

# Partition of $\pi$ -electrons between faces of polyhedral carbon aggregates

Alexandru T. Balaban\*

*Texas A&M University at Galveston, 5007 Ave. U, Galveston, TX 77551, USA*  
E-mail: balabana@tamug.edu

Milan Randić

*National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia*

Damir Vukičević

*Department of Mathematics, University of Split, Nikole Tesle 12, HR-21000 Split, Croatia*

Received 6 December 2006; Revised 24 January 2007

We report for the trivalent regular and semiregular polyhedra (three Platonic and seven Archimedean carbon polyhedra) the  $\pi$ -electron partition between rings of various sizes based on considering all their resonance structures. It was found that small odd-membered (3- and 5-membered) faces are assigned a lower share of  $\pi$ -electrons than that corresponding to equipartition (i.e.,  $1/3$  of an electron for carbon atoms shared between three rings). In contrast, 4-membered rings obtain a larger share of  $\pi$ -electrons than that corresponding to equipartition.

**KEY WORDS:** Regular (Platonic) polyhedra, semiregular (Archimedean) polyhedra, Partition of  $\pi$ -electrons between faces

## 1. Introduction

The partition of  $\pi$ -electrons between individual rings of polycyclic conjugated molecules (whose hydrogen-depleted graphs consist only of  $sp^2$ -hybridized carbon atoms) allows a simple characterization of such molecules by averaging  $\pi$ -electron ring partitions over all possible Kekulé structures. The partition is based on the assumption that a shared bond between two condensed rings assigns one electron to each of these rings, whereas a bond that is not shared assigns two electrons to that ring [1]. In a series of communications, various classes of benzenoid and nonbenzenoid hydrocarbons [2–7] or aza-derivatives [8] have been thus investigated and the  $\pi$ -electron partitions in their ring have been reported.

\*Corresponding author.

In a recent publication, fullerenes  $C_V$  have been similarly analyzed [9]. In particular, it was found that in buckminsterfullerene ( $C_{60}$ , with 20 hexagons and 12 pentagons) 2.16  $\pi$ -electrons are assigned to the 6-membered rings and 1.40  $\pi$ -electrons are assigned to the 5-membered rings. Should the 60  $\pi$ -electrons be equipartitioned between all rings in buckminsterfullerene, this would entail assigning 1/3 of an electron to each carbon atom that is common to three rings. This equipartition would then assign to a benzenoid ring two  $\pi$ -electrons and to a five-membered ring  $5/3 = 1.67$   $\pi$ -electrons, totaling as expected  $(20 \times 6)/3 + (12 \times 5)/3 = 60$   $\pi$ -electrons. One can conclude that in this case, although this electron count does not take into consideration the Hückel Rule or Clar structures, yet benzenoid rings get a larger share of  $\pi$ -electrons than 5-membered rings. This is in agreement with the Fries structure of buckminsterfullerene, in which all double bonds are exocyclic to pentagons, so that all bonds shared between two hexagons are double, forming aromatic sextets. The question then arises whether this larger share of  $\pi$ -electrons for benzenoid rings than that corresponding to equipartition is a general phenomenon for trivalent polyhedral structures.

## 2. Partition of $\pi$ -electrons in trivalent Platonic and Archimedean polyhedral $C_V$ aggregates

Taking into account that the skeletal structure of buckminsterfullerene is that of a truncated icosahedron, one of the semiregular polyhedra, we have examined in the present communication all regular (Platonic) and semiregular (Archimedean) polyhedra that can be represented as trivalent (cubic) graphs, i.e., regular graphs of degree three, representing systems formed from  $sp^2$ -hybridized carbon atoms. This may offer some insight on how are  $\pi$ -electrons partitioned between faces other than hexagons and pentagons.

For obtaining the numbers  $K$  of Kekulé structures, and the partitions according to Kekulé structures averaged with equal weights, a specially devised computer program was developed. The program is based on the construction of all Kekulé structures using a back-tracking algorithm. For each Kekulé structures the distribution of  $\pi$ -electrons is obtained and the averages have been calculated. A more efficient method using Pfaffian orientation could be also applied.

On denoting the total number of vertices, edges, and  $m$ -gonal faces by  $V$ ,  $E$ , and  $F$ , respectively, the well-known Euler relationship is represented by equation (1).

$$V + F = E + 2. \quad (1)$$

Taking into account that in all trivalent (cubic) graphs equation (2) is observed, Euler's relationship can be transformed for cubic graphs into equation (3).

$$2E = 3V, \quad (2)$$

$$2F = V + 4. \quad (3)$$

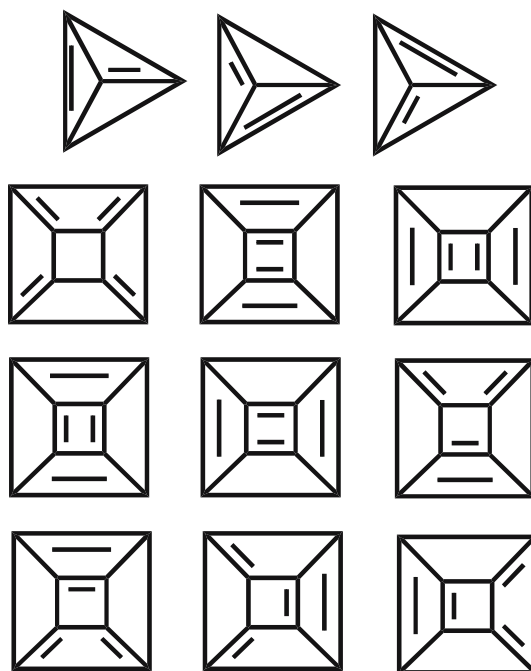


Figure 1. Kekulé structures of regular trivalent polyhedral systems: tetrahedron and cube.

All resonance structures for the two smallest regular polyhedra and one semiregular polyhedron are presented in figures 1 and 2, respectively, using Schlegel diagrams. In table 1, we present all trivalent regular and semiregular polyhedra with their share of  $\pi$ -electrons that would result both in accordance to Kekulé structures averaged with equal weights, and by equipartition (i.e., assigning  $m/3$   $\pi$ -electrons to each  $m$ -gonal face) using rational fractions. In the Symbol column ( $F^m$ ) the exponents count the number  $m$  of  $F$ -sized faces. When all faces  $F_1$  are the same type of regular polygons, the polyhedra are Platonic, and when two or three types of regular polygons ( $F_1$ ,  $F_2$ , and  $F_3$ ) are involved, one has Archimedean polyhedra. The partitions ( $P_1$ ,  $P_2$ , and  $P_3$ ) and numbers of  $m$ -gonal faces ( $P_i$ ) with different sizes  $m_i$  for semiregular polyhedra corresponding to different types of polygonal faces are arranged according to increasing  $m_i$ -values. In the case of equipartitions, a face with a given size  $m$  always receives the same partition  $P$  of  $\pi$ -electrons, i.e.,  $P = m/3$ , but this is not true for partitions according to averaged resonance structures.

The semiregular trivalent polyhedra can be grouped into two classes, namely binary (with two types of polygons) and ternary (with three types of polygons). In table 2, we present all trivalent regular and semiregular polyhedra with their  $K$ -values and their share of  $\pi$ -electrons that result both in accordance

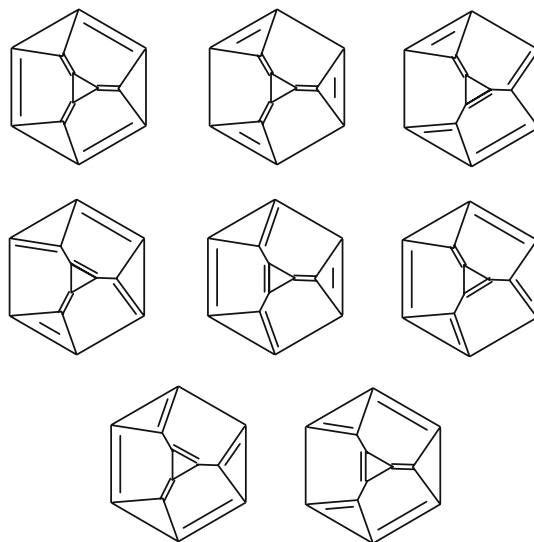


Figure 2. Kekulé structures of a trivalent semiregular polyhedral system, truncated tetrahedron.

to Kekulé structures averaged with equal weights, and according to equipartitions, on two decimals.

It can be seen from table 1 that for binary and ternary semiregular polyhedra, relationships (4) and (5) hold, respectively.

$$2m_1F_1 = m_2F_2, \quad (4)$$

$$m_1F_1 = m_2F_2 = m_3F_3. \quad (5)$$

Another evident relationship is equation (6) involving polygon sizes and the numbers of edges and of vertices. For regular polyhedra equation (7) holds.

$$\sum_i m_i F_i = 2E = 3V, \quad (6)$$

$$F(6 - m) = 12. \quad (7)$$

From tables 1 and 2 it can be seen that for Platonic polyhedra the partition according to averaged Kekulé structures agree with equipartitions; for Archimedean polyhedra triangles and pentagons have a lower partition according to averaged Kekulé structures than to equipartitions, whereas for squares the reverse holds. Therefore in semiregular trivalent polyhedral systems the 6-membered rings have a higher share of  $\pi$ -electrons than 2  $\pi$ -electrons when the smaller rings are 3- or 5-membered, as in the case of buckminsterfullerene, and a lower share than 2  $\pi$ -electrons when the smaller rings are 4-membered. In other words, on a diagram of partitions versus  $m$  for semiregular polyhedra, there is a straight line for equipartitions, and the points for the partitions according to averaged Kekulé structures are above that line for  $m = 3$  and 5, below that line

Table 1  
Trivalent polyhedra with their  $\pi$ -electron partitions according to (i) averaged Kekulé structures and (ii) equipartitions.

Platonic regular polyhedron	Symbol	V	E	F	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	Average Kekulé structures			Equipartitions		
								P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>
Tetrahedron	3 <sup>4</sup>	4	6	4	4			1			1		
Cube	4 <sup>6</sup>	8	12	6	6			3/4			4/3		
Dodecahedron	5 <sup>12</sup>	20	30	12	12			5/3			5/3		
<b>Archimedean semiregular polyhedron</b>	<b>Symbol</b>	<b>V</b>	<b>E</b>	<b>F</b>	<b>F<sub>1</sub></b>	<b>F<sub>2</sub></b>	<b>F<sub>3</sub></b>	<b>Average Kekulé structures</b>			<b>Equipartitions</b>		
								<b>P<sub>1</sub></b>	<b>P<sub>2</sub></b>	<b>P<sub>3</sub></b>	<b>P<sub>1</sub></b>	<b>P<sub>2</sub></b>	<b>P<sub>3</sub></b>
<b>Binary semiregular polyhedron</b>													
Truncated tetrahedron	3 <sup>4</sup> 6 <sup>4</sup>	12	18	8	4	4		3/4	9/4		1	2	
Truncated cube	3 <sup>8</sup> 8 <sup>6</sup>	24	36	14	8	6		3/4	3		1	8/3	
Truncated octahedron	4 <sup>6</sup> 6 <sup>8</sup>	24	36	14	6	8		20/13	24/13		4/3	2	
Truncated dodecahedron	3 <sup>20</sup> 10 <sup>12</sup>	60	90	32	20	12		3/4	15/4		1	10/3	
Truncated icosahedron	5 <sup>12</sup> 6 <sup>20</sup>	60	90	32	12	20		35/25	54/25		5/3	2	
<b>Ternary semiregular polyhedron</b>													
Great rhombicuboctahedron	4 <sup>12</sup> 6 <sup>8</sup> 8 <sup>6</sup>	48	72	26	12	8	6	13/8	15/8	18/8	4/3	2	8/3
Great rhombicosidodecahedron	4 <sup>30</sup> 6 <sup>20</sup> 10 <sup>12</sup>	120	180	62	30	20	12	5/3	106/56	150/56	4/3	2	10/3

Table 2  
 Trivalent polyhedra with their  $K$ -values and  $\pi$ -electron partitions according to (i) averaged Kekulé structures and (ii) equipartitions.

Platonic regular polyhedron	Faces meeting at a vertex	Average Kekulé structures			Equipartitions			$K$
		$P_1$	$P_2$	$P_3$	$P_1$	$P_2$	$P_3$	
Tetrahedron	3 triangles	1			1			4
Cube	3 squares	1.33			1.33			9
Dodecahedron	3 pentagons	1.67			1.67			36
Archimedean semiregular polyhedron	Faces meeting at a vertex	Average Kekulé structures			Equipartitions			$K$
		$P_1$	$P_2$	$P_3$	$P_1$	$P_2$	$P_3$	
<b>Binary semiregular polyhedron</b>								
Truncated tetrahedron	2 hexagons + 1 triangle	0.75	2.25		1	2		8
Truncated cube	2 octagons + 1 triangle	0.75	3		1	2.67		32
Truncated octahedron	1 square + 2 hexagons	1.54	1.85		1.33	2		169
Truncated dodecahedron	1 triangle + 2 decagons	0.75	3.75		1	3.33		2,048
Truncated icosahedron	1 pentagon + 2 hexagons	1.4	2.16		1.67	2		12,500
<b>Ternary semiregular polyhedron</b>								
Great rhombicuboctahedron	1 square + 1 hexagon + 1 octagon	1.63	1.88	2.25	1.33	2	2.67	16,384
Great rhombicosidodecahedron	1 square + 1 hexagon + 1 decagon	1.67	1.89	2.68	1.33	2	3.33	21,956,126,976

for  $m = 4$ , and on both sides of that line for  $m = 6, 8$ , and  $10$  depending on the smaller-size polygon with  $m = 3, 4$ , or  $5$  involved in these semiregular polyhedra.

For cata-condensed benzenoids that have no anthracenic subgraphs (fibonacenes [10, 11]), the unique resonance structure having double bonds for all bonds shared by two benzenoid rings is called a Fries structure. In accordance with Hückel's Rule, one could award a favored situation to  $\pi$ -electrons sextets in 6-membered rings instead of equal weights. In this case, the unique Fries electronic structure exemplified by the first formula in figure 2, or the unique Fries structure of buckminsterfullerene where in the truncated icosahedron all pentagons have exocyclic double bonds (or the Clar structures of the two ternary semiregular polyhedra where there are no bonds shared by a pair of hexagons) would receive a greater weight than other resonance structures. Such an approach has been discussed for benzenoids [12].

A final remark concerns the fact that the complexity of all regular and semiregular polyhedra has been examined using different criteria [13, 14].

### 3. Conclusion

In conclusion, regular polyhedra have  $\pi$ -electron partitions corresponding exactly to equipartitions, but for semiregular polyhedra small odd-membered (3- and 5-membered) faces are assigned a lower share of  $\pi$ -electrons than that corresponding to equipartition, and by contrast, 4-membered rings obtain a larger share of  $\pi$ -electrons than that corresponding to equipartition. As a result, 6-, 8-, and 10-membered faces of the semiregular polyhedra may obtain either a higher share of  $\pi$ -electrons (when in semiregular polyhedra 3- or 5-membered rings are involved), or a lower share (when 4-membered rings are involved).

### References

- [1] M. Randić, *Chem. Rev.* 103 (2003) 3449.
- [2] M. Randić and A.T. Balaban, *Polycyclic Arom. Comp.* 24 (2004) 173.
- [3] A.T. Balaban and M. Randić, *J. Chem. Inf. Comput. Sci.* 44 (2004) 50.
- [4] A.T. Balaban and M. Randić, *New J. Chem.* 28 (2004) 800.
- [5] D. Vukičević, M. Randić, and A.T. Balaban, *J. Math. Chem.* 36 (2004) 271.
- [6] A.T. Balaban and M. Randić, *J. Chem. Inf. Comput. Sci.* 44 (2004) 1701.
- [7] A.T. Balaban and M. Randić, *J. Math. Chem.* 37 (2005) 443.
- [8] A.T. Balaban, B. Furtula, I. Gutman and R. Kovačević, *Polycyclic Arom. Comp.* 27 (2007) 51.
- [9] M. Randić, H. Kroto and D. Vukičević, *J. Chem. Inf. Model.* 47 (2007) 897.
- [10] A.T. Balaban, *MATCH, Commun. Math. Comput. Chem.* 24 (1989) 29.
- [11] I. Gutman, A.T. Balaban, M. Randić and C. Kiss-Tóth, *Z. Naturforsch.* 60a (2005) 171.
- [12] M. Randić and A.T. Balaban, *J. Chem. Inf. Model.* 46 (2006) 57.
- [13] A.T. Balaban and D. Bonchev, *MATCH, Commun. Math. Comput. Chem.* 54 (2005) 137.
- [14] S.M. Rajtmajer, A. Miličević, N. Trinajstić, M. Randić and D. Vukičević, *J. Math. Chem.* 39 (2006) 119.