On the π-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 π-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 π-electron content of a ring is equal to the sum of the π-electron contents of the carbon-carbon bonds forming this ring. We show that in benzenoid hydrocarbons the π-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 π-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; π-Electron Content (of a Carbon-Carbon Bond); π-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 π-electron content of the bond \( rs \). More precisely, if the π-electrons of the benzenoid molecule are viewed as being distributed among the carbon-carbon bonds, then the π-electron content of the bond \( rs \) would be \( 2P_{rs} \).

Bearing this latter interpretation in mind, we could conceive the π-electron content of a ring \( R \) by adding the π-electron contents of the carbon-carbon bonds forming this ring. If the bond \( rs \) belongs solely to \( R \), then it contributes to the π-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 π-electron content of \( R \) is \( P_{rs} \) and to the π-electron content of \( R' \) also \( P_{rs} \). Thus, the π-electron content of the ring \( R \) of a polycyclic conjugated hydrocarbon \( H \) is computed by means of the expression

\[
EC = EC(R) = EC(R \mid H) = 2 \sum_s P_{rs} + \sum_{rs} P_{rs} \tag{1}
\]

with \( \sum_s \) and \( \sum_{rs} \) 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 π-electron-ring-content was conceived only quite recently [18, 19].
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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 $π$-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 $π$-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. If a bond $rs$ is single in all Kekulé structures, then it is referred to as an essential single bond. For it $P_{rs} = 0$. If a bond $rs$ is double in all Kekulé structures, then it is referred to as an essential double bond. For it $P_{rs} = 1$. 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 $0 \leq P_{rs} \leq 1$. 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 $0 < P_{rs} < 1$. 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.
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Fig. 3. The general form of a ring with zero \( \pi \)-electron content (3a) and an example of a benzenoid system containing it (3b). For details see Fig. 1 and text.

**Proving Theorem 1**

The \( \pi \)-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 \( \pi \)-electron content it must share its \( \pi \)-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 \( \pi \)-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 \( K_a, K_b, \) and \( K_c \) Kekulé structures of \( H \) of the form 4a, 4b, and 4c, respectively. Then,

\[
EC(R|H) = \frac{6K_a + 5K_b + 4K_c}{K_a + K_b + K_c}
\]

It is easily seen that \( K_a = K_b \). Therefore

\[
EC(R|H) = \frac{11K_a + 4K_c}{2K_a + K_c} = 5.5 - \frac{1.5K_c}{2K_a + K_c}.
\]

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 \( K_c = 0 \). 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.

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 es-
ential 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), $K = (a + 1)^3 + 1$, $K_{rs} = 1$, and $K_{st} = (a + 1)^2$, cf. Figure 5. Consequently,

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

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

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

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

An analogous calculation for the benzenoid system 5b yields $K = 2(a + 1)^2 + 1$, $K_{ts} = K_{uv} = K_{wr} = (a + 1)^2$, and $K_{st} = K_{av} = (a + 1)^2 + 1$. Consequently,

$$P_{ts} = P_{tu} = P_{av} = P_{wr} = \frac{(a + 1)^2}{2(a + 1)^2 + 1};$$

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

which, in view of (1) results in

$$EC(R) = 2(P_{ts} + P_{st} + P_{tu} + P_{av} + P_{wr}) + P_{wt} = \frac{11(a + 1)^2 + 4}{2(a + 1)^2 + 1} = \frac{5.5}{2(a + 1)^2 + 1} - \frac{1.5}{2(a + 1)^2 + 1}.$$

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.