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A simple method for the calculation of π-bond orders in alternant hydrocarbons*,**

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A new method for the calculation of bond orders in alternant hydrocarbons is presented. The method requires a summation over the contributions of various superposition diagrams. Quantitatively, the method is almost as reliable as PPP, and due to its simplicity it can be used for fast and relatively accurate calculation of bond orders. In addition some simple rules are derived, which in many cases can be used to predict the signs of bond orders between nonbonded atoms.

Key words: Alternant hydrocarbons — Bond orders — Bond orbital resonance theory (BORT)

1. Introduction

The aim of this paper is to present a simple graphical method for the calculation of π-bond orders in alternant hydrocarbons. The method is derived within the framework of the Bond Orbital Resonance Theory (BORT) approach [1]. The basic approximation used in the derivation of this method is the assumption, justified in the paper, that the ground state of an alternant hydrocarbon is relatively well approximated as a linear combination of positive BORT Kekulé structures, all these structures being contained in the ground state with the same coefficient.

The method implies a simple rule which can be in many cases used in order to predict the sign of the bond order between nonbonded atoms. In all cases

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

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*** *Permanent address*: Rugjer Bošković Institute, POB 1016, 4-41001 Zagreb, Yugoslavia considered, the sign thus predicted is correct. Quantitatively, the method is found to be almost as reliable as PPP. Since numerically this method involves only a simple summation over contributions of various superposition diagrams, it can be used as a method of choice for the fast and relatively reliable predictions of bond orders in alternant hydrocarbons.

Recently there has been a revival interest in various aspects of bond orders [2-14]. Politzer and Ranganathan [2] in their study of relative strengths of chemical bonds considered bond order-bond energy correlation. Peter [3] investigated the well known relationship between bond lengths and bond orders as well as the correlation with electronegativity for homo- and heteronuclear bonds. In his study of the exactly solvable Hubbard model for linear polyenes Hashimoto [4] investigated bond length and bond order dependence of the optical transition energies. Mizoguchi [5] considered the correlation of bond orders with magnetic properties, while Brown and Altermatt [6] derived bond valence parameters from a systematic analysis of the inorganic crystal structure data. Bond orders were also investigated in the relatively large conjugated systems, such as long polymere chains [7], soccerballene C_{60} and related systems [8, 9], carbon honeycomb lattice [10], etc.

In spite of the undeniable importance due to the strong correlation with many physical and chemical properties, there is in the literature no uniquely accepted definition of bond orders [11-14]. Essentially there are two approaches; one can define bond orders either in terms of the "standard" density matrix [12], or in terms of the density matrix in the Löwdin orthonormalized basis [13]. The latter approach seems to perform better and to be more stable [14], and that is the way how bond orders are defined in this paper.

We will consider only π-bond orders of alternant hydrocarbons. This restriction is not essential, and the BORT approach can be also applied to the more interesting non-alternant case [15]. However, the treatment of nonalternant molecules requires a different set of approximations than the treatment of alternant molecules, and nonalternant hydrocarbon are hence not included in the present paper.

2. The method

In the simple varient of the Bond Orbital Resonance Theory (BORT) the $2n$-particle ground state ψ of the closed shell conjugated system is spin-separated [16]

$$\psi = \mathscr{A}\phi\bar{\phi}, \tag{1}$$

where $\mathscr{A}$ is the antisymmetrizer, while ϕ and $\bar{\phi}$ are n-particle spin-α and spin-β substates, respectively. The state ϕ (and equally the state $\bar{\phi}$) is a linear combination of "regular" resonance structures (RRS) S_a (see Appendix)

$$\phi = \sum_a \lambda_a S_a. \tag{2}$$

There is some formal graphical similarity between regular resonance structures and valence bond (VB) resonance structures. However, except for this graphical similarity, these structures are quite different. In the case of RRSs a single nonoriented bond represents a nonexcited bond orbital (BO) which accomodates one particle, while in the case of the VB structure it represents a two-particle state which accomodates two spin paired particles. In addition, RRSs may contain oriented bonds which represent excited bond orbitals, while VB structures may be ionic.

Ground state ϕ of an alternant hydrocarbon containing at least one Kekulé structure can be approximated with [17]

$$\phi = \sum_a K_a^+, \tag{3}$$

where K_a^+ are positive Kekulé RRSs. The approximation (3) is supported by the following points:

(i) The contribution of BORT Kekulé structures to the ground state of a conjugated hydrocarbon is dominant. In addition, this contribution is significantly larger than the corresponding contribution of VB Kekulé structures. For example, a single butadiene BORT Kekulé structure contains approximately 95% of the *ab initio* SCF butadiene ground state [18], while the corresponding VB Kekulé structure contains only ~20% of this state [19]. Similarly, the two BORT Kekulé structures associated with the benzene molecule contain (jointly) ~90% of the benzene SCF ground state [18], while the corresponding VB Kekulé structures contain (jointly) only ~5% of this state [19]. In conclusion, BORT Kekulé structures are well suited to represent ground states of conjugated hydrocarbons, and in the first approximation one can neglect BORT non-Kekulé structures.

(ii) The set $R(n)$ of all n-particle regular resonance structures can be partitioned into subsets $R^+(n)$ and $R^-(n)$ containing "positive" and "negative" structures, respectively [1]. Under rather general assumptions, which include Hamiltonians substantially beyond the PPP model, all RRSs contained in the ground state of an alternant hydrocarbon are of the same parity [1]. In particular, all BORT Kekulé structures contained in this ground state are of the same parity. By definition, this parity can be chosen to be positive. It is interesting that in the case of the Kekulé structures, this partition into positive and negative structures coincides with the Dewar and Longuet-Higgins [20] partition into positive and negative Kekulé structures.

(iii) BORT Kekulé structures contained in the ground state of an alternant hydrocarbon are coherent. In other words, all these structures are contained in the ground state ϕ with the same sign. Moreover, in the case of hydrocarbon compounds containing up to ~30 carbon atoms, the corresponding coefficients λ_a in (2) are approximately constant with a standard deviation ~10% to maximum ~15% [17].

The above three points justify ansatz (3). This ansatz differs from the analogous VB ansatz in that ϕ contains only positive Kekulé structures. Of course, there is in addition a substantial difference in the interpretation of BORT and VB Kekulé structures, as well as in the spin separation assumption (1) characteristic of BORT.

Using ansatz (3) the expectation value of a spin-independent operator $\mathcal{O}$ in the state (1) is

$$\langle\mathcal{O}\rangle = 2 \sum_{a,b} \langle K_a^+|\mathcal{O}|K_b^+\rangle \Big/ \sum_{a,b} \langle K_a^+|K_b^+\rangle. \tag{4}$$

This relation is quite easy to implement. All one needs is a systematic way for the calculation of overlaps $\langle K_a^+|K_b^+\rangle$ and matrix elements $\langle K_a^+|\mathcal{O}|K_b^+\rangle$. This is done elsewhere [1]. Expression (4) can be further simplified, since the summations over overlaps and matrix elements can be conveniently reformulated in terms of the summations over various superposition diagrams. One can thus use relation (4) as a simple tool for an easy approximate calculation of ground state properties of alternant hydrocarbons. It was recently shown that this relation, in conjuncture with the simple Hückel Hamiltonian, reproduces quite reliably PPP resonance energies [17]. The correlation coefficient between the two sets of data is corr = 0.997 [17]. We will now show that this relation is equally reliable in the prediction of bond orders.

3. Some qualitative relations concerning bond orders

In the case of the bond orders between atoms of the same parity, expression (4) predicts that these bond orders vanish (see Appendix). This is in accord with the well known result derived originally within the MO theory and based on the pairing theorem [21].

In the case of the bond orders between atoms of the opposite parity one has

$$P_{ij} = 2 \sum_{a,b} \langle K_a^+|p_{ij}|K_b^+\rangle \Big/ \sum_{a,b} \langle K_a^+|K_b^+\rangle, \tag{5}$$

where P_{ij} is the bond order between atoms (i) and (j), while p_{ij} is the corresponding bond order operator. The rules for the evaluation of overlaps $\langle K_a^+|K_b^+\rangle$ and matrix elements $\langle K_a^+|p_{ij}|K_b^+\rangle$ are given in the Appendix. These rules are quite simple, and in many cases some qualitative predictions are possible.

Overlaps $\langle K_a^+|K_b^+\rangle$ are nonnegative. Further, matrix element $\langle K_a^+|p_{ij}|K_b^+\rangle$ is nonzero if and only if the superposition $G_{ab} = K_a^+ \oplus K_b^+$ of structures K_a^+ and K_b^+ contains no $4m$-type cycle, and if in addition bond $s \equiv (i, j)$ is "internal" to G_{ab}. Thus in Fig. 1 one has $\langle K_a^+|p_{14}|K_b^+\rangle \neq 0$ since G_{ab} contains bond $s \equiv (1, 4)$ internally, and $\langle K_a^+|p_{89}|K_b^+\rangle = 0$ since G_{ab} contains bond $s \equiv (8, 9)$ externally. Moreover, provided nonzero, matrix element $\langle K_a^+|p_{ij}|K_b^+\rangle$ is positive if bond s forms a $(4m+2)$-type cycle over G_{ab}, and it is negative if this bond forms a $4m$-type cycle over G_{ab}. Thus $\langle K_a^+|p_{14}|K_b^+\rangle < 0$ since bond (1, 4) forms a 4-cycle over G_{ab}, while $\langle K_a^+|p_{12}|K_b^+\rangle > 0$ since bond (1, 2) forms a 2-cycle over G_{ab}.

The above rules concerning the sign of matrix elements can be in many cases used in order to estimate the sign of the bond order P_{ij}. It is convenient to define

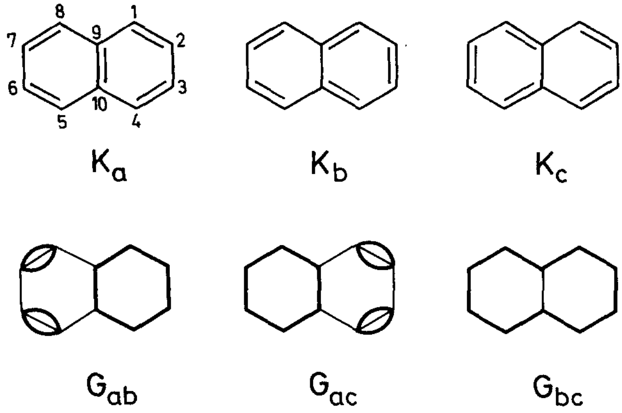


Fig. 1. Naphthalene Kekulé structures and some superposition diagrams. "Diagonal" superposition diagrams G_{aa}, G_{bb}, and G_{cc} are not shown. These diagonal superposition diagrams topologically coincide with Kekulé structures K_a, K_b, and K_c, respectively

a "superposition distance" $d_{ij}(G_{ab})$ between vertices (i) and (j). If bond $s \equiv (i, j)$ is internal to the superposition G_{ab}, the superposition distance is defined as the shortest distance between (i) and (j) on G_{ab}. If this bond is external to G_{ab}, superposition distance $d_{ij}(G_{ab})$ needs not be defined, since in this case the superposition G_{ab} does not contribute to P_{ij}. It follows from the above discussion that if $d_{ij}(G_{ab})$ modulo $4 = 1$, then the contribution of G_{ab} to P_{ij} is positive, while if $d_{ij}(G_{ab})$ modulo $4 = 3$, then this contribution is negative. Thus in Fig. 1 one has $d_{14}(G_{ab})$ modulo $4 = 3$, and $d_{14}(G_{bc})$ modulo $4 = 3$. Both superpositions give a negative contribution to $P_{1,4}$. No other superposition contributes to $P_{1,4}$ and hence $P_{1,4} < 0$. This prediction agrees with HMO, which is a sufficiently accurate method to check such a qualitative prediction.

The above rule is very easy to apply. One needs to examine only these superpositions which contribute to P_{ij}. An example is shown in Fig. 2. One finds $P_{1,4} < 0$, $P_{1,5} > 0$, $P_{1,16} < 0, \ldots, P_{2,15} < 0$, $P_{2,6} > 0, \ldots$ etc., in complete agreement with HMO.

In some cases this simple method does not work. This happens whenever there are superpositions which contribute positively to P_{ij} as well as superpositions which contribute negatively to P_{ij}. Thus in the case of pyrene (Fig. 3), the superposition I contributes positively to $P_{1,14}$, while the superposition II contributes negatively to $P_{1,14}$. Similarly, superpositions III and IV contribute, respectively, positively and negatively to $P_{1,14}$. In BORT these contributions

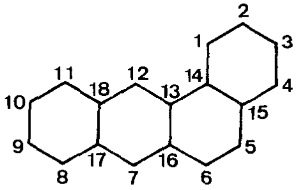


Fig. 2. 1,2-Benz-anthracene. The signs of all bond orders in this compound can be easily derived using the rules described in the text

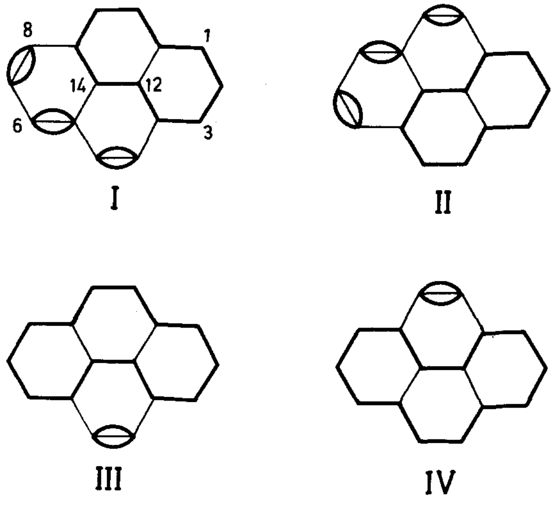
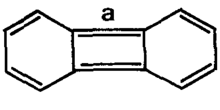


Fig. 3. Superposition diagrams which contribute to the bond order $P_{1,14}$ in pyrene. Contributions of diagrams I and III are positive, while contributions of diagrams II and IV are negative. In BORT these contributions cancel

cancel, and relation (5) predicts $P_{1,14}=0$. In HMO one has $P_{1,14}=-0.02868$ [22]. This is quite small, in qualitative agreement with BORT. Except for bond orders $P_{3,14}=P_{6,12}=P_{8,12}$ which are related to the bond order $P_{1,14}$ by symmetry, no other bond order in pyrene has both, positive and negative contributions. All these other bond orders are predicted with the correct sign.

An interesting case can happen if the hydrocarbon contains $4m$-type rings. In this case beside positive the hydrocarbon can also have negative Kukulé structures. Thus biphenylene has five Kekulé structures, four positive and one negative. In the simplest resonance theory (RT) all these structures contribute to the ground state [23]. Due to the presence of the negative structure V (Fig. 4) the central ring in biphenylene is wrongly predicted to be aromatic. Bond order P_a is also predicted to be large, and bond (a) to be short. One way to treat nonbenzenoid hydrocarbons within the (covalent) VB approach is to take into account the contribution of cyclic permutations [24, 25]. However, in order to obtain satisfactory results one has to include permutations of higher order [24]. The simple RT can hence not be applied. This and similar results prompted strong criticism of RT. Thus in discussing biphenylene example Dewar states that RT has "no firm foundation in the wave properties of matter" [26].

The reason for this and similar failures of RT is easily explained in BORT. Since structure V has negative parity, it is not contained in the ground state. The central ring in biphenylene is hence not aromatic, and bond order P_a is predicted to be



V

Fig. 4. Negative Kekulé structure of biphenylene. In RT the presence of this structure leads to the wrong conclusion that the central ring in biphenylene is aromatic. In BORT this structure does not contribute to the ground state and the central biphenylene ring is not predicted to be aromatic

zero. The failure of RT is thus due to the inclusion of negative structures in the ground state. If one interprets Kekulé structures in the BORT rather than in the simple RT sense, these structures should be omitted. Resonance theory at least partly regains "firm foundation in the wave properties of matter", and its predictions improve.

The above remark concerning RT can be supported in yet another way. One can simplify relation (5) by assuming the zero overlap approximation between Kekulé structures

$$\langle K_a^+ | K_b^+ \rangle = \delta_{ab}. \tag{6}$$

Approximation (6) was rather successfully used in the VB approach [27], it can be imposed a priori on the resonance structures without specifying their nature [28], and it is implicitly assumed in the simple resonance theory.

Using ($A2$) relation (5) reduces to [16]

$$P_{ij} \approx \sum_a^+ f_{aa}^s / N^+. \tag{7}$$

In the above relation the summation $\sum_a^+$ is performed only over positive Kekulé structures, and N^+ is the number of such structures. This relation gives vanishing bond order P_{ij}, unless atoms (i) and (j) are directly bonded. Provided there are no negative structures, bond orders (7) are the same as the well known Pauling bond orders. This shows that in the absence of negative Kekulé structures Pauling bond orders are an approximation to the bond orders (5). However, when negative Kekulé structures are present, Pauling bond orders differ from (7), and they do not approximate (5). It is known that in this latter case Pauling bond orders are quite inaccurate [26]. The reason for this failure is again the improper inclusion of negative Kekulé structures.

4. Comparison with HMO and PPP

Let us now see in more detail how well relation (5) predicts bond orders. In Fig. 5 are shown some benzenoid hydrocarbons and in Table 1 are the corresponding bond orders. HMO, PPP and BORT results are given. Since the PPP results are much more reliable than HMO, the comparation of BORT bond orders with PPP bond orders is crucial.

One first notices that BORT bond orders are systematically smaller than PPP bond orders. This is not such a serious defect. What matters and what is physically most relevant is the relative ordering of bond orders, and this is predicted quite reliably with BORT. Thus in the case of naphthalene (I) BORT predicts $b > d > a, c$ (BORT bond orders P_a and P_c are the same) in agreement with the PPP result $b > d > c > a$. Similarly, in the case of phenanthrene (II) BORT predicts $i > b, d > g > a, c, e > f, h$, again in agreement with the PPP result $i > b, d > g > c > e > a > h > f$. In general, if PPP predicts bond x to have larger bond order than bond y, then BORT predicts bond x to have either larger or the same bond order as bond y. This is true for all compounds in Fig. 5. With only few exceptions it

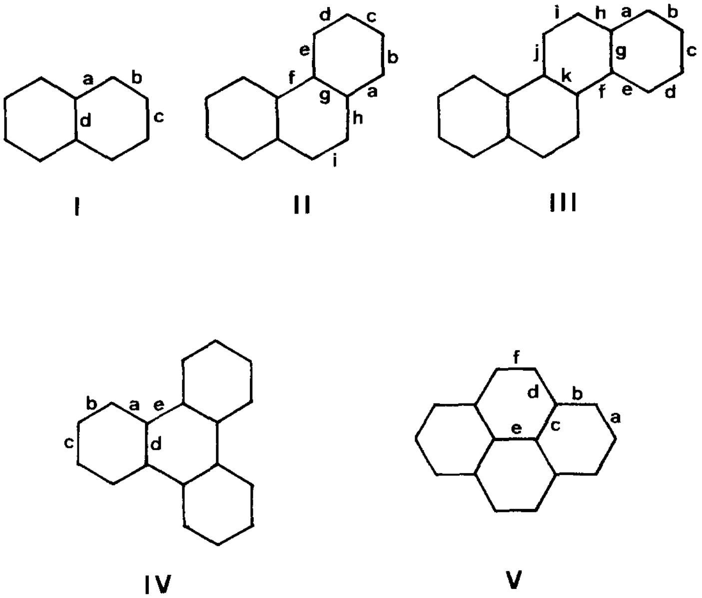


Fig. 5. Some typical benzenoid compounds. The corresponding bond orders are given in Table 1

is also true more generally, if one compares bond orders associated with different compounds in this figure. Of course, the agreement obtained in the case of the above compounds is no guarantee that the descending sequence of bond orders as predicted by BORT will always agree with the descending sequence of bond orders as predicted by PPP. Nevertheless, the compounds in Fig. 5 are some typical benzenoid compounds, and the obtained results indicate a strong correlation between BORT and PPP bond orders.

HMO bond orders do not correlate so well with PPP bond orders. Thus in the case of the naphthalene HMO predicts $b > c > a > d$ in disagreement with the PPP result $b > d > c > a$. Similar disagreement can be found in the case of all other compounds in Fig. 5. These results show that BORT bond orders correlate quite well with PPP bond orders, and they correlate less well with the HMO bond orders. This is encouraging, since the PPP bond orders are more reliable than the HMO bond orders.

Another way to estimate relative merits of HMO and BORT bond orders is to compare the corresponding correlation coefficients in the correlation with PPP. These correlation coefficients are also given in Table 1. Thus in the case of naphthalene the correlation of BORT bond orders with PPP bond orders (corr = 0.996) is much better than the correlation of HMO bond orders with PPP bond orders (corr = 0.763). In general, the correlation of BORT results with PPP results is very good, the correlation coefficient in the worst case (compound V) being corr = 0.992.

In view of such a good correlation, one can successfully emulate PPP bond orders

Table 1. Bond orders of the molecules in Fig. 5

Molecule		*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	Corr. coeff.
Naphthalene(I)	BORT[a]	0.3939	0.7576	0.3939	0.5151								0.996
	HMO[b]	0.5547	0.7246	0.6032	0.5182								0.763
	PPP[c]	0.500	0.789	0.530	0.608								
Phenanthrene(II)	BORT	0.4864	0.6887	0.4864	0.6887	0.4864	0.2218	0.5447	0.2218	0.8755			0.997
	HMO	0.5751	0.7068	0.6228	0.7016	0.5900	0.4605	0.5423	0.5059	0.7747			0.944
	PPP	0.560	0.741	0.584	0.741	0.566	0.380	0.627	0.398	0.862			
Chrysene(III)	BORT	0.4488	0.7169	0.4488	0.7169	0.4488	0.2922	0.5212	0.2922	0.8284	0.2922	0.6434	0.996
	HMO	0.5684	0.7122	0.6171	0.7071	0.5831	0.4759	0.5353	0.5209	0.7540	0.5376	0.5729	0.886
	PPP	0.536	0.759	0.566	0.759	0.542	0.416	0.621	0.434	0.831	0.452	0.687	
Triphenylene(IV)	BORT	0.5437	0.6449	0.5437	0.5770	0.1123							0.996
	HMO	0.6026	0.6904	0.6366	0.5617	0.4281							0.920
	PPP	0.602	0.705	0.621	0.627	0.325							
Pyrene(V)	BORT	0.5809	0.5809	0.4635	0.1873	0.3397	0.9016						0.992
	HMO	0.6695	0.5944	0.5235	0.5034	0.5364	0.7765						0.928
	PPP	0.669	0.627	0.572	0.380	0.440	0.874						

[a] Results of the relation (5)

[b] Taken from [22] and rounded to four significant figures

[c] Derived from the PPP bond lengths in [20] (given to three significant figures) and rounded to three significant figures. Correlation coefficients are calculated prior to round off

with BORT bond orders. The least square fit yields

$$P_{\mathrm{ppp}} = 0.731 P_{\mathrm{bort}} + 0.224. \tag{8}$$

This relation reproduces PPP bond orders in Table 1 with the correlation coefficient corr = 0.995 and with a standard deviation $\Delta = 0.014$. The analogous emulation of PPP bond orders with HMO bond orders yields

$$P_{\mathrm{ppp}} = 1.435 P_{\mathrm{hmo}} - 0.262. \tag{9}$$

This relation reproduces PPP bond orders with the correlation coefficient corr = 0.916 and with a standard deviation $\Delta = 0.057$. BORT bond orders are obviously much more reliable than HMO bond orders.

One should not attach too much importance to the actual numerical values of the above correlation coefficients. Depending on the parametrisation, bond orders as calculated by different PPP implementations may differ from each other. We have here compared BORT bond orders with PPP bond orders as calculated by Dewar and Gleicher [29]. The comparison with some other PPP bond orders should give slightly different results. In addition, numerical data in [29] are given only up to three significant figures, and this introduces a substantial error in the last digit of the correlation coefficients. This error is not likely to improve the correlation but rather to make it appear worse. Moreover, the correlation between two different PPP calculations can in some cases be of the same order of magnitude as the correlation between BORT and PPP. One can hence say that BORT bond orders correlate with PPP bond orders approximately as well as bond orders calculated by one PPP method correlate with bond orders calculated by some other PPP method. In conclusion, bond orders calculated using relation (8) and BORT values (5) for P_{bort} are almost as reliable as PPP bond orders. Since BORT bond orders (5) can be very easily calculated, the BORT approach can be used as a method of choice.

Appendix

A1. BORT *resonance structures*

In the bond orbital resonance theory each resonance structure S_a is a normalised determinant containing mutually disconnected excited and/or nonexcited bond orbitals (BO) [1]. Graphically, excited and nonexcited BOs are represented as oriented and nonoriented bonds, respectively. An n-particle resonance structure contains n such bonds and it involves $2n$ vertices.

The above resonance structures are linearly dependent, and it is sufficient to consider only "regular" resonance structures (RRS). In order to define these structures one has first to partition the set of all $2n$ vertices into two subsets containing n "source" and n "sink" vertices, respectively. By definition, each RRS contains only such BO's which connect a source vertex with a sink vertex, i.e. bond orbitals connecting either two source or two sink vertices are not allowed [1]. Figure 6 shows RRSs for $n = 2$. In the case of alternant hydrocarbons it is convenient, if possible, to choose such a partition on sink and source vertices which coincides with the usual partition into starred and nonstarred atoms.

A2. Superpositions of resonance structures and active and passive cycles

For the evaluation of overlaps and matrix elements between RRSs the notion of the superposition of RRSs and the distinction between "active" and "passive" cycles is important.

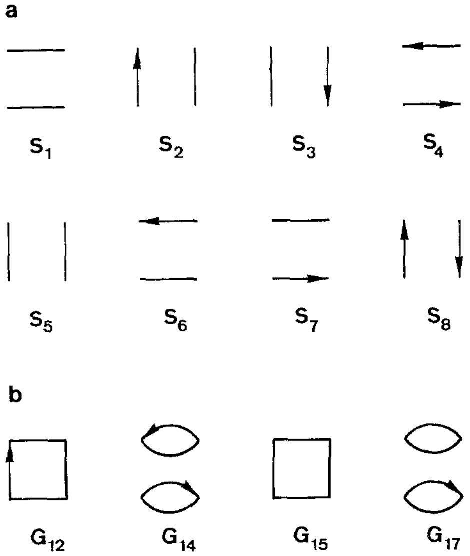


Fig. 6. **a** Regular resonance structures for $n=2$. Structures S_1 through S_4 are positive, while structures S_5 through S_8 are negative. **b** Some superpositions of RRSs in **a**. Superposition G_{12} contains one active cycle, superposition G_{14} contains two passive cycles, superposition G_{15} contains one passive cycle, and superposition G_{17} contains one active and one passive cycle

A superposition $G_{ab}=S_a \oplus S_b$ between RRSs S_a and S_b consists of disconnected even cycles. Each of these cycles contains oriented and/or nonoriented bonds. A cycle $c_\mu \in G_{ab}$ is "active" if $(n_\mu + m_\mu)$ is odd, where $2n_\mu$ is the number of bonds in c_μ, while m_μ is the number of oriented bonds in c_μ. Otherwise the cycle c_μ is "passive" (see Fig. 6b). In particular, if $S_a \equiv K_a$ and $S_b \equiv K_b$ are Kekulé resonance structures, G_{ab} contains no oriented bonds. In this case each active cycle $c_\mu \in G_{ab}$ is a $(4m+2)$-type cycle, while each passive cycle $c_\mu \in G_{ab}$ is a $4m$-type cycle.

A3. Positive and negative resonance structures

The set $R(n)$ of all n-particle RRSs splits into subsets $R^+(n)$ and $R^-(n)$ containing "positive" (S_a^+) and "negative" (S_a^-)RRSs, respectively. Structures S_a and S_b are of the same parity if the superposition G_{ab} contains an even number of passive cycles. Otherwise they are of the opposite parity [1]. In the case of alternant hydrocarbons matrix element of the PPP-type Hamiltonian between structures of the opposite parity vanishes [1]. Nondegenerate ground states of alternant hydrocarbons hence contain resonance structures of only one parity, which can be conveniently defined to be positive [1].

A4. Overlaps and matrix elements of bond order operators

Overlap $S_{ab} \equiv \langle S_a | S_b \rangle$ between n-particle RRSs S_a and S_b is [1]

$$S_{ab} = 2^{p-n} \begin{cases} 1 & \text{if all cycles } c_\mu \in G_{ab} \text{ are active} \\ 0 & \text{otherwise,} \end{cases} \tag{A1}$$

where p is the number of cycles in G_{ab}.

In particular, if $S_a \equiv K_a$ and $S_b \equiv K_b$ are Kekulé resonance structures, overlap S_{ab} vanishes whenever the superposition G_{ab} contains at least one $4m$-type cycle.

Let p_{ij} be a bond order operator involving vertices (i) and (j). If these vertices are of the same parity, then the matrix element $\langle S_a | p_{ij} | S_b \rangle$ vanishes for all structures S_a and S_b of the same parity [1]. Since ground states of alternant hydrocarbons contain only positive structures [1], bond orders in alternant hydrocarbons vanish between atoms of the same parity.

If vertices (i) and (j) are of the opposite parity, then matrix element $\langle S_a | p_{ij} | S_b \rangle$ equals [1]

$$\langle S_a | p_{ij} | S_b \rangle = \tfrac{1}{2}(-1)^{n_s'+m_s'+1} f_{ab}^s S_{ab}, \tag{A2}$$

where:

(i) $f^s_{ab} = 1$ if vertices (i) and (j) which define bond $s \equiv (i, j)$ are contained in the same cycle $c_\mu \in G_{ab}$. Otherwise, i.e. if vertex (i) is contained in one cycle $c_\mu \in G_{ab}$ and vertex (j) in another cycle $c_\nu \in G_{ab}$, then $f^s_{ab} = 0$.

(ii) (defined if $f^s_{ab} \neq 0$). Vertices (i) and (j) identify two segments on c_μ. These segments, together with the bond $s \equiv (i, j)$, from overlapping cycles c'_μ and c''_μ. By definition, $2n'_s$ is the number of bonds in c'_μ, while m'_s is the number of oriented bonds in c'_μ.

(iii) S_{ab} is overlap given by (A1).

According to (i) through (iii) matrix element (A2) is different from zero if and only if the superposition G_{ab} contains no passive cycle, and if in addition bond $s \equiv (i, j)$ is "internal" to G_{ab} (i.e. if vertices (i) and (j) are contained in one and the same cycle $c_\mu \in G_{ab}$). If nonzero, this matrix element is positive if bond s forms an active cycle over G_{ab}, and it is negative if this bond forms a passive cycle over G_{ab}.

A5. Graphical rules for the evaluation of bond orders in alternant hydrocarbons

It is convenient to reformulate summations in (5) in terms of the summations over superposition diagrams. One has to evaluate two sums:

$$
\begin{aligned}
S &= \sum_{a,b} \langle K_a^+ | K_b^+ \rangle \\
D_{ij} &= 2 \sum_{a,b} \langle K_a^+ | p_{ij} | K_b^+ \rangle.
\end{aligned}
\tag{A3}
$$

D_{ij} are "nonnormalised" bond orders, and S is the normalisation constant.

Using relations (A1) and (A2) and the fact that K_a^+ and K_b^+ are positive Kekulé structures, one derives following rules for the evaluation of these sums:

Evaluation of S:

(i) Consider only these superposition diagrams G_{sup} which contain no $4m$-cycle. In addition, G_{sup} should be reproducible as a superposition of positive Kekulé structures.

(ii) Each superposition diagram G_{sup} with the above properties contributes $2^{2\rho-\rho_2-n}$ to S. Here ρ is the number of all cycles in G_{sup}, while ρ_2 is the number of 2-cycles in G_{sup}.

(iii) S is the total sum of the above contributions.

Evaluation of D_{ij}:

(i) Consider only these superposition diagrams G_{sup} which contain no $4m$-cycle, which are reproducible as superpositions of positive Kekulé structures, and which in addition contain bond $s \equiv (i, j)$ internally.

(ii) Each G_{sup} with the above properties contributes in the absolute value $2^{2\rho-\rho_2-n}$ to D_{ij}.

(iii) The contribution of G_{sup} to D_{ij} is positive if bond $s \equiv (i, j)$ forms a $(4m+2)$-cycle over G_{sup}, and it is negative if this bond forms a $4m$-cycle over G_{sup}.

(iv) D_{ij} is the total sum of the above contributions.

The quantity $2^{2\rho-\rho_2-n}$ appearing in the above rules can be also expressed as $2^{2\rho'-n'}$, where ρ' is the number of all cycles in G_{sup} excluding 2-cycles, while $2n'$ is the number of all bonds in G_{sup} excluding bonds contained in 2-cycles. Note also that the condition that G_{sup} should be reproducible as a superposition of positive Kekulé structures can be usually omitted, except in some cases when the hydrocarbon has at least two $4m$-type rings. Namely, only in such cases it can happen that the superposition diagram originates from two negative Kekulé structures.

The above rules are easy to implement. Thus G_{ab} in Fig. 1 contributes 1/2 to $D_{1,2}$ ($\rho = 3$, $\rho_2 = 2$ and $n = 5$), $-1/2$ to $D_{1,4}$, 0 to $D_{1,5}$ etc. Similarly, G_{bc} contributes 1/8 to $D_{1,2}$ ($\rho = 1$, $\rho_2 = 0$, $n = 5$), $-1/8$ to $D_{1,4}$, 1/8 to $D_{1,5}$, etc.

The above rules, supplemented with some iterative relations which further simplify the calculation of S and D_{ij} were used in the calculation of BORT bond orders in Table 1.

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