Coding and Ordering Kekulé Structures[†]

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The concept of numerical Kekulé structures is used for coding and ordering geometrical (standard) Kekulé structures of several classes of polycyclic conjugated molecules: catacondensed, pericondensed, and fully arenoid benzenoid hydrocarbons, thioarenoids, and [N]phenylenes. It is pointed out that the numerical Kekulé structures can be obtained for any class of polycyclic conjugated systems that possesses standard Kekulé structures. The reconstruction of standard Kekulé structures from the numerical ones is straightforward for catacondensed systems, but this is not so for pericondensed benzenoid hydrocarbons. In this latter case, one needs to use two codes to recover the geometrical Kekulé structures: the Wiswesser code for the benzenoid and the numerical code for its Kekulé structure. There is an additional problem with pericondensed benzenoid hydrocarbons; there appear numerical Kekulé structures that correspond to two (or more) geometrical Kekulé structures. However, this problem can also be resolved.

1. INTRODUCTION

Recently, Randić introduced in this journal[1] a novel description of Kekulé structures by replacing their standard representation by what he called *algebraical* representation. Consequently, Randić named Kekulé structures thus presented as *algebraical* Kekulé structures, while their standard representation was called *geometrical* Kekulé structures. It is not surprising that Randić introduced this new concept— his belief in and search for *hidden* properties of Kekulé structures is clearly visible in his article on aromaticity of polycyclic conjugated hydrocarbons which appeared last year (2003) in *Chemical Reviews.*[2]

We find the algebraic representation of Kekulé structures useful for linear coding and lexicographical ordering Kekulé structures of various polycyclic conjugated systems. However, we should like to replace the term *algebraical* with the term *numerical*, since this term better fits this novel representation of Kekulé structures and will better serve our purpose. Randić has also used this term in his paper.[1]

The idea behind the construction of numerical Kekulé structures is rather simple: Each double bond in a geometrical Kekulé structure gets the number 2 for two π-electrons making up the double bond, and if the double bond is shared by two rings it gets only the number 1. Then the numbers assigned to each bond in a ring are added up. Thus, every Kekulé structure gives rise to a numerical Kekulé structure which can simply be presented by a linear code. Linear codes can straightforwardly be handled by a computer and used for example to enumerate Randić's conjugated circuits,[2,3] if one wishes to compute the resonance energy of some conjugated molecule. But, they can also be used for other purposes.

An example of transforming geometrical Kekulé structures into numerical Kekulé structures is given in Figure 1.

We also point out that the numerical Kekulé structures can be generated for any class of conjugated systems, hydrocarbons or heterosystems, possessing geometrical Kekulé structures by applying the recipe mentioned above, as it will be shown in sections 5 and 6.

2. NUMERICAL KEKULÉ STRUCTURES OF CATACONDENSED BENZENOID HYDROCARBONS

The numerical Kekulé structures of benzo[*c*]phenanthrene are given in Figure 2.

Below they are listed in the *reverse* lexicographical order:

6	3	4	5
6	3	3	6
6	2	6	4
5	4	4	5
5	4	3	6
5	3	6	4
4	6	3	5
4	6	2	6

From these numbers, the geometrical Kekulé structures can be generated without any problem—the number of digits in the code determines the number of hexagons in the catacondensed benzenoid hydrocarbon, and the sum of digits gives the total π-electron count in the benzenoid. For example, the code 5526 allows the construction of one of seven Kekulé structures belonging to benzo[*a*]anthracene:
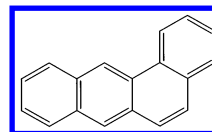
The codes presented above for the Kekulé structures of benzo[*c*]phenanthrene give a partitioning of its total number of π-electrons to benzene rings making up the benzenoid.

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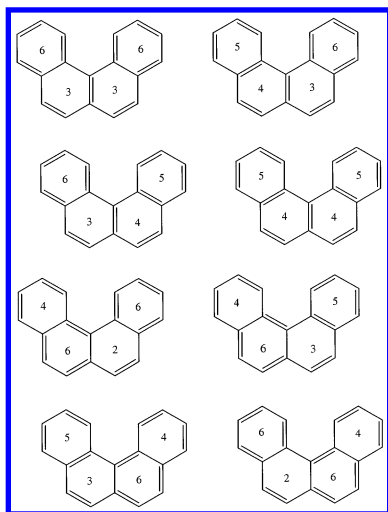**416** *J. Chem. Inf. Comput. Sci., Vol. 44, No. 2, 2004*

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Figure 1. Geometrical Kekulé structures of benzo[c]phenanthrene with written-in numbers characterizing numerical Kekulé structures.
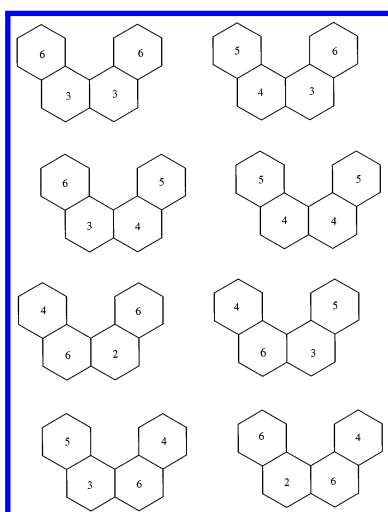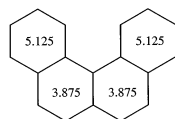

Figure 2. Numerical Kekulé structures of benzo[c]phenanthrene.

The average π-electron content of rings in benzo[c]phenanthrene (obtained by dividing the total π-electron content of each ring with the number of Kekulé structures) is shown below:

Note, the relationship between the terminal and inner rings in benzo[c]phenanthrene is 1:0.76.

In the past we have been interested in characterizing local features in benzenoids and have devised the *Clar index* for measuring the contribution of each ring to the resonance energy of a benzenoid in terms of (4n+2) and (4n) conjugated circuits.[4] The relationship between the terminal and inner rings in benzo[c]phenanthrene in terms of their Clar indices is 1:0.74. Both approaches indicate that the π-electron content of terminal rings is higher than that of the inner rings. In Figure 3 we give a few catacondensed benzenoids, and their π-electron contents are calculated in both ways.
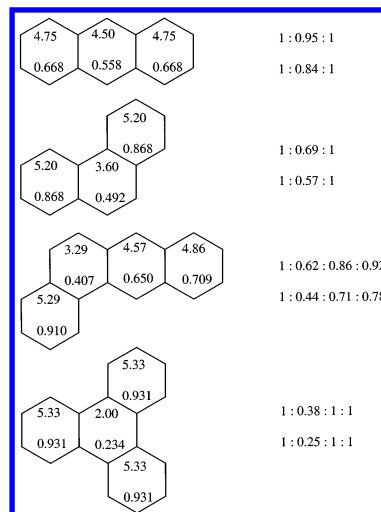

Figure 3. Relationship between the terminal and inner rings of a few catacondensed benzenoids based on the π-electron content of each ring devided by the number of Kekulé structures (the first line) and the Clar indices of each ring (the second line).
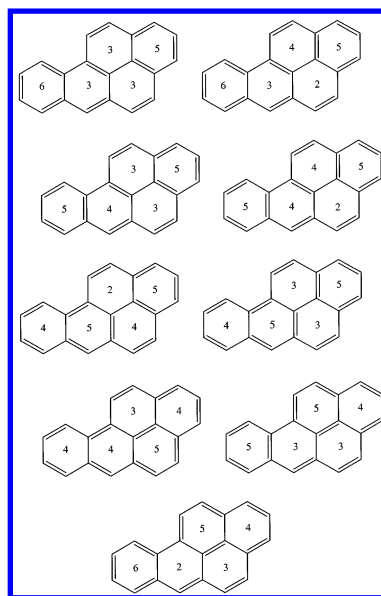

Figure 4. Geometrical Kekulé structures of benzo[a]pyrene with numbers in each ring characterizing its numerical Kekulé structures.

3. NUMERICAL KEKULÉ STRUCTURES OF PERICONDENSED BENZENOID HYDROCARBONS

In Figure 4, we give as an example geometrical Kekulé structures of benzo[a]pyrene and the distribution of their π-electrons between the five rings constituting this benzenoid.

The coding of numerical Kekulé structures of pericondensed benzenoid hydrocarbons is not as simple as it is in the case of catacondensed benzenoids. One way is by using the Wiswesser coding system devised for benzenoid hydrocarbons.[5] Wiswesser used the *tilted* Cartesian coordinate system in which the y axis is at an angle of 60° to the x axis. Then, he placed a network in the xy plane and placed a benzenoid onto this network in such a way that x,y intersections appear at each of its hexagons. An example is shown in Figure 5.

The position of each hexagon is determined by x,y coordinates fixing the position of its center denoted by a
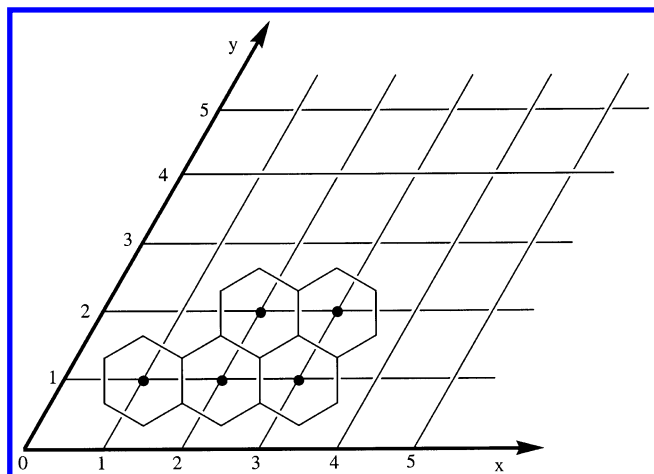
Figure 5. The tilted Cartesian coordinate system with 60° angle between *x* and *y* axes and benzo[*a*]pyrene placed onto the network in the *xy* plane.

Figure 6. Creation of the Wiswesser code for benzo[*a*]pyrene.

dot[6] in Figure 5. The rule for constructing the Wiswesser code is to give always all *y* values for the same *x* value before proceeding to the next *x* value. The construction of the Wiswesser code for benzo[*a*]pyrene is given in Figure 6.

It should be noted that the orientation of a benzenoid in the *xy* plane should be such that the first entry is always unity or in some cases, e.g., perylenes, coronoids, the smallest possible number. This requirement eliminates all other orientations which would give lexicographically higher Wiswesser codes.[7] Using this convention, the Wiswesser codes for benzenoids are straightforwardly produced by inscribing the appropriate number in each ring of a benzenoid. It is applicable both to catacondensed and pericondensed benzenoids. Several examples are presented in Figure 7.

Following the ideas of Wiswesser, exposed above, we will order in the same way the counts of π-electrons within individual rings in a benzenoid. The numerical Kekulé structures of benzo[*a*]pyrene, given in this way, are listed in the *reverse* lexicographical order as follows:

6	3	4	2	5
6	3	3	3	5
6	2	5	3	4
5	4	4	2	5
5	4	3	3	5
5	3	5	3	4
4	5	3	3	5
4	5	2	4	5
4	4	3	5	4

From these numbers, the geometrical Kekulé structures can be recovered by keeping in mind that they were constructed using the Wiswesser rules. For example, a Kekulé structure of dibenzo[*def,p*]chrysene with the Wiswesser code 131212 can easily be recovered in three steps from the following set of numbers: 663225 (see Figure 8). Therefore, the input must be two sets of numbers: the Wiswesser code of a given benzenoid and numerical codes of its Kekulé structures.
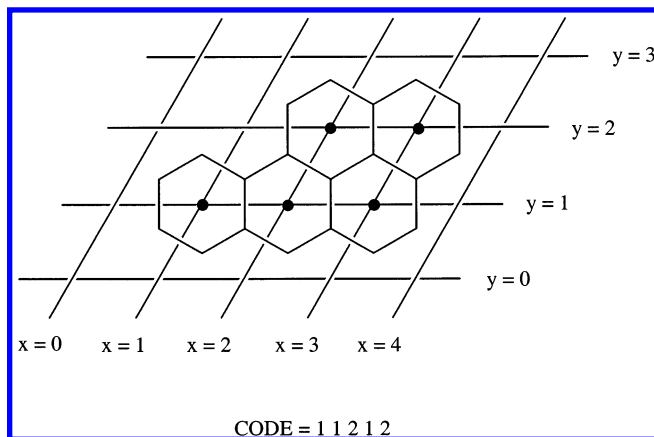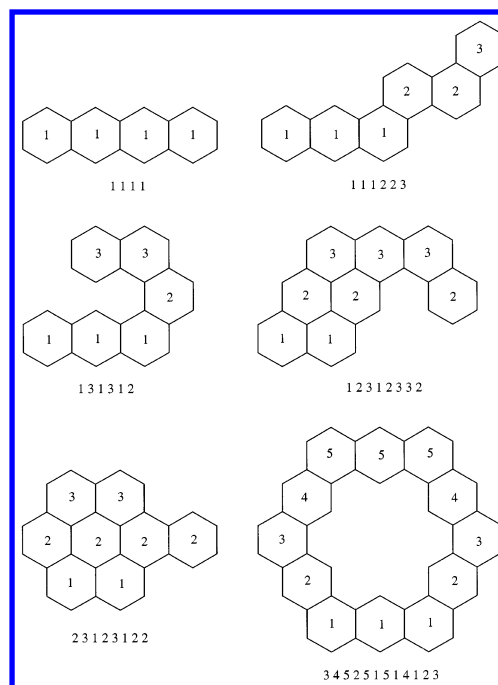

Figure 7. Several catacondensed and pericondensed benzenoids and their Wiswesser codes.

As soon as we started to generate numerical Kekulé structures of peri-benzenoids, we observed an interesting fact: There exists pericondensed systems with distinct geometrical Kekulé structures but the same numerical Kekulé structures—the smallest example of such a case is pyrene. This is shown in Figure 9.

Geometrical Kekulé structures of pyrene denoted by **B** and **C** possess the same numerical Kekulé structure 5335. Therefore, there is not a one-to-one correspodence between geometrical and numerical Kekulé structures of some pericondensed benzenoid hydrocarbons. In such cases the recovery of standard Kekulé structures requires an additional condition, that is, the knowledge of the number of Kekulé structures. If the number of recovered Kekulé structures does not match the total number of Kekulé structures, one must systematically search for the missing structure(s) until one finds those that have the same numerical code as structures already recovered but with a different location of double bonds as can be seen by comparing structures **B** and **C** in Figure 9. There are many methods available for the enu-
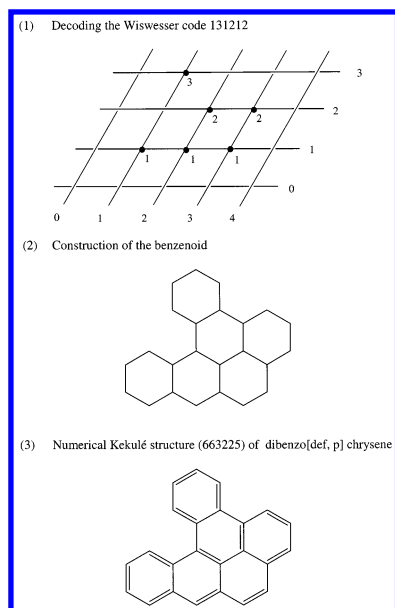
Figure 8. Recovery of a geometrical Kekulé structure of dibenzo-[def,p]chrysene from the corresponding Wiswesser code 131212 and the code 663325 reflecting the π-electron content in rings of a looked-for standard Kekulé structure.
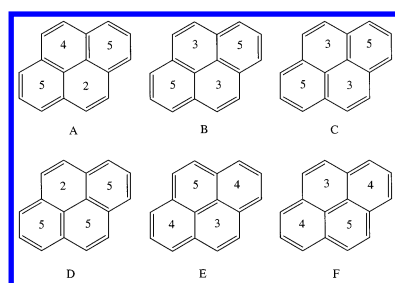

Figure 9. Pyrene is an example of a pericondensed benzenoid in which two distinct geometrical Kekulé structures correspond to two identical numerical Kekulé structures.

meration of Kekulé structures as discussed for example in refs 8−10.

4. NUMERICAL KEKULÉ STRUCTURES OF FULLY ARENOID BENZENOIDS AND HETEROARENOIDS

The concept of fully arenoid benzenoids was discussed by several authors.[11−13] A more general concept is the concept of fully benzenoids[14] (Gutmand and Cyvin used the term all-benzenoids in their book[15]) that includes as special cases fully arenoid benzenoids.[13] In our earlier study,[11] we computed Clar indices for fully arenoid benzenoids and have found, for example, the Clar index to be zero for a ring between two naphthalene-like subunits in perylene:
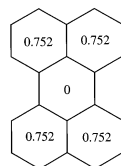
The same was observed for all naphthalenoid systems and systems similarly designed.[11,12] Now we generated numerical Kekulé structures of perylene (see Figure 10) in order to see within this concept the π-electron content of a ring that has been earlier indicated to be "empty".
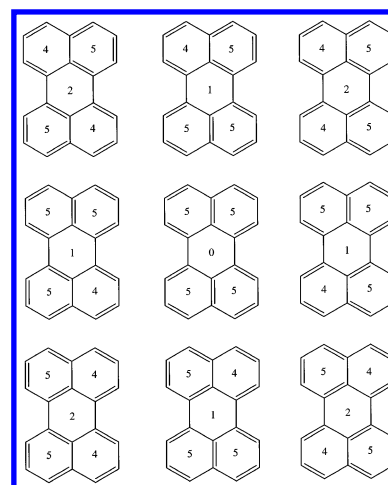

Figure 10. Geometrical Kekulé structures of perylene with the written-in numbers characterizing numerical Kekulé structures.
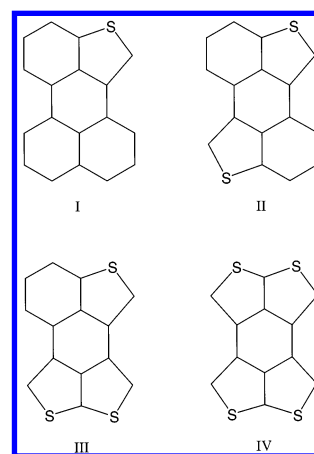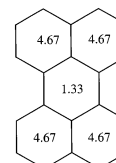

Figure 11. Diagrams of four thio-derivatives of perylene.

The *reverse* lexicographical order of numerical Kekulé structures of perylene—its Wiswesser code being 31231—are

$$
\begin{array}{ccccc}
5 & 5 & 2 & 4 & 4 \\
5 & 5 & 1 & 5 & 4 \\
5 & 5 & 1 & 4 & 5 \\
5 & 5 & 0 & 5 & 5 \\
5 & 4 & 2 & 4 & 5 \\
5 & 4 & 1 & 5 & 5 \\
4 & 5 & 2 & 5 & 4 \\
4 & 5 & 1 & 5 & 5 \\
4 & 4 & 2 & 5 & 5 \\
\end{array}
$$

The average π-electron content of rings in perylene is given below:

The ratio between the π-electron content of the outer rings and the inner ring is 1:0.29, thus, disproving our earlier

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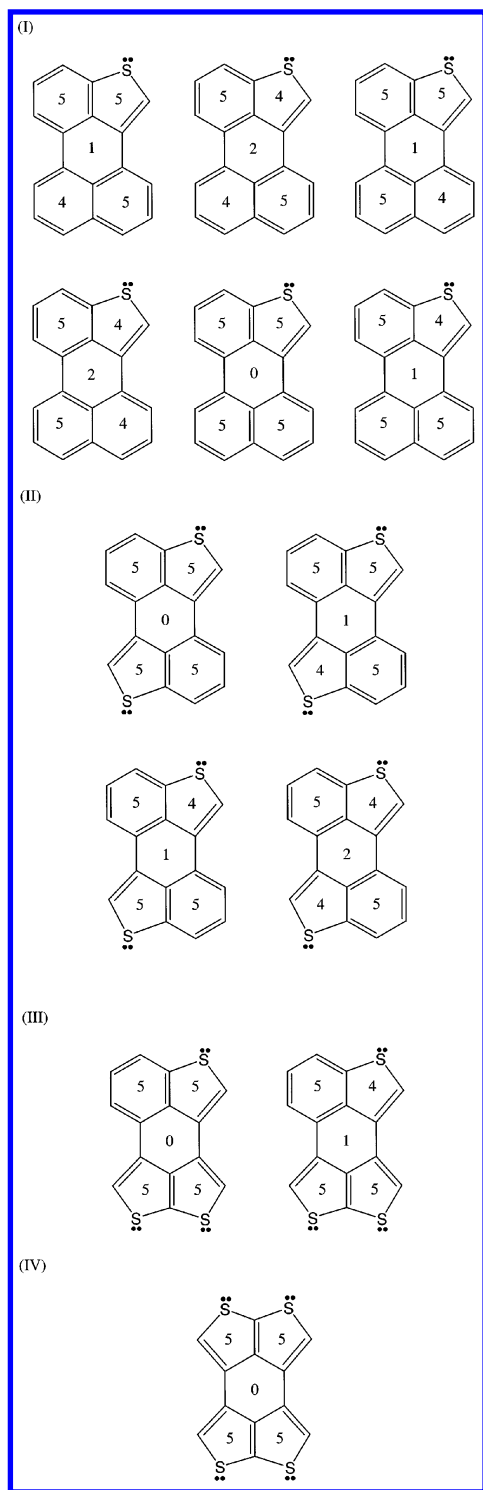*J. Chem. Inf. Comput. Sci., Vol. 44, No. 2, 2004* **419**

Figure 12. Geometrical Kekulé structures of four thio-perylenes with inscribed numbers characterizing the corresponding numerical Kekulé structures.

Figure 13. Average π-electron content of four thio-perylenes. The six-membered ring in structure **IV** appears to be devoid of π electrons.

If we consider, for example, the thio-derivatives of perylene, that is, a class of thio-conjugated systems generated by a gradual replacement of six-membered rings in perylene with thiophene-like five-membered rings, the inner six-membered ring is loosing its π-electron content. It should also be noted that there is no difficulty in extending the concept of numerical Kekulé structures to heteroconjugated systems. We consider the set of thio-derivatives of perylene depicted in Figure 11.

Their Kekulé structures and the corresponding π-electron contents are given in Figure 12.

Finally, we give the average π-electron ring content of considered thio-perylenes in Figure 13.

The six-membered ring in **IV** appears to be *empty* within the model used.

This set of thioarenoids is considered because one of its members—thio-perylene **II** (3,4:3′4′-dibenzo[*b*]thiophene)—is known[18] and possesses properties similar to perylene. For example, **II** forms an iodine complex with very similar properties to the known perylene-iodine solids, including electrical conductivity.

5. NUMERICAL KEKULÉ STRUCTURES OF [N]PHENYLENES

The concept of numerical Kekulé structures can simply be extended to include [N]phenylenes (N = the number of six-membered rings). In this class of conjugated systems four- and six-membered rings alternate—the six-membered rings being always terminal rings. The best studied compound in this class is biphenylene ([2]phenylene), known since 1941.[19,20] Members of the phenylene class are either *linear* or *bent* depending on the mode of annelation. The most studied higher members of the class are linear [3]phenylene and bent [3]phenylene.[21] Vollhardt and his group are mostly responsible for the contemporary development of the phenylene chemistry.[21,22]

In Figure 14 we give five geometrical Kekulé structures of biphenylene and the distribution of π-electrons between its three rings.

conclusion that the inner ring is empty. It is worth pointing out a remarkable coincidence with the ratio 1:0.25 obtained from the calculated π-electron "ring-current" intensities in the outer rings (0.970) and the inner ring (0.239).[16]

The class of fully arenoid benzenoids is of research interest because of the possibility that there are among them molecules possessing a favorable π-electronic structure for semiconductivity.[17]
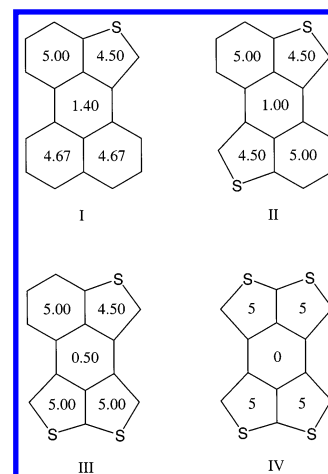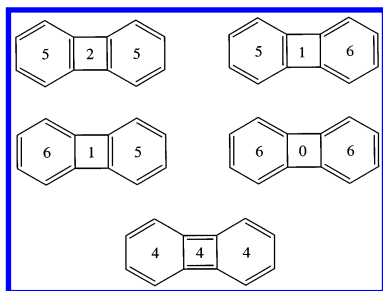
Figure 14. Geometrical Kekulé structures of biphenylene with the ring-labels reflecting the ring π-electron content in numerical Kekulé structures.
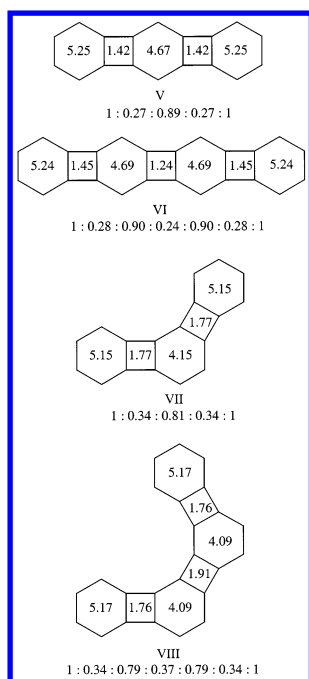

Figure 15. Average π-electron content of linear [3]- (**V**) and [4]-phenylene (**VI**) and bent [3]- (**VII**) and [4]phenylene (**VIII**).

The reverse lexicographical order of numerical Kekulé structures of biphenylene follows:

$$6 \ 1 \ 5$$
$$6 \ 0 \ 6$$
$$5 \ 2 \ 5$$
$$5 \ 1 \ 6$$
$$4 \ 4 \ 4$$

The average π-electron content of rings in biphenylene is much larger for the outer than the inner rings—the ratio being 1:0.31:

In Figure 15 we give the partition of π-electrons in linear [3]- and [4]phenylene and bent [3]- and [4]phenylene.

Terminal six-membered rings are richer in π-electron content than inner six-membered rings. Four-membered rings have a much smaller π-electron content. This π-electron distribution correlates with the nucleus-independent chemical shift values inside the rings of [N]phenylenes.[23]

6. CONCLUDING REMARKS

We have used the concept of numerical Kekulé structures for coding and ordering geometrical Kekulé structures and pointed out that this concept can be extended to any class of polycyclic conjugated systems that possess standard Kekulé structures. Thus, to support this claim the numerical Kekulé structures have been derived for thio-derivatives of perylene and [N]phenylenes.

We have also shown how one can obtain geometrical Kekulé structures from numerical ones for pericondensed benzenoids by using the Wiswesser linear coding system for benzenoids. We observed while deriving the numerical Kekulé structures of the pericondensed benzenoids that a numerical Kekulé structure corresponding to two (perhaps even three or more) geometrical Kekulé structures may appear. In such a case, to recover the geometrical Kekulé structures from the corresponding numerical Kekulé structures of a pericondensed benzenoid, it is necessary to know its number of Kekulé structures in order to construct the missing geometrical Kekulé structures.

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