# On the $\pi$-Electron Content of Bonds and Rings in Benzenoid Hydrocarbons

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The Pauling bond order can be viewed as a measure of the $\pi$-electron content of the respective carbon-carbon bond. In benzenoid hydrocarbons its values lie between 0 (in the case of essential single bonds) and 1 (in the case of essential double bonds). If the benzenoid molecule does not possess essential single and double bonds, then the Pauling bond orders are greater than 0 and less than 1, but may assume values arbitrarily close to 0 and 1. The $\pi$-electron content of a ring is equal to the sum of the $\pi$-electron contents of the carbon-carbon bonds forming this ring. We show that in benzenoid hydrocarbons the $\pi$-electron content of any (six-membered) ring lies between 0 and 5.5. If the molecule does not possess essential single and double bonds, then the $\pi$-electron content of any ring is greater than 0 and less than 5.5, but may assume values arbitrarily close to 0 and 5.5.

*Key words:* Pauling Bond Order; Benzenoid Hydrocarbons; $\pi$-Electron Content (of a Carbon-Carbon Bond); $\pi$-Electron Content (of a Ring).

## Introduction

Molecular-topology-based considerations have a long tradition in organic chemistry [1 – 3] and have proven to be particularly suitable and efficient in the case of benzenoid hydrocarbons [4 – 6]. Kekulé structures and their counts play an outstanding role in the theory of benzenoid hydrocarbons (for details see the book [5], the review [7] and elsewhere [8 – 10]).

In order to rationalize the variations in the carbon-carbon bond lengths in polycyclic aromatic compounds, Pauling, Brockway, and Beach [11] considered the quantities $P_{rs}$ (nowadays known under the name "*Pauling bond orders*"), equal to the ratio of the number $K_{rs}$ of Kekulé structures in which the carbon atoms $r$ and $s$ are connected by a double bond, and the total number $K$ of Kekulé structures. This very simple and easily calculable "bond order" enables a surprisingly accurate prediction of interatomic distances, as demonstrated by numerous examples [12 – 17].

Another way to interpret $P_{rs}$ would be to consider it as a measure of the $\pi$-electron content of the bond $rs$. More precisely, if the $\pi$-electrons of the benzenoid molecule are viewed as being distributed among the carbon-carbon bonds, then the $\pi$-electron content of the bond $rs$ would be $2P_{rs}$.

Bearing this latter interpretation in mind, we could conceive the $\pi$-electron content of a ring $R$ by adding the $\pi$-electron contents of the carbon-carbon bonds forming this ring. If the bond $rs$ belongs solely to $R$, then it contributes to the $\pi$-electron content of $R$ by $2P_{rs}$. If, however, this bond is shared by two rings, say $R$ and $R'$, then its contribution to the $\pi$-electron content of $R$ is $P_{rs}$ and to the $\pi$-electron content of $R'$ also $P_{rs}$. Thus, the $\pi$-electron content of the ring $R$ of a polycyclic conjugated hydrocarbon $H$ is computed by means of the expression

$$EC = EC(R) = EC(R|H) = 2\sum_{*} P_{rs} + \sum_{**} P_{rs} \quad (1)$$

with $\sum_{*}$ and $\sum_{**}$ indicating summation over bonds belonging solely to $R$, and shared by $R$ and another ring of $H$, respectively.

Whereas the Pauling-bond-order concept was put forward in the 1930s [11] and fully elaborated in the 1970s [12, 13], the closely related $\pi$-electron-ring-content was conceived only quite recently [18, 19].

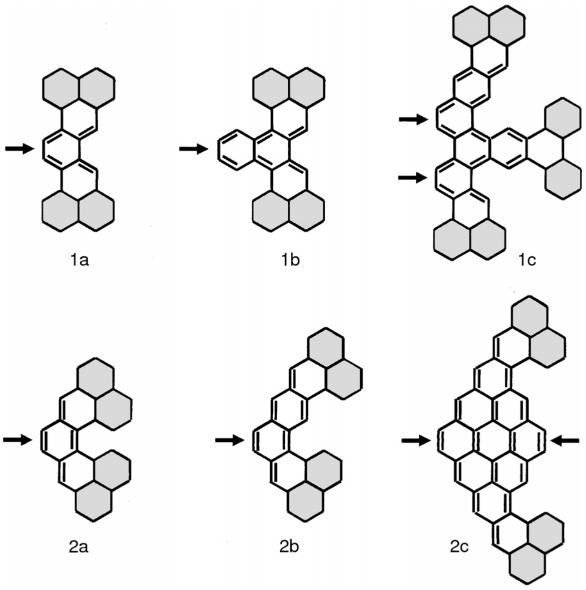

Fig. 1. Benzenoid hydrocarbons possessing essential single (2,2)-bonds (**1a**, **1b**, and **1c**) and essential double (2,2)-bonds (**2a**, **2b**, and **2c**). These bonds are indicated by arrows. By shading are indicated the domains in which delocalization occurs, i. e., in which the Pauling bond orders differ from 0 and 1.

The aim of the present paper is to determine the values which $EC(R)$ may assume in the case of benzenoid hydrocarbons, and to reveal the structure of those benzenoids in which $EC(R)$ is extremal [20]. For these polycyclic conjugated systems $R$ always stands for a six-membered cycle (a hexagon).

Our main results are the following two theorems.

**Theorem 1.** If $H$ is a Kekuléan benzenoid hydrocarbon, and $R$ is one of its rings, then $0 \leq EC(R) \leq 5.5$. The $\pi$-electron content of $R$ may be equal to 0, and may be equal to 5.5.

**Theorem 2.** If $H$ is a Kekuléan benzenoid hydrocarbon without essential single and double bonds, and $R$ is one of its rings, then $0 < EC(R) < 5.5$. The $\pi$-electron content of $R$ may be arbitrarily close to 0, and may be arbitrarily close to 5.5.

In order to prove the above bounds for $EC$ we need some preparation. In particular, we need to find lower and upper bounds for the Pauling bond order.

## Bounds for the Pauling Bond Order

In what follows we shall be especially interested in carbon-carbon bonds of benzenoid hydrocarbons in which both involved carbon atoms have exactly two carbon-atom neighbors. In line with the terminology of the book [5] we refer to these as $(2,2)$-bonds. Each benzenoid system possesses at least six $(2,2)$-bonds.

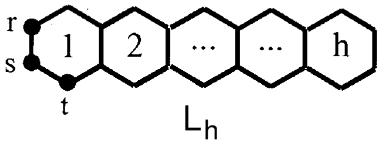

Fig. 2. The linear polyacene with $h$ hexagons has $K = h+1$ Kekulé structures. For the sites $r,s,t$, as indiacetd in the diagram, $K_{\mathrm{rs}} = 1$ whereas $K_{\mathrm{st}} = h$. Consequently, $P_{\mathrm{rs}} = 1/(h+1)$ whereas $P_{\mathrm{st}} = h/(h+1)$. With increasing $h$, the Pauling bond orders of rs and st tend to their limit values 0 and 1, respectively.

If a bond *rs* is single in all Kekulé structures, then it is referred to as an *essential single bond*. For it $P_{\mathrm{rs}} = 0$. If a bond *rs* is double in all Kekulé structures, then it is referred to as an *essential double bond*. For it $P_{\mathrm{rs}} = 1$. Evidently, 0 is the minimum and 1 the maximum possible value of the Pauling bond order.

There exist benzenoid hydrocarbons in which some bonds are essential single and some essential double [21–23]. Furthermore, such essential bonds may be $(2,2)$-bonds. In Fig. 1 are depicted examples of such benzenoid systems.

From the examples given in Fig. 1 we arrive at an obvious conclusion [16]:

**Theorem 3.** If *rs* is a bond of a Kekuléan benzenoid hydrocarbon, then $0 \leq P_{\mathrm{rs}} \leq 1$. The Pauling bond order of *rs* may be equal to 0, and may be equal to 1. The Pauling bond order of a $(2,2)$-bond may be equal to 0, and may be equal to 1.

However, we may say a bit more:

**Theorem 4.** If *rs* is a bond of a Kekuléan benzenoid hydrocarbon without essential single and double bonds, then $0 < P_{\mathrm{rs}} < 1$. The Pauling bond order of *rs* may be arbitrarily close to 0, and may be arbitrarily close to 1. The Pauling bond order of a $(2,2)$-bond may be arbitrarily close to 0, and may be arbitrarily close to 1.

In order to verify Theorem 4 it is sufficient to find a homologous series of benzenoid hydrocarbons for which the Pauling bond orders of $(2,2)$-bonds tend to zero and unity. An elementary example of this kind is depicted in Figure 2.

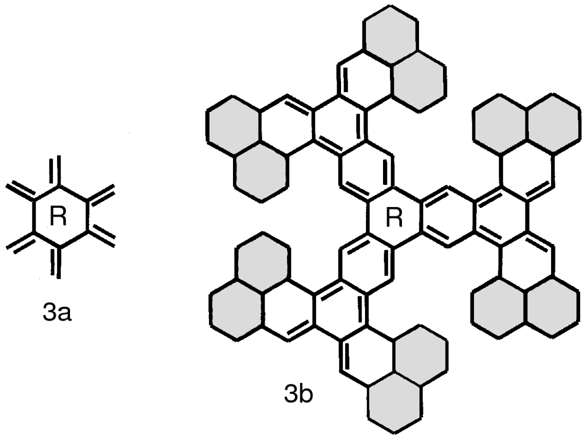

Fig. 3. The general form of a ring with zero π-electron content (**3a**) and an example of a benzenoid system containing it (**3b**). For details see Fig. 1 and text.

### Proving Theorem 1

The π-electron content of a ring $R$ of a benzenoid hydrocarbon $H$ is zero if and only if in all Kekulé structures of $H$ the arrangement of double bonds is as indicated in diagram **3a** in Figure 3. This is achieved if three benzenoid fragments possessing $(2,2)$-bonds with zero Pauling bond order (cf. Fig. 1) are connected to $R$ via their $(2,2)$-bonds. An example is the system **3b** in Fig. 3, constructed from three fragments **1b**.

In order that a ring $R$ in a benzenoid hydrocarbon $H$ has as large as possible π-electron content it must share its π-electrons with as few as possible other rings. Thus a ring with maximum $EC$-value must have exactly one neighboring ring. Then the Kekulé structures of $H$ may be of the type **4a**, **4b**, and **4c**, as shown in Figure 4. Each Kekulé structure of the type **4a** contributes by 6 to the π-electron content of $R$. The analogous contributions of the Kekulé structures of the type **4b** and **4c** are 5 and 4, respectively.

Let there be $K_\mathrm{a}$, $K_\mathrm{b}$, and $K_\mathrm{c}$ Kekulé structures of $H$ of the form **4a**, **4b**, and **4c**, respectively. Then,

$$EC(R|H) = \frac{6K_\mathrm{a} + 5K_\mathrm{b} + 4K_\mathrm{c}}{K_\mathrm{a} + K_\mathrm{b} + K_\mathrm{c}}$$

It is easily seen that $K_\mathrm{a} = K_\mathrm{b}$. Therefore

$$EC(R|H) = \frac{11K_\mathrm{a} + 4K_\mathrm{c}}{2K_\mathrm{a} + K_\mathrm{c}} = 5.5 - \frac{1.5K_\mathrm{c}}{2K_\mathrm{a} + K_\mathrm{c}}.$$

We thus see that $EC \leq 5.5$. Equality $EC = 5.5$ will occur if there are no Kekulé structures of the type **4c**, i. e. if $K_\mathrm{c} = 0$. This, in turn, will happen if $H$ is obtained by connecting to the ring $R$ a benzenoid fragment possessing a $(2,2)$-bond with unit Pauling bond order (cf. Fig. 1) via this $(2,2)$-bond. An example is the system **4d** in Fig. 4, obtained from the fragment **2b**.

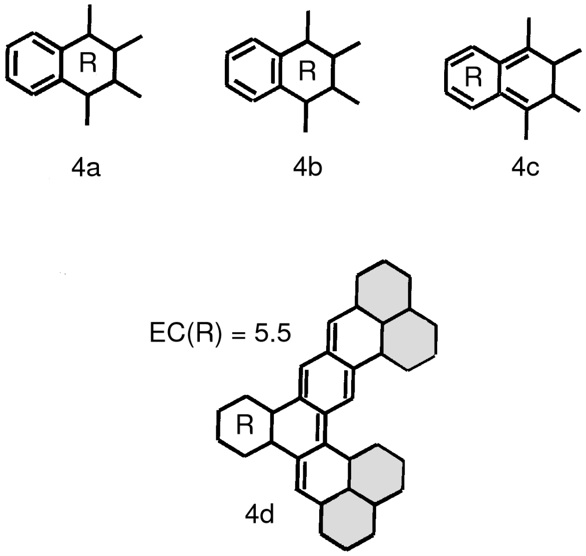

Fig. 4. The three different types of arrangements of double bonds in a terminal 6-membered ring (**4a**, **4b**, **4c**) and a benzenoid hydrocarbon (**4d**) in which the ring $R$ has maximum possible π-electron content.

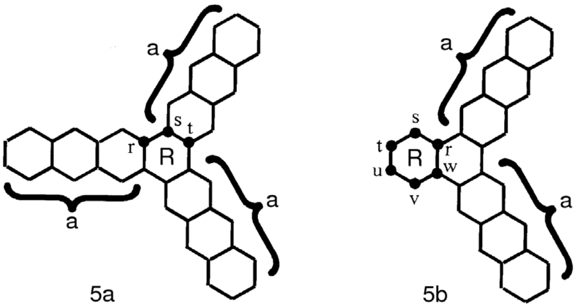

Fig. 5. Two benzenoid systems without essential single and double bonds. With increasing value of the parameter $a$, the π-electron content of the ring $R$ in **5a** tends to zero, whereas in **5b** it tends to 5.5. For details see text.

By this we completed the demonstration of the validity of Theorem 1.

### Proving Theorem 2

From the considerations in the previous section we see that if either $EC(R|H) = 0$ or $EC(R|H) = 5.5$, then the benzenoid system $H$ necessarily possesses essential single and double bonds. We have also demonstrated that $EC(R|H)$ cannot exceed 5.5. Thus, if essential single and double bonds are not permitted, it must be $0 < EC(R) < 5.5$.

The fact that $EC(R)$ may become arbitrarily close to either 0 or 5.5 is verified by means of the examples shown in Figure 5.

Using standard methods for Kekulé structure enumeration [5, 7–10], it is shown that for the benzenoid molecules of the type **5a** (symmetric starphenes), $K = (a+1)^3+1$, $K_{\mathrm{rs}} = 1$, and $K_{\mathrm{st}} = (a+1)^2$, cf. Figure 5. Consequently,

$$P_{\mathrm{rs}} = \frac{1}{(a+1)^3+1}; \quad P_{\mathrm{st}} = \frac{(a+1)^2}{(a+1)^3+1}.$$

Bearing in mind equation (1) and the symmetry of the molecule **5a**, we get

$$EC(R) = 6P_{\mathrm{rs}} + 3P_{\mathrm{st}} = \frac{6+3(a+1)^2}{(a+1)^3+1} = \frac{3a^2+6a+9}{a^3+3a^2+3a+2},$$

implying that $EC(R)$ tends to zero as the parameter $a$ tends to infinity.

An analogous calculation for the benzenoid system **5b** yields $K = 2(a+1)^2+1$, $K_{\mathrm{rs}} = K_{tu} = K_{vw} = K_{\mathrm{wr}} = (a+1)^2$, and $K_{\mathrm{st}} = K_{uv} = (a+1)^2+1$. Consequently,

$$P_{\mathrm{rs}} = P_{\mathrm{tu}} = P_{\mathrm{uv}} = P_{\mathrm{wr}} = \frac{(a+1)^2}{2(a+1)^2+1};$$

$$P_{\mathrm{st}} = P_{\mathrm{uv}} = \frac{(a+1)^2+1}{2(a+1)^2+1}$$

which, in view of (1) results in

$$EC(R) = 2(P_{\mathrm{rs}} + P_{\mathrm{st}} + P_{\mathrm{tu}} + P_{\mathrm{uv}} + P_{\mathrm{vw}}) + P_{\mathrm{wr}} = \frac{11(a+1)^2+4}{2(a+1)^2+1} = 5.5 - \frac{1.5}{2(a+1)^2+1}.$$

The fact that for $a \to \infty$ the $\pi$-electron content of the rings $R$ in **5b** tends to 5.5 (from below) is now evident.

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