

Electron content of rings of fully benzenoid hydrocarbons

IVAN GUTMAN^{1,*#}, BORIS FURTULA¹, SVETLANA JEREMIĆ¹ and NEDŽAD TURKOVIĆ²

¹Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac and ²Technical High School, 31300 Prijepolje, Serbia and Montenegro

(Received 1 March 2005)

Abstract: The distribution of π -electrons in rings of fully benzenoid hydrocarbons was investigated. It was found that the electron content EC of “full” rings varies significantly (between 5.5 and 2.5 electrons), and depends on the annelation mode, mainly on the number of adjacent rings. “Full” rings belonging to the same annelation class have nearly equal EC -values. The EC -values of all “empty” rings are also nearly equal (around 2 electrons).

Keywords: fully benzenoid hydrocarbons, π -electron content of ring, “full” rings, “empty” rings.

INTRODUCTION

The use of Kekulé structural formulas in the analysis of the π -electron structure of benzenoid hydrocarbons dates back to the 1930s, and since then has become one of the standard methods of the theoretical chemistry of conjugated molecules.^{1,2} It is therefore somewhat surprising that the idea of assessing the distribution of π -electrons into rings by means of Kekulé structures was put forward only quite recently.^{3,4}

According to the proposed method,^{3,4} the π -electron content of a ring R , denoted by $EC(R)$, is computed as follows. In each Kekulé structure the π -electrons are assumed to be distributed in the rings according to the positions of the double bonds: a double bond belonging solely to the ring R , contributes two π -electrons to R ; a double bond shared by R and another ring contributes one π -electron to R . The $EC(R)$ is the arithmetic average of the respective electron contents of all Kekulé structures.

It has been shown⁵ that $EC(R)$ can be computed by means of the formula

$$EC(R) = 2 \sum_{*} p_{rs} + \sum_{**} p_{rs} \quad (1)$$

* Author for correspondence.

Serbian Chemical Society active member.

doi: 10.2298/JSC0510199G

where p_{rs} is the Pauling bond order pertaining to the carbon–carbon bond rs , and where \sum^* and \sum^{**} indicate, respectively, summation over bonds that belong solely to the ring R , and bonds that are shared by R and another ring. For additional details on EC , as well as for illustrative examples see some of the numerous recent papers concerned with this matter.^{3–21}

FULLY BENZENOID HYDROCARBONS

In the Clar aromatic sextet theory,^{2,22} the so-called *fully benzenoid* (or *all-benzenoid*) *hydrocarbons* play an outstanding role. These are the benzenoid systems in which all π -electrons can be (formally) grouped into “aromatic sextets”. Thus the fully benzenoid hydrocarbons are represented by a single Clar formula in which there are no double bonds. The rings in which aromatic sextets are located (indicated by circles) are said to be “full” whereas the other rings are “empty”. Examples of Clar formulas of fully benzenoid hydrocarbons are given in Fig. 1.

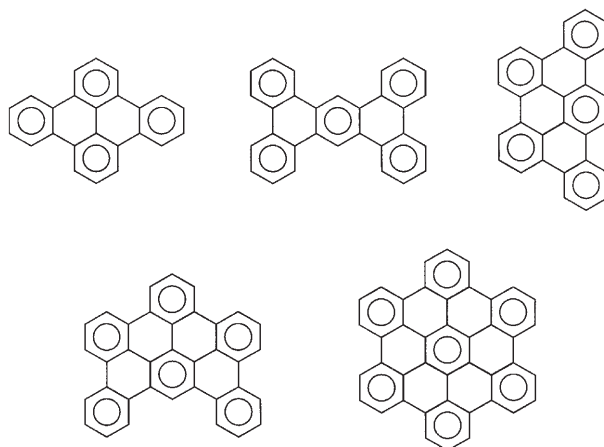


Fig. 1. Clar formulas of some typical fully benzenoid hydrocarbons.

Fully benzenoid hydrocarbons are the most stable benzenoids and, due to a new method for their synthesis,²³ their chemistry is nowadays in great expansion. Fully benzenoids were subjected to numerous theoretical studies, with particular emphasis being placed on the relations between their structural and π -electron features.^{24–30}

Various theoretical approaches^{31,32} agree that in the “full” and “empty” rings of fully benzenoid hydrocarbons, the extent of cyclic conjugation is, respectively, very strong and very weak.^{28–30} From the point of view of the concept of electron content, one may expect that “full” and “empty” rings have, respectively, large and small EC -values.

The aim of this study was to check this latter assertion and, if possible, reveal the finer structural details influencing the EC -values of the rings of fully benzenoid hydrocarbons.

NUMERICAL WORK

In order to investigate the π -electron contents of “full” and “empty” rings, 67 fully benzenoid hydrocarbons were considered. These were chosen in such a manner that each of the twelve possible annelation modes (*cf.* Fig. 3) be present several times. These benzenoids possess 11–19 hexagons, most of them being pericondensed. The method of calculation of EC , based on Eq. (1), has been described elsewhere.^{15–17}

Some characteristic EC -values for the rings indicated in Fig. 2 are given in Table I.

TABLE I. The π -electron content (EC) of rings of fully benzenoid hydrocarbons from Fig. 1. The labeling of these rings is indicated in Fig. 2. In accordance with Fig. 3, the “full” rings are denoted by $A_1, \dots, A_4, B_1, \dots, B_5, C_1, E_1, H_1$, and L_1 . The “empty” rings are denoted by e_1, \dots, e_7 . Note that the rings labelled by the same character have equal or nearly equal EC -values

Ring	EC	Ring	EC	Ring	EC	Ring	EC
A_1	5.35	B_1	4.80	C_1	4.80	e_1	1.85
A_2	5.35	B_2	4.80	E_1	4.13	e_2	1.90
A_3	5.33	B_3	4.80	H_1	3.60	e_3	1.93
A_4	5.35	B_4	4.80	L_1	2.40	e_4	1.73
		B^5	4.80			e_5	1.80
						e_6	1.85
						e_7	1.80

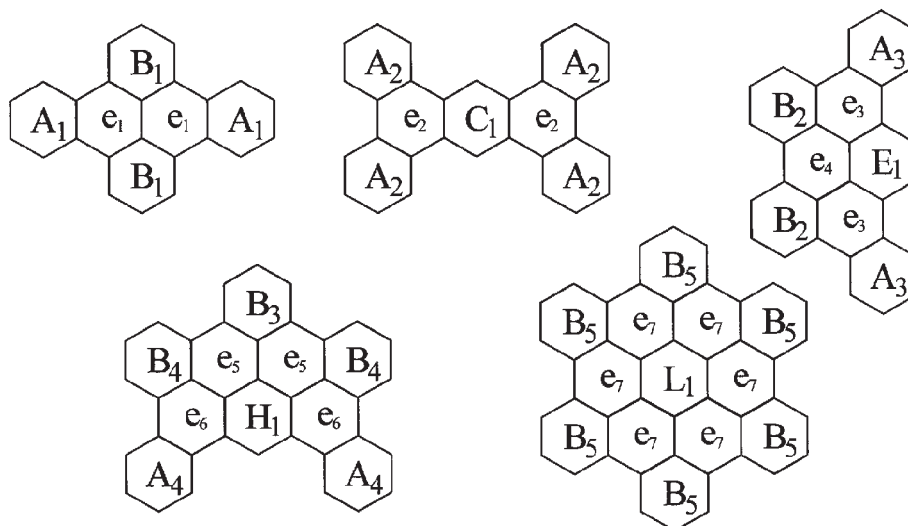


Fig. 2. Labeling of the rings of the fully benzenoid hydrocarbons from Fig. 1. The symbols used agree with the annelation modes shown in Fig. 3. The respective electron contents are given in Table I.

RESULTS AND DISCUSSION

By inspection of the data given in Table I, it can be seen that whereas all “empty” rings have nearly equal *EC*-values, the π -electron contents of “full” rings vary significantly. A detailed examination revealed that the main structural factor influencing the *EC*-value of a “full” ring is its annelation mode and, in particular, the number of “empty” rings attached to it.

Twelve distinct annelation modes may occur in the “full” rings of fully benzenoid hydrocarbons. These are shown in Fig. 3.

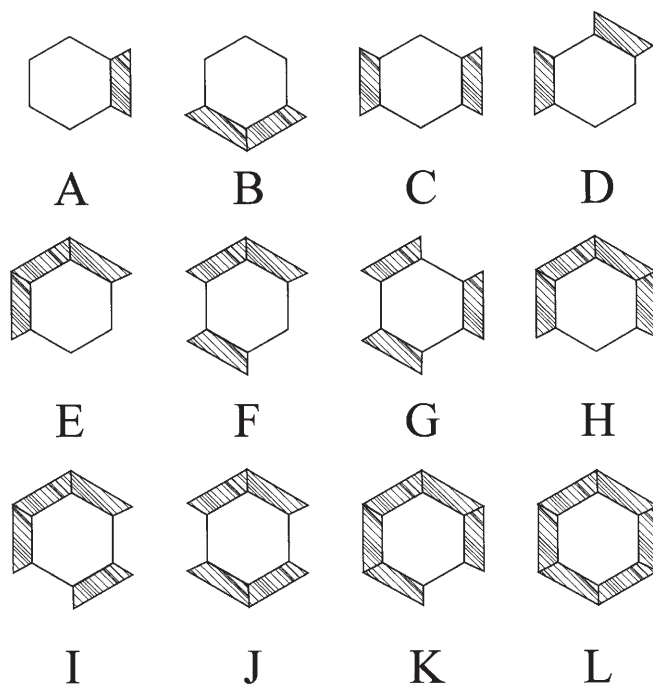


Fig. 3. The twelve possible annelation modes of the “full” rings of fully benzenoid hydrocarbons.

Although the π -electron contents of different “full” rings of the same annelation mode need not be equal, they vary within remarkably narrow intervals. Details on these intervals are given in Table II.

TABLE II. Minimal and maximal π -electron contents of equally annelated rings of fully benzenoid hydrocarbons. The labeling of the annelation models of “full” rings is shown in Fig. 3

Ring type	Annelation mode	Minimal <i>EC</i>	Maximal <i>EC</i>
“Empty”	All	1.67	2.18
“Full”	A	5.28	5.36
	B	4.60	4.82
	C	4.79	4.82

TABLE II. Continued

Ring type	Annellation mode	Minimal EC	Maximal EC
"Full"			
	D	4.54	4.58
	E	4.05	4.16
	F	4.12	4.15
	G	3.65	3.68
	H	3.58	3.60
	I	3.29	3.34
	J	3.59	3.61
	K	2.83	2.95
	L	2.37	2.40

The results can be summarized in the following rules:

Rule 1. All "empty" rings of fully benzenoid hydrocarbons have nearly the same π -electron contents. Contrary to the Clar-formula-based electron distribution pattern, "empty" rings contain around two π -electrons.

Rule 2. The π -electron content of "full" rings of fully benzenoid hydrocarbons varies significantly and mainly depends on the number of attached "empty" rings. The greater the number of neighboring rings is, the smaller is the EC -value of a "full" ring. Rings possessing a single neighbor (annellation mode A) contain more than five π -electrons; those possessing six neighbors (annellation model L) contain less than 2.5 π -electrons.

Thus the final conclusion is that in fully benzenoid hydrocarbons neither are the "empty" rings devoid of π -electrons, nor do the "full" rings contain (around) six π -electrons. Consequently, caution is needed when the electron structure (and from it, the chemical and physico-chemical properties) of benzenoid hydrocarbons are inferred from their Clar aromatic sextet formulas.

ИЗВОД

ЕЛЕКТРОНСКИ САДРЖАЈ У ПРСТЕНИМА СВЕБЕНЗЕНОИДНИХ УГЉОВОДОНИКА

ИВАН ГУТМАН, БОРИС ФУРТУЛА, СВЕТЛАНА ЈЕРЕМИЋ и НЕЏАД ТУРКОВИЋ

Природно-математички факултет у Крагујевцу и Техничка школа, Пријепоље

Проучавана је расподела π -електрона у прстенима свебензеноидних угљоводоника. Нађено је да електронски садржај EC "пуних" прстена значајно варира (између 5,5 и 2,5 електрона), и да зависи од начина анелације, а нарочито од броја суседних прстена. "Пуни" прстени који припадају истој класи анелације имају приближно једна-

ке *EC*-вредности. *EC*-вредности свих "празних" прстена су такође скоро исте (око 2 електрона).

(Примљено 1. марта 2005)

REFERENCES

1. A. Graovac, I. Gutman, N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules*, Springer-Verlag, Berlin, 1977
2. S. J. Cyvin, I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer-Verlag, Berlin, 1988
3. M. Randić, *J. Chem. Inf. Comput. Sci.* **44** (2004) 365
4. M. Randić, A. T. Balaban, *Polyc. Arom. Comp.* **24** (2004) 173
5. I. Gutman, T. Morikawa, S. Narita, *Z. Naturforsch.* **59a** (2004) 295
6. I. Gutman, *Bull. Chem. Technol. Maced.* **22** (2003) 105
7. A. T. Balaban, M. Randić, *J. Chem. Inf. Comput. Sci.* **44** (2004) 50
8. I. Gutman, D. Vukičević, A. Graovac, M. Randić, *J. Chem. Inf. Comput. Sci.* **44** (2004) 296
9. A. T. Balaban, M. Randić, *J. Chem. Inf. Comput. Sci.* **44** (2004) 1701
10. A. T. Balaban, M. Randić, *New J. Chem.* **28** (2004) 800
11. D. Vukičević, M. Rnadić, A. T. Balaban, *J. Math. Chem.* **36** (2004) 271
12. I. Gutman, *Indian J. Chem.* **43A** (2004) 1615
13. I. Gutman, Ž. Tomović, K. Müllen, J. P. Rabe, *Chem. Phys. Lett.* **397** (2004) 412
14. D. Vukičević, D. J. Klein, *J. Math. Chem.* **37** (2005) 163
15. I. Gutman, B. Furtula, N. Turković, *Polyc. Arom. Comp.* **25** (2005) 87
16. B. Furtula, I. Gutman, N. Turković, *Indian J. Chem.* **44A** (2005) 9
17. I. Gutman, S. Milosavljević, B. Furtula, N. Cmiljanović, *Indian J. Chem.* **44A** (2005) 13
18. I. Gutman, S. Gojak, N. Turković, B. Furtula, *MATCH Commun. Math. Comput. Chem.* **53** (2005) 139
19. I. Gutman, A. T. Balaban, M. Radnić, C. Kiss-Toth, *Z. Naturforsch.* **60a** (2005) 171
20. I. Gutman, N. Turković, *Monatsh. Chem.*, in press
21. I. Gutman, G. Stojanović, Ž. Bošković, N. Radulović, P. Rašić, *Polyc. Arom. Comp.* **136** (2005) 713
22. E. Clar, *The Aromatic Sextet*, Wiley, London, 1972
23. M. D. Watson, A. Fechtenkötter, K. Mülen, *Chem. Rev.* **101** (2001) 1267
24. O. E. Polansky, D. H. Rouvray, *MATCH Commun. Math. Comput. Chem.* **2** (1976) 91
25. B. N. Cyvin, J. Brunvoll, S. J. Cyvin, I. Gutman, *MATCH Commun. Math. Comput. Chem.* **23** (1988) 163
26. I. Gutman, S. J. Cyvin, *MATCH Commun. Math. Comput. Chem.* **23** (1988) 175
27. I. Gutman, D. Babić, *J. Mol. Struct. (Theochem)* **251** (1991) 367
28. I. Gutman, *Rep. Mol. Theory* **1** (199) 115
29. M. Randić, *J. Mol. Struct. (Theochem)* **229** (1991) 139
30. I. Gutman, V. Ivanov-Petrović, J. R. Dias, *Polyc. Arom. Comp.* **18** (2000) 221
31. M. Randić, *Chem. Rev.* **103** (2003) 3449
32. I. Gutman, *Monatsh. Chem.* **136** (2005) 1055.