Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 78 (9) 1351–1357 (2013)
JSCS–4502
UDC 547.53+547.535:544.112:
548.1.023:548.115
Original scientific paper

On benzenoid systems with a minimal number of inlets

ROBERTO CRUZ[1], IVAN GUTMAN[2,3*#] and JUAN RADA[1]

[1]Instituto de Matemáticas, Universidad de Antioquia, Medellín, Colombia, [2]Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia and [3]Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

(Received 18 February, revised 21 March 2013)

Abstract. Inlets are features on the perimeter of a benzenoid system that determine numerous of its electronic and topological properties. A class of large benzenoid systems is constructed, having a small number of inlets. It is shown that the minimal number of inlets in a benzenoid system with h hexagons is less than or equal to $\sqrt{3(h-1)}$.

Keywords: benzenoid molecule; benzenoid hydrocarbon; perimeter (of benzenoid system); hexagonal system; inlet; number of inlets.

INTRODUCTION

Recent experimental methods have made it possible to synthesize very large benzenoid molecules, sometimes referred to as "graphenes".[1–3] These have found unprecedented applications as organic materials for electronic and optoelectronic devices.[2,3] As large benzenoid systems have countless possible isomers,[4–6] it is a task of theoretical chemistry to help indicate those species that may possess interesting properties.

The fact that numerous electronic and topological properties of benzenoid systems are determined by the structural features on their perimeter was established a long time ago.[7–9] These features are shown in Fig. 1; their more precise definitions are given in the literature.[10] The total number of fissures, bays, coves and fjords in a benzenoid system B is called[11] its number of inlets and is denoted by $r = r(B)$.

By means of $r(B)$, several topological properties of B are directly determined. Thus, let B be a benzenoid molecule with n carbon atoms and h hexagons. If m_{ij} denotes the number of edges of the molecular graph of B, connecting vertices of degree i and j, then:[11]

* Corresponding author. E-mail: gutman@kg.ac.rs
# Serbian Chemical Society member.
doi: 10.2298/JSC130218033C

$$m_{22} = n - 2h - r + 2 \quad (1)$$

$$m_{23} = 2r \quad (2)$$

$$m_{33} = 3h - r - 3 \quad (3)$$

Recall that m_{22}, m_{23} and m_{33} are the number of carbon–carbon bonds of the type CH–CH, CH–C and C–C, respectively.[10]

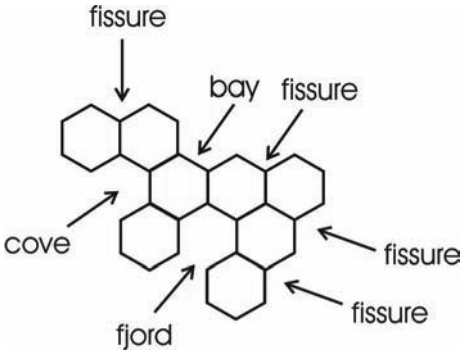

Fig. 1. Structural features on the perimeter of a benzenoid molecule.[10] The total number of fissures, bays, coves, and fjords is the number of inlets r. In this example, $r = 7$.

Equations (1)–(3) enable a large number of molecular structure descriptors of a benzenoid molecule to be expressed as a function of r. For instance:

$$GA(B) = n + h - 1 - \left(2 - \frac{4\sqrt{6}}{5}\right) r$$

$$ABC(B) = n + \left(\sqrt{8} - 2\right)(h - 1) + \frac{3 - \sqrt{8}}{3} r$$

$$H(B) = \frac{1}{2} n - \frac{1}{30} r$$

for the geometric–arithmetic,[12–14] atom–bond connectivity[15–17] and harmonic[18] indices, respectively; for more details see elsewhere.[11,19–23] Evidently, benzenoid molecules of a given size (*i.e.*, with fixed values of n and h), for which the number of inlets r is extremal (maximal or minimal), will possess extremal values of these structure descriptors and, therefore, may be expected to have extremal (or at least, outstanding) electronic and physicochemical properties. In this paper, the problem of constructing benzenoid systems with a minimal number of inlets and estimating its value as a function of h are considered.

The benzenoid system with maximal r-value is easy to characterize:[20] this is the linear acene with h hexagons, for which $r = r_{\max} = 2(h - 1)$. In Fig. 2 this is the benzenoid system denoted by R_{p1}, for which $h = p$.

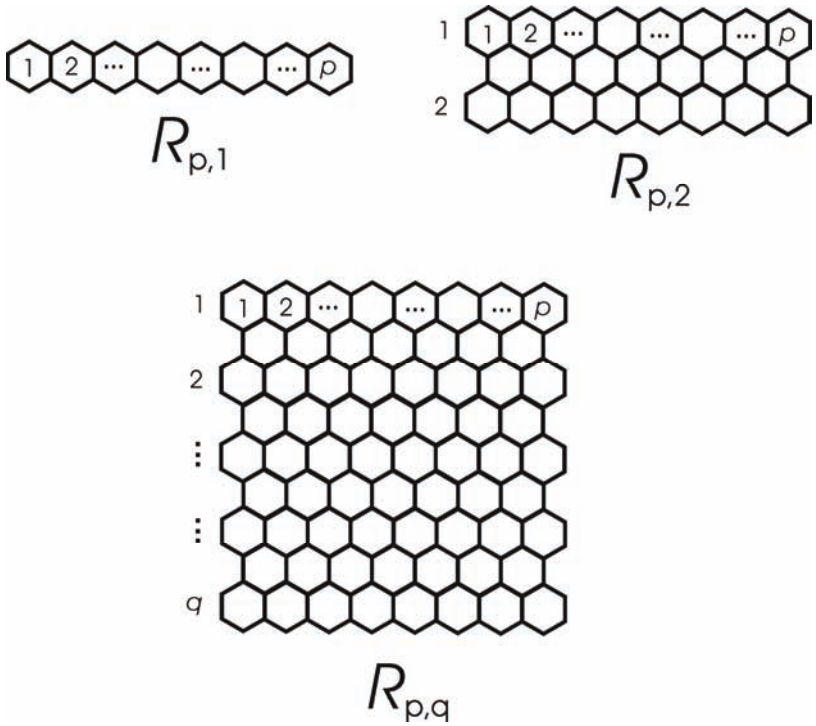

Fig. 2. Prolate rectangles,[24] consisting of $h(R_{pq}) = qp + (q-1)(p-1)$ hexagons. These possess $2(p-1)$ fissures and $2(q-1)$ bays, and thus, $r(R_{pq}) = 2(p-1) + 2(q-1)$ inlets.

CONSTRUCTING LARGE BENZENOID SYSTEMS WITH FEW INLETS

Consider the benzenoid systems R_{pq}, general formula of which is depicted in Fig. 2. These benzenoids are sometimes referred to[24] as "prolate rectangles".

As already pointed out, among the benzenoids with a fixed number of hexagons, the prolate rectangle with q = 1, namely R_{p1}, has the maximal number of inlets. First, one needs to observe that the transition from R_{p1} to R_{p2} (Fig. 2) almost triples the number of hexagons: $h(R_{p2}) = 3h(R_{p1}) - 1 = 3p - 1$, whereas the number of inlets is increased by only two: $r(R_{p2}) = r(R_{p1}) + 2 = 2p$. Continuing this rationale, one arrives at R_{pq} ; $q \geq 3$, for which:

$$h(R_{pq}) = 2pq - p - q + 1 \text{ and } r(R_{pq}) = 2p + 2q - 4$$

At this point, it is noteworthy that recent studies revealed that benzenoid systems of the form R_{p2} ; $p \geq 4$ possess unusual, "anomalous", π-electron[25,26] and magnetic[27] properties.

By means of the transformations indicated in Fig. 3, the number of hexagons was increased, but the *r*-value was decreased. Namely, by adding a new hexagon in a "dent" position, $R_{pq} \Rightarrow R'_{pq}$ (Fig. 3), the number of inlets was diminished by one. If p is even, then $p/2 - 1$ such "dents" could be added on the top of R_{pq}

(see R_{pq} in Fig. 3), and the same number on its bottom, a total of $p - 2$ "dents". By this, the number of hexagons was increased by $p - 2$, whereas the number of inlets was decreased by $p - 2$.

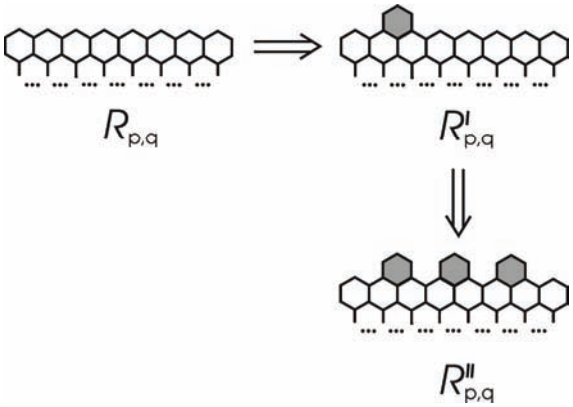

Fig. 3. Adding "dents" at the top (and bottom) of a prolate rectangle diminishes the number of inlets; for details, see text.

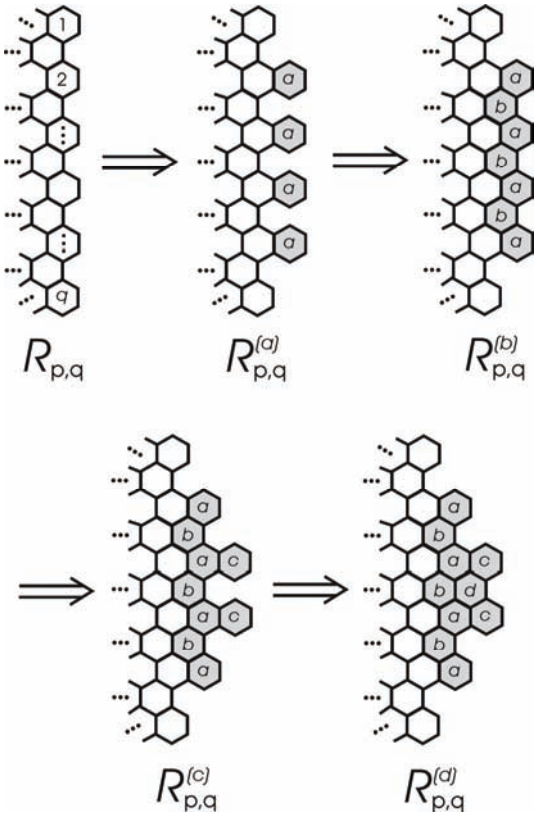

Fig. 4. Adding hexagons on to a prolate rectangle whereby the number of inlets remains the same.

A further series of transformations, indicated in Fig. 4, increases the number of hexagons, but leaves the number of inlets of R_{pq} unchanged.

First, $q-2$ hexagons are to be added to one side of R_{pq}, resulting in $R_{pq}^{(a)}$. Then an additional $q-3$ hexagons could be added, resulting in $R_{pq}^{(b)}$. Continuing this transformation, one arrives at $R_{pq}^{(c)}$, $R_{pq}^{(d)}$, *etc*. Thus:

$$(q-2)+(q-3)+\cdots+2+1=\frac{1}{2}(q-1)(q-2)$$

hexagons can be added on one side of R_{pq} without increasing its *r*-value. The same can also be realized on the other side of R_{pq}, and thus a total of $(q-1)(q-2)$ hexagons are added.

Combining the transformations indicated in Figs. 3 and 4, a class of benzenoid systems is arrived at, the general formula B_{pq} of which is shown in Fig. 5.

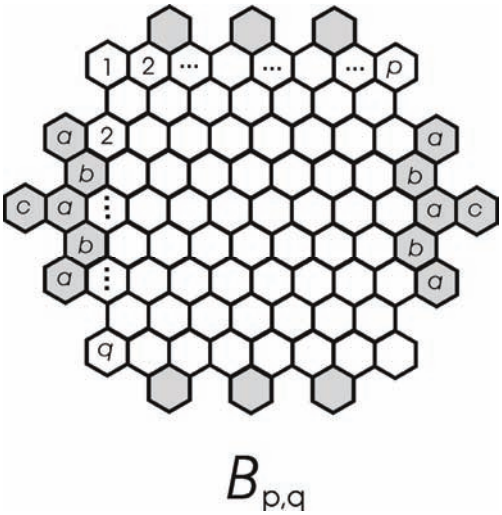

Fig. 5. A large benzenoid system with a small number of inlets. It has $h(R_{pq})+(p-2)+(q-1)(q-2)$ hexagons, but only $r(R_{pq})-(p-2)$ inlets, *cf*. Fig. 2.

By direct calculation (*cf*. Figs. 2 and 5), it could be shown that:

$$h(B_{pq})=2pq+q^2-4q+1 \text{ and } r(B_{pq})=p+2q-2$$

and B_{pq} may be considered as a candidate for a large benzenoid system, which for a given number of hexagons has the smallest number of inlets.

What remains is to choose the parameters *p* and *q*, in order to minimize the *r*-value for some fixed value of *h*. This is achieved by a standard Lagrange multiplier method, in which it is required that both derivatives:

$$\frac{\partial}{\partial p}\left[(p+2q-2)+\lambda\left(2pq+q^2-4q+1-h\right)\right]$$

and

$$\frac{\partial}{\partial q}\left[(p+2q-2)+\lambda\left(2pq+q^2-4q+1-h\right)\right]$$

are simultaneously equal to zero. This yields:

$$1+\lambda(2q)=0 \qquad \text{and} \qquad 2+\lambda(2p+2q-4)=0$$

which, by eliminating the multiplier λ, results in $q=p-2$. Consequently,

$$h=h(B_{p,p-2})=3p^2-12p+13 \tag{4}$$

and

$$r=r(B_{p,p-2})=3p-6 \tag{5}$$

Solving Eq. (4) in the parameter p, one obtains $p=2+\sqrt{(h-1)/3}$, which substituted back into Eq. (5) yields $r=\sqrt{3(h-1)}$.

CONCLUDING REMARKS

It has been shown how a large benzenoid system $B_{p,p-2}$ with h hexagons can be constructed, the number of inlets of which is only $\sqrt{3(h-1)}$. It was not proven that $B_{p,p-2}$ has the smallest possible number of inlets (for a given value of h), but – at least – it is deemed to be not too far from the true minimum. Nevertheless, what has been proven is that $r\le\sqrt{3(h-1)}$ for any benzenoid system with h hexagons. It is believed that this result could be useful in the design of graphenes with the desired properties.

И З В О Д

О БЕНЗЕНОИДНИМ СИСТЕМИМА СА МИНИМАЛНИМ БРОЈЕМ УСЕКА

ROBERTO CRUZ[1], ИВАН ГУТМАН[2,3] и JUAN RADA[1]

[1]Instituto de Matemáticas, Universidad de Antioquia, Medellín, Colombia, [2]Природно–математички факултет Универзитета у Крагујевцу и [3]Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Усеци су структурни детаљи на периметру бензеноидног система који одређују његова бројна електронска и тополошка својства. Конструисана је класа великих бензеноидних система који имају мали број усека. Показано је да је минималан број усека бензеноидног система са h хексагона мањи од или једнак $\sqrt{3(h-1)}$.

(Примљено 18. фебруара, ревидирано 21. марта 2013)

REFERENCES

1. M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **101** (2001) 1267
2. J. Wu, A. Pisula, K. Müllen, *Chem. Rev.* **107** (2007) 718
3. T. M. Figueira-Duarte, K. Müllen, *Chem. Rev.* **111** (2011) 7260
4. G. Brinkmann, G. Caporossi, P. Hansen, *MATCH Commun. Math. Comput. Chem.* **43** (2001) 133
5. M. Vöge, A. J. Guttmann, I. Jensen, *J. Chem. Inf. Comput. Sci.* **42** (2002) 456

6. G. Brinkmann, C. Grothaus, I. Gutman, *J. Math. Chem.* **42** (2007) 909
7. K. Balasubramanian, J. J. Kauffman, W. S. Koski, A. T. Balaban, *J. Comput. Chem.* **1** (1980) 149
8. I. Gutman, G. G. Hall, S. Marković, Z. Stanković, V. Radivojević, *Polyc. Arom. Comp.* **2** (1991) 275
9. D. Babić, I. Gutman, *J. Math. Chem.* **9** (1992) 261
10. I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer, Berlin, 1989
11. J. Rada, O. Araujo, I. Gutman, *Croat. Chim. Acta* **74** (2001) 225
12. D. Vukičević, B. Furtula, *J. Math. Chem.* **46** (2010) 1369
13. M. Mogharrab, G. H. Fath-Tabar, *MATCH Commun. Math. Comput. Chem.* **65** (2011) 33
14. K. C. Das, I. Gutman, B. Furtula, *MATCH Commun. Math. Comput. Chem.* **65** (2011) 595
15. E. Estrada, L. Torres, L. Rodríguez, I. Gutman, *Indian J. Chem.* **37A** (1998) 849
16. E. Estrada, *Chem. Phys. Lett.* **463** (2008) 422
17. I. Gutman, J. Tošović, S. Radenković, S. Marković, *Indian J. Chem., A* **51** (2012) 690
18. L. Zhong, *Appl. Math. Lett.* **25** (2012) 561
19. J. Rada, *MATCH Commun. Math. Comput. Chem.* **52** (2004) 167
20. R. Cruz, I. Gutman, J. Rada, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 97
21. I. Gutman, B. Furtula, *J. Serb. Chem. Soc.* **77** (2012) 1031
22. R. Cruz, H. Giraldo, J. Rada, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 501
23. I. Gutman, J. Tošović, *J. Serb. Chem. Soc.* **78** (2013) 805
24. S. J. Cyvin, I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer, Berlin, 1988
25. I. Gutman, J. Đurđević, Z. Matović, M. Marković, *J. Serb. Chem. Soc.* **77** (2012) 1401
26. I. Gutman, J. Đurđević, S. Radenković, Z. Matović, *Monatsh. Chem.* **143** (2012) 1649
27. S. Radenković, P. Bultinck, I. Gutman, J. Đurđević, *Chem. Phys. Lett.* **552** (2012) 151.