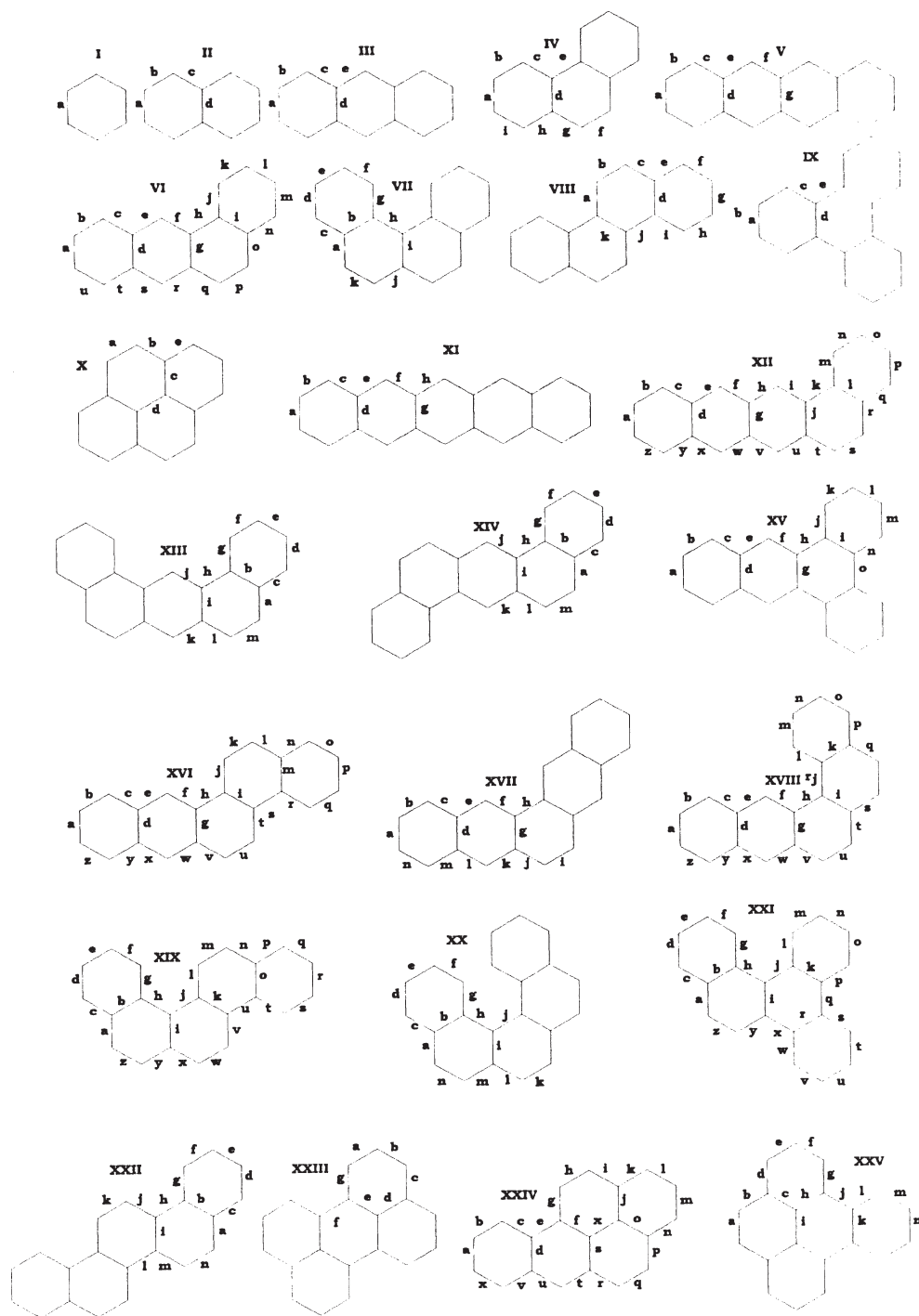


Figure 1. Benzenoid hydrocarbons having up to five fused rings and at least one Kekulé RRS.

This result is encouraging since a better approximation of the more sophisticated PPP model is preferable.

The best correlations are obtained with the basis sets containing only Kekulé RRSs (models **(I)** and **(IV)**). The correlation continuously deteriorates with the successive inclusion of mono-Claus RRSs (model **(II)**) and all other Claus RRSs (model **(III)**). Therefore, as far as the ground state energy is considered, there is no improvement if, besides Kekulé structures, one also includes Claus structures (and, possibly, some other excited RRSs). With the simple BORT models **(I)**–**(IV)**, the best results are obtained with Kekulé RRSs alone. In addition, as shown in table 2, the simple and very crude BORT ansatz produces surprisingly good results. The correlation coefficients for the BORT ansatz are only insignificantly smaller than the best correlation coefficients. In the case of the correlation with the PPP energies, the BORT-ansatz correlation coefficient is $r^P = 0.9991$, while the best correlation coefficient is $r^P = 0.9992$. Similarly, in the case of the correlation with the Hückel energies, the BORT-ansatz correlation coefficient is $r^H = 0.9977$, and the best correlation coefficient $r^H = 0.9978$ is only marginally better.

The above result shows that the simplest BORT model **(IV)** based on the BORT ansatz, which, unlike the other three models **(I)**–**(III)**, requires no diagonalization, produces very good ground state energies of BHs. In our opinion, this surprisingly good performance of such a crude model is due to its inner consistency. In any semi-empirical model one has to deal with the two types of approximations. On one hand, one has to approximate a Hamiltonian, and on the other hand, one has to approximate, or rather truncate, a space of states. In a well-behaved model these approximations should balance each other, i.e., a sophisticated approximation of a Hamiltonian should be combined with equally sophisticated approximation of a space of states, and vice versa. Thus, a very simple Hamiltonian should be combined with an equally simple space of states, and, if one combines such a Hamiltonian with more sophisticated space of states, one usually obtains not better, but worse results. This is exactly what happens here: model **(I)** combines a simple Hückel Hamiltonian with a simple space of states which is spanned only by Kekulé RRSs, and it gives the best results. In this model the Hamiltonian and the space of states are well balanced. If one improves the space of states by including either only mono-Claus RRSs (model **(II)**) or all Claus RRSs (model **(III)**), one obtains, as far as the ground-state energies are considered, worse results. The Hamiltonian and the space of states are not well balanced in models **(II)** and **(III)**. Finally, if one considers the BORT ansatz (model **(IV)**), the space of states is even more restricted than in model **(I)** since it is uniquely defined by the ansatz, and no calculation of the ground-state wave function is needed. This model is also very well balanced.

There are some other points which should be considered. Within all four models the energies obtained for the pairs of *cis*- and *trans*-isomers, such as pairs VII, VIII and XIII, XIV, are the same. The same energies are also obtained for the pair XVI, XVIII and the triplet XIX, XX and XXII. It can be shown that, as a consequence of a simple transformation performed on a molecular graph, all these BHs should have exactly the

Table 3
Energy correlation coefficients for the set of BHs I–XXV excluding linear acenes III, V and XI.

Coef. corr.	$E_{\pi}(\text{K})$	$E_{\pi}(\text{K+mC})$	$E_{\pi}(\text{K+C})$	$E_{\pi}(\text{A})$
$E_{\pi}(\text{P})$	0.9997	0.9991	0.9986	0.9996
$E_{\pi}(\text{H})$	0.9993	0.9985	0.9992	0.9992

same energies within the simple BORT approach [14]. Although the energies of BHs contained in the above pairs and triplet are not exactly the same neither in the Hückel nor in the PPP model, they are nevertheless very close to each other, especially in the PPP model. In general, the energies of these structural isomers calculated by more sophisticated models are also very similar [2–4].

Another point considers linearly condensed anthracene (III), naphthacene (V) and pentacene (XI). If one excludes these BHs and retains only branched isomers, the remaining subset of BHs has notably larger correlation coefficients. These correlation coefficients are given in table 3. Comparing tables 2 and 3, one finds that the exclusion of linearly condensed BHs improves the correlations at least twice and in some cases more than three times. The improvement is more pronounced in the case of larger basis sets which, besides the Kekulé RRSs, also include either only mono-Claus RRSs or all Claus RRSs. On the other hand, within the subset of only linear acenes, there are also good correlations of the BORT energies with the PPP and Hückel energies: for energies calculated in each BORT model, correlation coefficients r^{P} and r^{H} are equal 0.9999. Such a partition of the set of BHs into the two subsets can be ascribed to the different pace at which the number of Kekulé and/or Claus RRSs increases with the number of π -electrons for these systems: while for angular BHs the number of Kekulé and/or Claus RRSs increases approximately exponentially with the number of π -electrons, for linear acenes this increase is only linear. As a result, the energy changes occurring upon adding all Kekulé and/or Claus RRSs are noticeably different for these subclasses of BHs. This difference is more pronounced for the basis set including more resonance structures, and thus the improvement of r^{P} and r^{H} due to the neglect of acenes is greater for the basis sets which include both Kekulé and Claus RRSs.

2.2. Bond orders

π -electron bond order between atoms (i) and (j) is defined as the expectation value of the corresponding bond-order operator (equation (3) or (4)) [15,16]. BHs are alternant systems whose atoms can be partitioned into starred and unstarred subsets in such a way that no two adjacent atoms are from the same subset. According to the well-known pairing theorem originally derived within the MO approach, for each BH the calculated electron density is uniformly distributed over all conjugated atoms and the bond orders between atoms from the same subset vanish [1,9,11,12,16]. It is, therefore, sufficient to consider bond orders between atoms from different subsets.

Table 4
Bond-order correlation coefficients r^P for BHs II–XXV.

BH	Coefficients r^P of correlation with the PPP bond orders					
	K	K+mC	K+C	A	Pauling	H
II	0.9827	0.9478	0.9478	0.9974	0.9521	0.7964
III	0.9898	0.9730	0.9730	0.9983	0.9807	0.8539
IV	0.9895	0.9777	0.9721	0.9953	0.9895	0.9572
V	0.9866	0.9679	0.9679	0.9982	0.9820	0.8269
VI	0.9877	0.9749	0.9700	0.9949	0.9885	0.6798
VII	0.9839	0.9708	0.9692	0.9945	0.9883	0.9174
VIII	0.9833	0.9704	0.9688	0.9938	0.9871	0.9114
IX	0.9813	0.9755	0.9713	0.9875	0.9982	0.9534
X	0.9897	0.9762	0.9729	0.9903	0.9763	0.9475
XI	0.9887	0.9773	0.9773	0.9982	0.9894	0.8349
XII	0.9887	0.9784	0.9752	0.9960	0.9893	0.9197
XIII	0.9858	0.9737	0.9684	0.9943	0.9908	0.9445
XIV	0.9856	0.9736	0.9683	0.9941	0.9906	0.9431
XV	0.9832	0.9732	0.9688	0.9894	0.9884	0.9358
XVI	0.9883	0.9775	0.9756	0.9955	0.9840	0.9217
XVII	0.9915	0.9809	0.9778	0.9962	0.9892	0.9464
XVIII	0.9887	0.9778	0.9759	0.9960	0.9878	0.9261
XIX	0.9851	0.9723	0.9655	0.9945	0.9895	0.9326
XX	0.9858	0.9732	0.9659	0.9949	0.9907	0.9411
XXI	0.9799	0.9700	0.9640	0.9878	0.9909	0.9389
XXII	0.9854	0.9730	0.9656	0.9942	0.9892	0.9344
XXIII	0.9875	0.9788	0.9776	0.9903	0.9788	0.9182
XXIV	0.9827	0.9680	0.9642	0.9906	0.9806	0.9141
XXV	0.9825	0.9671	0.9606	0.9891	0.9859	0.9480
All	0.9856	0.9733	0.9692	0.9928	0.9850	0.9081

In table 4, the values of the coefficients r^P of correlation between the PPP bond orders and the bond orders calculated with the four BORT models are shown. The correlation coefficients r^P for the Pauling and Hückel bond orders are also given. The PPP method is used as a reference since it gives reliable predictions for bond orders as well as for other ground-state properties of the alternant systems [2].

Coefficients r^P in table 4 are obtained by taking into account only bond orders between directly bonded atoms. These bond orders are always positive. Assuming that these quantities can serve as a measure of bond strength, they are often related to the experimental bond lengths [1,5,10]. On the other hand, there is no direct physical interpretation for the bond orders between nonbonded atoms. These bond orders may be either positive or negative and they are, in absolute values, much smaller than bond orders between directly bonded atoms [15]. Their signs can be easily determined from relations (3) or (4) by using the simple algorithms for calculating overlap integrals and matrix elements of the corresponding bond-order operators between RRSs [12,15].

Table 5
Various π -bond orders, bond lengths and correlation coefficients for anthracene (III).

Bond	π -bond orders						Exp. bond length (Å)
	K	K+C	A	Pauling	H	P	
a	0.242	0.263	0.287	0.25	0.586	0.463	1.418
b	0.867	0.904	0.827	0.75	0.737	0.828	1.353
c	0.242	0.263	0.287	0.25	0.535	0.443	1.428
d	0.442	0.526	0.395	0.25	0.485	0.524	1.432
e	0.575	0.622	0.568	0.50	0.606	0.634	1.395
r^P	0.9898	0.9730	0.9983	0.9807	0.8539	–	0.9537
r^H	0.7712	0.7715	0.8380	0.9162	–	0.8539	0.9697
$ r^{\text{exp}} $	0.9017	0.8588	0.9456	0.9849	0.9697	0.9537	–

Table 6
Various π -bond orders, bond lengths and correlation coefficients for phenanthrene (IV).

Bond	π -bond orders							Exp. bond length (Å)
	K	K+mC	K+C	A	Pauling	H	P	
a	0.483	0.541	0.557	0.486	0.4	0.623	0.581	1.382
b	0.697	0.75	0.747	0.689	0.6	0.702	0.738	1.376
c	0.483	0.541	0.557	0.486	0.4	0.590	0.569	1.392
d	0.605	0.689	0.691	0.564	0.4	0.542	0.615	1.414
e	0.182	0.193	0.180	0.222	0.2	0.461	0.395	1.455
f	0.908	0.939	0.944	0.876	0.8	0.775	0.852	1.339
g	0.182	0.193	0.180	0.222	0.2	0.506	0.412	1.423
h	0.483	0.541	0.557	0.486	0.4	0.575	0.564	1.414
i	0.697	0.75	0.747	0.689	0.6	0.707	0.740	1.350
r^P	0.9895	0.9777	0.9721	0.9953	0.9895	0.9572	–	0.9162
r^H	0.9147	0.8912	0.8874	0.9350	0.9687	–	0.9572	0.9696
$ r^{\text{exp}} $	0.8762	0.8583	0.8568	0.8931	0.9166	0.9696	0.9162	–

Tables 5 and 6 show in more details bond orders between directly bonded atoms of anthracene (III) and phenanthrene (IV), respectively. Results obtained for these relatively simple π -electron systems illustrate general behaviour of results observed for all other linear and angular isomers considered. The last columns of tables 5 and 6 contain experimental bond lengths, while their last three rows show values of the correlation coefficients with the PPP (r^P) and Hückel (r^H) bond orders as well as with the experimental bond lengths ($|r^{\text{exp}}|$) [5]. Since the correlation between the bond orders and bond lengths is negative, the absolute value of the corresponding correlation coefficient $|r^{\text{exp}}|$ is given.

The bond order results generally follow the same pattern as the energy results. The BORT bond orders are better correlated with the PPP bond orders than with

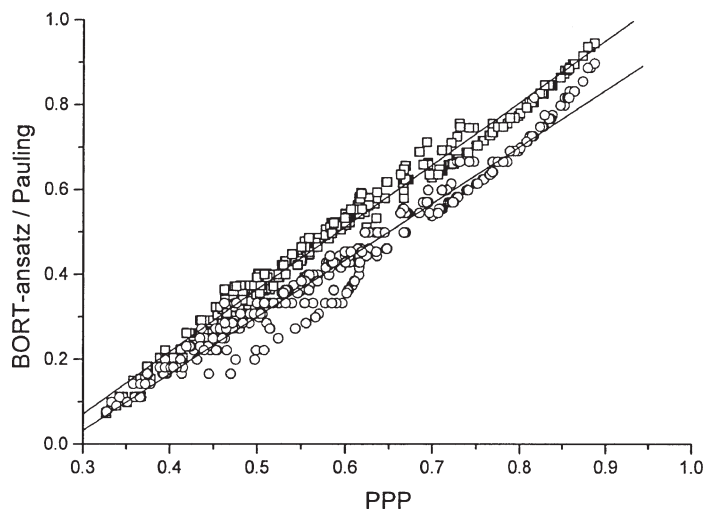


Figure 2. Comparison of correlations of the bond orders calculated by the BORT-ansatz (\square) and Pauling (\circ) bond orders with the PPP bond orders. Correlation coefficients r^P for the BORT-ansatz and Pauling bond orders are 0.9928 and 0.9850, respectively.

the Hückel bond orders, as the examples of anthracene (III) and phenanthrene (IV) demonstrate.

Concerning the relative performance of the four BORT models, results in table 4 show high regularity: for each benzenoid molecule, the best correlation is obtained with the BORT ansatz (model (IV)). The next is the correlation obtained with the Kekulé basis (model (I)), then the correlation obtained with the basis of Kekulé and mono-Claus RRSs (model (II)), and, finally, the correlation obtained with the basis of Kekulé and all Claus RRS (model (III)). As example, for the entire set of BHs I–XXV the coefficient r^P of correlation between the PPP bond orders and the bond orders calculated by model (IV) is 0.9928, while in the case of model (III), r^P is equal to 0.9692. In conclusion, by far the best results are obtained with the simple BORT ansatz (model (IV)).

The comparison of the BORT and Pauling bond orders is also interesting. Correlation coefficients r^P for the BORT-ansatz and Pauling bond orders in all BHs I–XXV are 0.9928 and 0.9850, respectively. Associated linear curves obtained by the least square fit are shown in figure 2. The dispersion of points (\square) corresponding to the BORT-ansatz bond orders is much less than that of points (\circ) corresponding to the Pauling bond orders. It can be noticed that the BORT bond orders, like the Pauling bond orders, show cumulating tendency – “ties” (two or more bonds of different lengths possess the same bond order). However, this property is less pronounced for the BORT bond orders, resulting in the improved correlation.

In general, the bond orders calculated by the BORT ansatz (model (IV)) correlate much better with the PPP bond orders than the Pauling bond orders. In table 4 one can find only two exceptions, triphenylene IX and benzo[g]chrysene XXI. The other

BORT models are less successful: model **(I)** is on an average equally successful as Pauling's model, while models **(II)** and **(III)** are much worse.

In the bond order calculation one can also notice different behaviour of subsets of linear and angular BHs. For example, with the ansatz bond orders, the best correlation coefficients r^P are obtained for linear anthracene **(III)** (0.9983), naphthalene **(V)** (0.9982) and pentacene **(XI)** (0.9982), while the worst correlation coefficients r^P are achieved for the fully benzenoid triphenylene **(IX)** (0.9875) and the most branched five-ring isomer **XXI** (0.9878) (table 4). The Hückel bond orders show the opposite trend: worse/better correlations are observed for more linear/angular isomers. The Pauling bond orders show behaviour similar to the Hückel bond orders. For example, BHs **IX** and **XXI** are the only exceptions for which Pauling's formula gives better predictions of bond orders than the BORT-ansatz relation (4).

The Hückel and Pauling bond orders also show similar behaviour in the correlation with the experimentally observed bond lengths [5]. On the whole, the Hückel and Pauling bond orders correlate better with the experimental bond lengths than the PPP and BORT bond orders. As the results for anthracene **(III)** (table 5) and phenanthrene **(IV)** (table 6) demonstrate, the values of coefficients $|r^{\text{exp}}|$ decrease from the Hückel and Pauling bond orders to the PPP bond orders and further to the BORT bond orders. For a set of BHs **I–V** and **VIII–X**, $|r^{\text{exp}}|$ are 0.9605, 0.9316 and 0.9233 for the Hückel, Pauling and PPP bond orders, respectively. With each particular BORT approximate wave function we obtained smaller values of coefficient $|r^{\text{exp}}|$. They are in the range from 0.9018 for the BORT-ansatz wave function to 0.8406 for the wave function defined in the basis of all Kekulé and Claus RRSs.

The comparison with experimental bond lengths seems contrary to our choice of the PPP method as a reliable reference approach for estimating the quality of bond order predictions. However, bond length is a complex quantity whose value depends on numerous factors, and π -electron distribution is only one of them. As a consequence, there is no strong correlation between the π -electron bond orders and the bond lengths. The good correlation with bond orders does not necessarily imply the good correlation with bond lengths. In this paper we put emphasis on the good correlation with bond orders.

In order to estimate the relative performance of the four BORT models, we have also done another statistical analysis. Since BORT models **(I)–(IV)** are relatively simple, one cannot expect these models to produce numerically very reliable bond orders. The same also holds for all other ground-state properties. As a consequence, there is corresponding uncertainty in interpreting the significance of the linear correlation coefficient r , which is calculated by using these numerical values. In particular, a greater correlation coefficient does not necessarily imply a greater significance [6].

In such cases when the exact numerical values are not very reliable, one can use nonparametric or rank correlation as a measure of correlation. The rank correlation does not deal with the exact numerical values of quantities considered, but rather with their relative order. For instance, in the case of two bond orders p_1 and p_2 , all

what is important is whether $p_1 < p_2$, $p_1 > p_2$, or $p_1 = p_2$. There are two popular nonparametric correlation coefficients: the Spearman rank-order correlation coefficient and Kendall's tau (τ) [6].

In table 7 we show values of Kendall's τ for the nonparametric correlations with the PPP bond orders. The results from this table and from table 4 are very similar. In particular, the best nonparametric correlation with the PPP bond orders is obtained with the simple BORT-ansatz model. If one compares relative performance of the BORT-ansatz model and Pauling's model, one finds that in almost all cases the BORT ansatz produces better nonparametric correlation with the PPP bond orders. In table 7, there is only one exception, benzo[e]pyrene XXV. This is even better result than in the case when as a measure of correlation one uses a linear correlation coefficient r^P where one finds two such exceptions (table 4). In general, the relative order of the PPP bond order values is quite well reproduced by the BORT model based on the ansatz wave function: if PPP predicts a bond **a** to have greater bond order than a bond **b**, then the simplest BORT model predicts the bond **a** to have greater or equal bond order as the bond **b**. Analogous statistical analysis, with similar results, can be performed for calculated energies of BHs.

Table 7
Bond-order Kendall's correlation coefficients τ^P for BHs II–XXV.

BH	Kendall's tau τ^P with the PPP bond orders					
	K	K+mC	K+C	A	Pauling	H
II	0.9129	0.9129	0.9129	0.9129	0.7071	0.3334
III	0.9487	0.9487	0.9487	0.9487	0.8367	0.6000
IV	0.9280	0.9280	0.9280	0.9280	0.8819	0.8334
V	0.9759	0.8783	0.8783	0.9759	0.8452	0.5238
VI	0.9017	0.8801	0.8801	0.9587	0.9129	0.4762
VII	0.9342	0.8564	0.8564	0.9342	0.9045	0.7818
VIII	0.9342	0.8564	0.8564	0.9342	0.9045	0.7818
IX	0.9487	0.9487	0.9487	0.9487	0.8367	0.6000
X	0.9661	0.9661	0.9661	0.9661	0.9310	0.8667
XI	0.9092	0.9092	0.9092	0.9820	0.8864	0.5714
XII	0.9578	0.9452	0.9452	0.9672	0.9266	0.7415
XIII	0.8120	0.8120	0.8120	0.9473	0.9268	0.8718
XIV	0.8120	0.8120	0.8120	0.9473	0.9268	0.8974
XV	0.9514	0.8925	0.8925	0.9363	0.9105	0.6952
XVI	0.9183	0.8930	0.8930	0.9353	0.9034	0.7292
XVII	0.9379	0.9379	0.9379	0.9379	0.8721	0.7802
XVIII	0.9183	0.8930	0.8930	0.9276	0.9017	0.7231
XIX	0.9332	0.9332	0.9332	0.9332	0.9132	0.7969
XX	0.9550	0.9550	0.9550	0.9550	0.9376	0.8462
XXI	0.9106	0.9106	0.9106	0.9236	0.8780	0.7723
XXII	0.9550	0.9550	0.9550	0.9550	0.9376	0.8022
XXIII	0.8997	0.8997	0.8997	0.8997	0.8165	0.7143
XXIV	0.9320	0.9173	0.9173	0.9613	0.9029	0.6957
XXV	0.7599	0.7599	0.7599	0.8817	0.9199	0.8840

There is an interesting connection between the BORT-ansatz and Pauling bond orders. It can be shown that if all Kekulé structures are of the same parity, the BORT-ansatz bond orders reduce to the Pauling bond orders, provided in the derivation of the BORT-ansatz bond orders one neglects nonorthogonality of Kekulé structures and if, in addition, in the derivation of relevant matrix elements one retains only the leading term. Hence, in the case of BHs which possess Kekulé structures which are all of the same parity, the Pauling bond orders can be considered to be a first approximation to the more accurate BORT-ansatz bond orders. Although, as shown above, in this case the Pauling bond orders are generally less accurate than the BORT-ansatz bond orders, they are still quite successful. However, in the case of alternant hydrocarbons which besides positive also contain negative Kekulé structures, the analogous first approximation of the BORT-ansatz bond orders is not identical to Pauling's method. For such systems, the Pauling bond orders correlate very poorly with the PPP bond orders, while the correlation of the BORT-ansatz bond orders with the PPP bond orders is still very successful [8].

3. Conclusions

Taking the PPP method as a reference approach, the calculation of energies and bond orders of π -electron ground states of BHs show that the BORT ansatz (model **(IV)**) provides a good method for describing these π -electron systems. Compared with the Hückel MO method, model **(IV)**, in which full computation can be easily performed by hand, provides not only better semiquantitative predictions but also the simple pictorial representation of the ground state wave functions in the sense of an organic chemist.

The BORT models **(I)**–**(III)**, which include more refined basis sets of RRSs in conjunction with the simple Hückel Hamiltonian, also give satisfactory predictions of benzenoid ground-state energies and bond orders. However, the predictions of all these models are less reliable than those given by the simplest model **(IV)** based on the ansatz wave function. The quality of prediction systematically reduces from the set of only Kekulé RRSs over the set comprising Kekulé and mono-Claus RRSs to the set of all Kekulé and Claus RRSs. Such a deterioration is a result of discrepancy between refinements of the Hamiltonian and the basis set. This shows that the improvement of the model subspace should be balanced with an equal improvement of the model Hamiltonian. The basis set including Kekulé and (mono-)Claus RRSs permits interactions between nonbonded carbons and also more expanded CI and, hence, requires an extension beyond the tight-binding and independent-particle approximations.

Concerning the comparison of the BORT bond orders with the Pauling bond orders, it was shown that the BORT-ansatz bond orders are much more reliable than the Pauling bond orders. Thus, if one requires a fast and relatively simple calculation of bond orders, one should utilise the BORT-ansatz method. This approach requires no diagonalisation and it is not much more numerically complex than Pauling's method.

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