Monatshefte für Chemie 136, 713–717 (2005)
DOI 10.1007/s00706-005-0287-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

On the Distribution of π-Electrons into Rings of Conjugated Hydrocarbons Containing a Linear Polyacene Fragment

Ivan Gutman[1,*] and **Nedžad Turković**[2]

[1] Faculty of Science, University of Kragujevac, P.O. Box 60, 34000 Kragujevac, Serbia and Montenegro
[2] Technical High School, Prijepolje, Serbia and Montenegro

Received September 7, 2004; accepted October 12, 2004
Published online April 22, 2005

Summary. A method for assessing the π-electron contents (EC) of rings of benzenoid hydrocarbons, based on the examination of their *Kekulé* structures, was recently put forward by *Balaban* and *Randić*. We now show that all hexagons belonging to a linear polyacene fragment of a conjugated hydrocarbon (not necessarily benzenoid) have mutually equal EC-values.

Keywords. π-Electron content; π-Electron distribution; Polyacenes.

Introduction

In a series of recently published papers [1–4] *Balaban* and *Randić* proposed a theoretical method for (formally) distributing the π-electrons into the rings of polycyclic conjugated molecules. Their approach was soon further elaborated by other authors [5–8]. In Ref. [8] it was shown that the π-electron content $EC(R)$ of a ring R can be computed by means of the *Pauling* bond orders as shown by Eq. (1) where P_{rs} stands for the *Pauling* bond order of the carbon–carbon bond rs, whereas $\sum_*$ and $\sum_{**}$ indicate, respectively, summation over bonds that solely belong to the ring R, and over bonds that are shared between R and another ring.

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

The sum of the $EC(R)$-values of all rings is equal to the total number of π-electrons.

Recall that the *Pauling* bond order is defined by Eq. (2) [9, 10] where K is the number of *Kekulé* structures of the underlying conjugated molecule, and K_{rs} is the

* Corresponding author. E-mail: gutman@knez.uis.kg.ac.yu

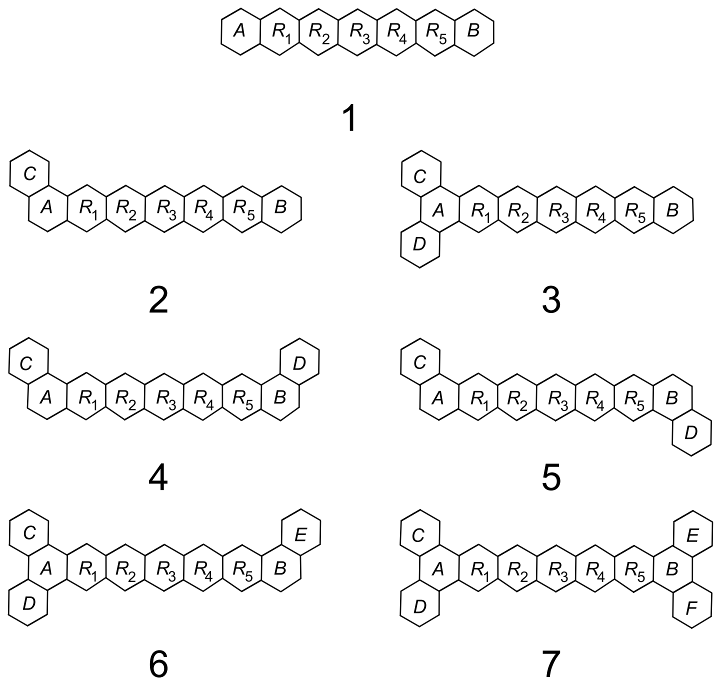

Fig. 1. Heptacene and its benzo-annelated derivatives, and the labeling of its hexagons; the respective π-electron contents are given in Table 1

number of *Kekulé* structures in which the bond *rs* is double.

$$P_{rs} = \frac{K_{rs}}{K} \tag{2}$$

The condition $K > 0$ is essential for the *Balaban–Randić* definition of the π-electron content of a ring. In view of this, in what follows we assume that all conjugated systems considered *Kekuléan*, *i.e.*, possess at least one *Kekulé* structural formula [10].

In Ref. [5] it was demonstrated that in the case of linear polyacenes, all hexagons, except the two terminal hexagons, have equal *EC*-values. In a number of catacondensed benzenoid molecules, whose π-electron contents were reported in Ref. [2], an analogous regularity could be envisaged. Some typical examples of this kind are given in Fig. 1 and Table 1. (One may observe that compounds **4** and **5** have coinciding *EC*-values. This is to be expected in view of the fact that *EC* is defined on the basis of *Kekulé* structures, and that **4** and **5** are isoarithmic species, in which all *Kekulé*-structure-based properties necessarily coincide [11, 12].

In order to clarify this situation we have undertaken extensive numerical studies of benzenoid molecules containing a linear polyacene fragment, after which it became possible to establish the following general regularity.

Let X and Y be arbitrary conjugated hydrocarbon fragments, not necessarily catacondensed and not necessarily benzenoid. Let G be a conjugated molecule, the structure of which is depicted in Fig. 2.

Rule 1. If G is *Kekuléan*, then for arbitrary X and Y and for any $h \geq 2$, the hexagons $1, 2, \ldots, h$ of G have equal π-electron contents.

Table 1. The π-electron contents of the rings of heptacene (**1**) and its benzo-annelated derivatives; for notation see Fig. 1

Compound	$EC(R_i)$ $i = 1,2,3,4,5$	$EC(A)$	$EC(B)$	$EC(C)$	$EC(D)$	$EC(E)$	$EC(F)$
1	4.2500	4.3750	4.3750	–	–	–	–
2	4.2667	2.8667	4.4000	5.4000	–	–	–
3	4.2759	1.3103	4.4138	5.4483	5.4483	–	–
4	4.2857	2.8929	2.8929	5.3929	5.3929	–	–
5	4.2857	2.8929	2.8929	5.3929	5.3929	–	–
6	4.2963	1.3333	2.9074	5.4444	5.4444	5.3929	–
7	4.3077	1.3462	1.3462	5.4423	5.4423	5.4423	5.4423

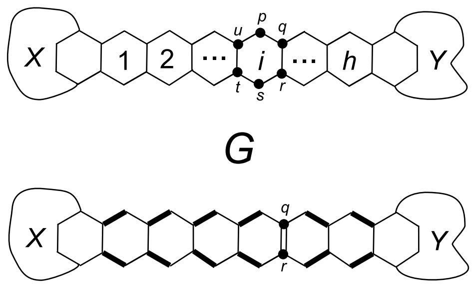

Fig. 2. The general structure of a conjugated hydrocarbon containing a linear polyacene fragment and the notation used in the proof of Rule 1; in the *Kekulé* structures of G in which the bond rq is double, also the bonds marked by thick lines must be double

Verifying Rule 1

In order to demonstrate the validity of Rule 1 we shall compute the electron content of the i-th ring of G, and show that its value is independent of i. Bearing in mind Eq. (1) and the labeling of the atoms of the i-th ring, shown in Fig. 2, we get Eq. (3).

$$EC(i) = 2(P_{pq} + P_{up} + P_{rs} + P_{st}) + (P_{qr} + P_{tu}) \tag{3}$$

The first term on the right-hand side of Eq. (3) is equal to 4. Namely, the sum of *Pauling* bond orders over all bonds that terminate in an atom is equal to unity [13]. Therefore, $P_{pq} + P_{up} = 1$ and $P_{rs} + P_{st} = 1$. We thus have Eq. (4) and what remains to be calculated is P_{qr} and P_{tu}.

$$EC(i) = 4 + (P_{qr} + P_{tu}) \tag{4}$$

Because G is assumed to be *Kekuléan*, the number of carbon atoms in the fragments X and Y must be either both even or both odd. The interesting case is when both X and Y have even number of atoms, which we examine first.

Using standard techniques for the enumeration of *Kekulé* structures [14, 15] it can be shown that Eq. (5) is valid where the meaning of the symbols X_0 and Y_0 is seen from Fig. 3.

$$K\{G\} = (h-1)\,K\{X\}\,K\{Y\} + K\{X\}\,K\{Y_0\} + K\{X_0\}\,K\{Y\} \tag{5}$$

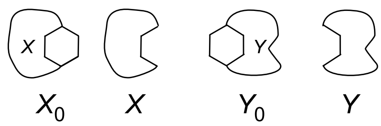

Fig. 3. The fragments encountered in connection with Eq. (5) and elsewhere

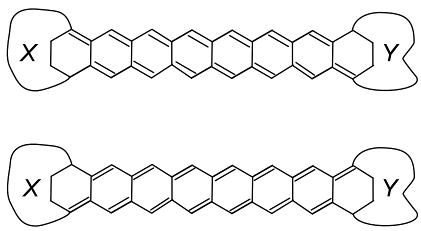

Fig. 4. The two types of *Kekulé* structures of the conjugated system G in the case when the fragments X and Y are odd; in each particular *Kekulé* structure, each ring $1, 2, \ldots, h$ of G possesses four π-electrons; therefore, the average of the π-electron count over all *Kekulé* structures is also equal to four

In order to apply Eq. (2), in addition to $K\{G\}$ we have to calculate $K\{G_{pr}\}$ and $K\{G_{tu}\}$. If the bond pr is chosen to be double, then a number of other bonds of G must also be double, see Fig. 2. Consequently, $K\{G_{pr}\} = K\{X\}\,K\{Y\}$, *cf.* Figs. 2 and 3. By the very same argument, $K\{G_{tu}\} = K\{X\}\,K\{Y\}$. Substituting these expressions back into Eq. (4) we arrive at our main result (Eq. (6)) where the denominator is given by Eq. (5). According to the notation explained in Fig. 2, the parameter i in Eq. (6) may assume any value between 1 and h. As we shall see in a while, Eq. (6) is valid also in the case when X and Y have an odd number of atoms.

$$EC(i) = 4 + \frac{2\,K\{X\}\,K\{Y\}}{K\{G\}} \qquad (6)$$

The right-hand side of Eq. (6) is independent of i, which is tantamount to the claim of Rule 1.

To complete our considerations, we need to analyze also the case when X and Y have an odd number of atoms. If so, then there exist only two types of *Kekulé* structures, shown in Fig. 4. It is easily seen that in each individual *Kekulé* structure exactly 4 π-electrons belong to each of the rings $1, 2, \ldots, h$. Consequently, $EC(i) = 4$ for all $i = 1, 2, \ldots, h$.

This conclusion is in harmony with Eq. (6), because if X and Y are of odd size, then necessarily $K\{X\} = K\{Y\} = 0$.

More Regularities for the π-Electron Content

From Eq. (6) it immediately follows:

Rule 2. If G is *Kekuléan*, then for arbitrary X and Y, the π-electron content of the hexagons $1, 2, \ldots, h$ of G is at least 4. It is equal to 4 if and only if the fragments X and/or Y are non-*Kekuléan*.

Rule 3. With the increasing length of the linear polyacene chain in G, the π-electron contents of the hexagons $1, 2, \ldots, h$ monotonically decrease, approaching a limit value equal to 4.

Rule 3 is a consequence of the fact that $K\{X\}$ and $K\{Y\}$ are independent of h, whereas $K\{G\}$ is a linear (increasing) function of h [14].

All the above stated regularities, as well as Eq. (6), are applicable also in the special cases when either X or Y or both are missing. If so, one simply has to set $K\{X\} = 1$ and/or $K\{Y\} = 1$.

In particular, in the case of (unsubstituted) linear polyacenes (with $h + 2$ hexagons), we get Eqs. (7) and (8), the expressions previously reported in Ref. [5]. The EC-values given in Table 1 pertain to the case $h = 5$ (heptacene).

$$EC(1) = EC(2) = \cdots = EC(h) = 4 + \frac{2}{h+3} \tag{7}$$

$$EC(A) = EC(B) = \frac{1}{2}\left[4(h+2) + 2 - h\left(4 + \frac{2}{h+3}\right)\right] = 5 - \frac{h}{h+3} \tag{8}$$

Concluding this paper we would like to point out that Rule 1 and its consequences, Rules 2 and 3, seem to be the very first generally valid results in the *Balaban–Randić* theory of the distribution of π-electrons into rings of conjugated molecules.

References

[1] Balaban AT, Randić M (2004) J Chem Inf Comput Sci **44**: 50
[2] Randić M, Balaban AT (2004) Polyc Arom Comp **24**: 173
[3] Balaban AT, Randić M (2004) New J Chem **28**: 800
[4] Balaban AT, Randić M (2004) J Chem Inf Comput Sci **44**: 000 (in press)
[5] Gutman I (2003) Bull Chem Technol Maced **22**: 105
[6] Gutman I, Vukičević D, Graovac A, Randić M (2004) J Chem Inf Comput Sci **44**: 296
[7] Miličević A, Nikolić S, Trinajstić N (2004) J Chem Inf Comput Sci **44**: 415
[8] Gutman I, Morikawa T, Narita S (2004) Z Naturforsch **59a**: 295
[9] Pauling L, Brockway LO, Beach JY (1935) J Am Chem Soc **57**: 2705
[10] Gutman I, Cyvin SJ (1989) Introduction to the Theory of Benzenoid Hydrocarbons. Springer, Berlin Heidelberg New York Tokyo
[11] Balaban AT, Tomescu I (1983) MATCH Commun Math Chem **14**: 155
[12] Balaban AT (1985) J Chem Inf Comput Sci **25**: 334
[13] Gutman I (1977) MATCH Commun Math Chem **3**: 121
[14] Gutman I (1982) Croat Chem Acta **55**: 371
[15] Cyvin SJ, Gutman I (1988) Kekulé Structures in Benzenoid Hydrocarbons. Springer, Berlin Heidelberg New York Tokyo