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The Calculations of Ring Current of Some Benzenoids Using Randić Model

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Abstract: ***The ring currents of some benzenoids were calculated using a graph theoretical model as called Randić. This model follows the first law of Kirchhoff. And it gives a qualitative visualization of currents expressive as plotted maps. The currents in the maps are decomposed into perimeter and interior bond currents. The results showed that the currents of bonds on perimeter of all molecules were diatropic (anticlockwise). And all the molecules were aromatic (diamagnetic). But the current of interior bonds of some molecules were paratropic (clockwise) (KF9, KF17 and KF19). The numerical values indicated that the currents were affected by the shape and the size of molecules.***

Keywords: currents, Randić, diatropic, conjugated circuits, diamagnetic

1. Introduction

The ring currents as described by Pauling[1] and Lonsdale[2], is a freedom of movement of electrons in P_z orbital of benzene and other aromatic hydrocarbons between adjacent carbon atoms. Itis occurred in the presence of an external magnetic field to form interatomic π currents aboveandbelow the molecular plane.[1,2]It considereda prominent feature of aromatic compounds. Aromatic and antiaromatic systems can be distinguished according to their magnetic properties.[3]Since an aromatic species have the ability to support a diatropic ring current (anticlockwise, opposed ring current circulation), but antiaromatic compounds support a paratropic ring currents (clockwise, aligned ring current circulation).[4]Therelation between aromaticity and ring currents was proved by nuclear magnetic resonance spectroscopyNMR.[5]

Theoretically, the ring current was calculated using different methods such as conjugated circuits CC.A conjugated circuit CC model was introduced by Randić in early 2000.[6]Randić[7] assumed that the currents flow in the set of conjugated circuits which are defined as those circuits in Kekulé valence structures*K*(alternation of single and double bonds).The CC necessarily even, and they were counted as two perfect matching $K(K-1)/2$.[5]The matchings are defined as a single conjugated circuits or a set of disjoint conjugated circuits.[8]

Randić model weighs all conjugated circuits (single and set of disjoint) that contributes to each bond as $\pm 2[m(G-C)]^2$, where the sign is determined by the orientation of conjugated circuit, (+) for anticlockwise direction of 4n+2 cycles, (-) for clockwise direction of 4n cycles and *m*is the perfect matching of conjugated circuit *C*in the molecular graph *G*.[8]Thismodel obeys Kirchhoff's first law thus the currents of two bonds with the same values and different directions are cancelled.[9]Randić model gives a qualitative insight of ring current. Nevertheless it has a drawback that it has a lake of distinguish between the systems withsimilargeometrybut different magnetic responsesuch as benzene and borazine.[8]In the present work, the ring currents of a set of benzenoids were calculated using CC model of Randić. The unnormalised values were plotted as maps and the normalised currents were listed.

2. The Method of Calculation

The set of molecules consists of 19 benzenoids. The molecules were classified according to their dualist graphs to catacondensed with no carbon atom common with three benzenoid rings, for which the dualist graphs are acyclic[10](KF1, KF2, KF3, KF4, KF5, KF6, KF7, KF10, KF13 and KF15) and pericondensed which contain some carbon atoms common to three benzenoid rings and their dualist graphs include threemembered rings[11]such as (KF8, KF9 and KF17).The set of molecules was chosen because it considers a good source of different size and shape of benzenoids.[12]

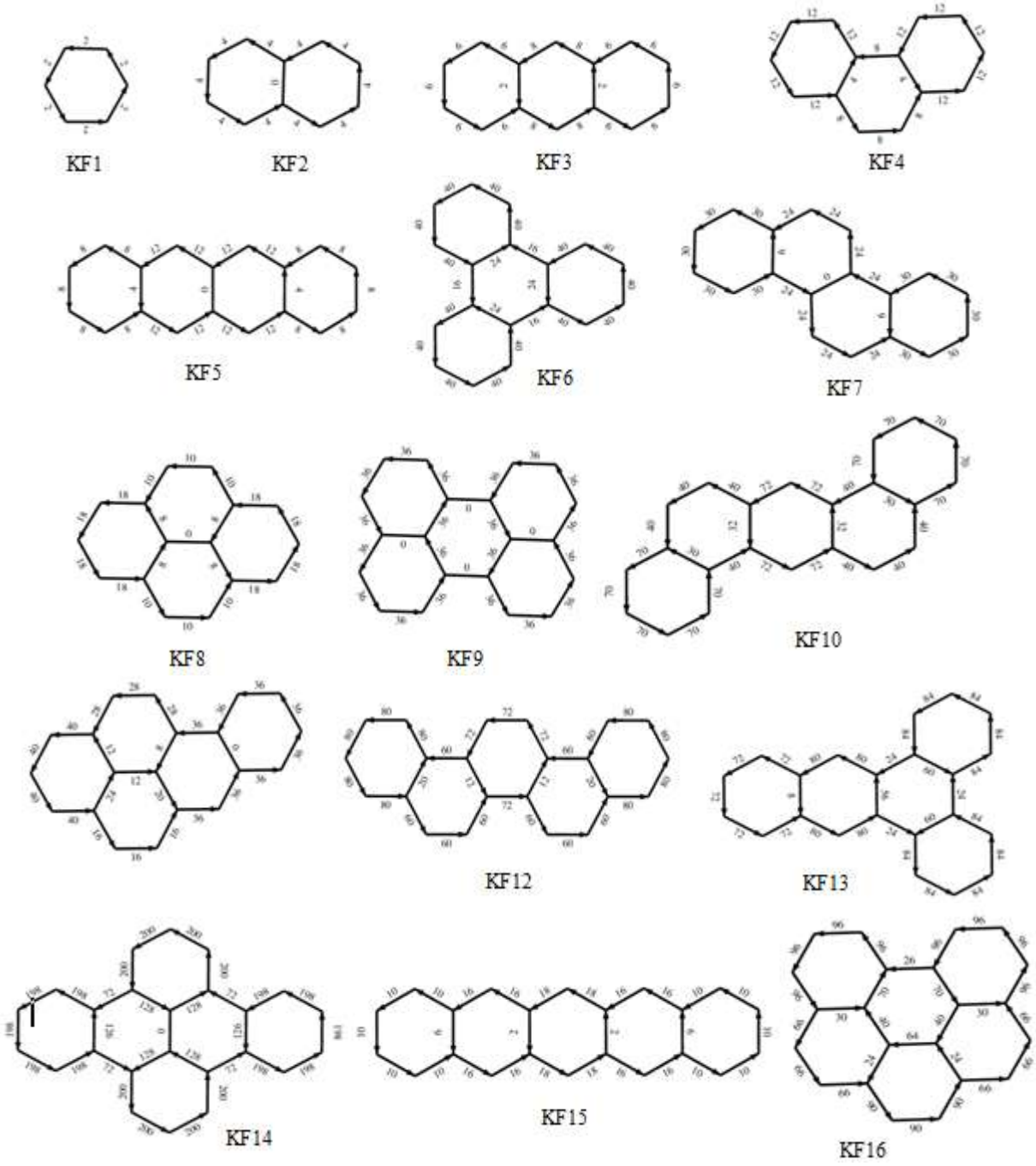
Thebenzenoids were drawn using ChemDraw (Ultra 10).[13]Then the ring currents were predicted using Randić model[7,8]and the maps of currents were plotted.For a prediction, a program that involved the formula$\pm 2[m(G-C)]^2$was used, where *m*is the perfect matching of conjugated circuit *C*in the molecular graph *G*.For instant, the current of benzene KF1 is 2*N*, where *N* is the number of benzene rings. Hence, each ring containing two Kekulé structures. And the currents of bonds on perimeter of anthracene were (2*N* for the first ring, 4*N*-4 for the mid ring, and 6*N*-12 for the last ring).And the currents of interior bonds were (2*N*-4 for the first ring, 2*N*-8 for the mid ring, and 2*N*-12 for the last ring).[14]The obtained unnormalised currents were normalised by dividing the valuesby the conjugated circuits of molecule*K*(*K*-1) and the results were listed in table (1).For each molecule, to obtain the scaled currents of Randić, the unnormalised currents were multiplied by a scale factor (highest value of current).

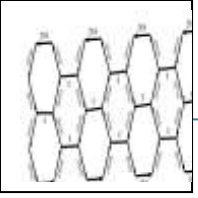
3. Results

The ring currents were calculated using Randić model.The unnormalised ring currents were predicted and the maps of ring current were plotted Fig. 1. The maps showed that the current of bonds on perimeter of all molecules were

anticlockwise (diatropic).But, the current of central inner ring of some molecules(KF9, KF16, KF17, KF18 and KF19) were paratropic (clockwise). Thus, it is expected that the aromaticity of later molecules will be less than the former molecules.

For linear catacondensed benzenoids (naphthalene, anthracene, tetracene, and pentacene), thecontributions to the current of central rings were bigger than it of terminal rings. For non-linear catacondensed, thesize and the shape of molecules affect the currents. Hence, the numerical values of current were increased as the number of rings increased. And the currents of catafusenes were bigger than those of perifusenes. For some molecules; naphthalene, tetracene, triphynelene, pyrene, perylene, 3,4-benzopyrene, dibenzo [fg,op] tetracene, coronene, benzo [fg,gi] phenanthro [9,10,1,2,3-pqrst] pentaphene and quatrylene, it noticed that the ring currents of interior bondswere zero (the currents of two bonds with the same values and different directions are cancelled). For other molecules, it is also showed that the currents on periphery of catacondensed and pericondensed benzenoids were bigger than currentsof interior.Normalised ring currents of Randić were calculated by dividing the unnormalised currentsby the perfect matching number *K*(*K*-1), and listed in table 1. In comparison with benzene, the results of normalization showed that benzene has the biggest value of ring current (1.000) and the minimum value of current was related to coronene (0.4421). The scaled values of ring currents were obtained by multiplying the ring current of each bond in a molecule by a scale factor (the biggest value of current of molecule). Fig.2b showed the scaled currents of anthracene.





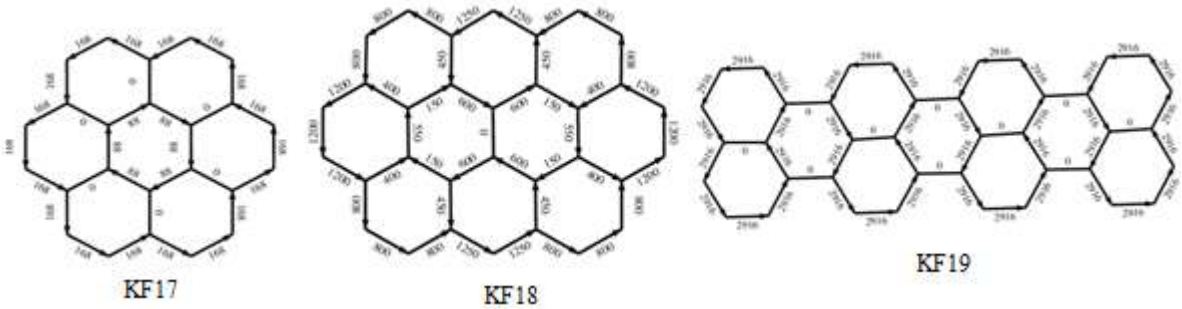


Figure 2: (a) the normalised ring currents and (b) the scaled ring currents of Randić of anthracene

Table 1: The normalised currents of Randićof the set ofbenzenoids

Molecules	Symboles	The normalised currents of Randić
benzene	KF1	1.0000
napthalene	KF2	0.6667
anthracene	KF3	0.5000
phenanthrene	KF4	0.6000
tetracene	KF5	0.6000
triphynelene	KF6	0.5556
chrysene	KF7	0.5357
pyrene	KF8	0.6000
perylene	KF9	0.5000
1,2,5,6-dibenzoanthracene	KF10	0.5455
3,4-benzopyrene	KF11	0.5000
picene	KF12	0.5128
dibenzo [a,c] anthracene	KF13	0.5385
dibenzo [fg,op] tetracene	KF14	0.5263
pentacene	KF15	0.6000
benzo [ghi] perylene	KF16	0.5275
coronene	KF17	0.4421
ovalene	KF18	0.5102
quatrylene	KF19	0.4500

4. Conclusion

It is concluded that the Randić model of currents is a simple and useful tool to predict currents of benzenoids. It gives quantitative and qualitative maps. The plotted maps showed that all the molecules under studying are diatropic (anticlockwise). And the currents on perimeter bonds are greater than those in interior. Also it showed that the obtained values were affected by the size of molecules since the currents were increased with increasing the number hexagons. As well as, the shape of molecule affects the currents. Thus the currents of catacondensed benzenoids are greater than currents of pericondensed benzenoids.

References

[1] Pauling,L.The Diamagnetic Anisotropy of Aromatic Molecules. *J. Chem. Phys.***1936**, *4*, 673.
[2] Lonsdale,K.Magnetic Anisotropy and electronic Structure of Aromatic Molecules. *Proc. R. Soc. Ser. A.***1937**, 149–161.
[3] De Proft,F.; Fowler,P. W.;Havenith,R. W. A.; Schleyer, P. V. R.;Van Lier G. G. and Geerlings,P. Ring Currents as Probes of the Aromaticity of Inorganic Monocycles: P_5^-, As_5^-, S_2N_2, $S_3N_3^-$, $S_4N_3^+$, $S_4N_4^{2+}$, $S_5N_5^+$, S_4^{2+} and Se_4^{2+}. *Chemistry*.**2004**, *10*, 940–950.
[4] Fowler, P. W.;Steiner,E.; Havenith, R. W. A. and Jenneskens,L. W. Current Density, Chemical Shifts and Aromaticity. *Magn. Reson. Chem.***2004**, *42*, S68–S78.
[5] Randić,M. Electron Currents in Polycyclic Conjugated Hydrocarbons of Decreasing Aromatic Character and a Novel Structural Definition of Aromaticity. *The Open Organic Chemistry Journal*.**2011**, *5*, 11-26.
[6] Randić,M. Aromaticity of Polycyclic Conjugated Hydrocarbons. *Chem. Rev.***2003**, *103*, 3492.
[7] Randić,M.;BalabanA. T. and Plavšić,D. Applying the Conjugated Circuits Method to ClarStructures of [n]Phenylenes for Determining Resonance Energies. *Phys. Chem. Chem. Phys.***2011**, *13*, 20644–20648.
[8] FowlerP. W. and Myrvold,W. The "Anthracene Problem": Closed-Form ConjugatedCircuit Models of Ring Currents in Linear Polyacenes. *J. Phys. Chem. A.***2011**, *115*, 13191–13200.
[9] Soncini,A.;Fowler,P. W.; Jenneskens,L. W. and Road,S. Ring Currents in Large [4 n + 2]-Annulenes. *Phys. Chem. Chem. Phys.***2004**, *6*, 277–284.
[10] Balaban,A. T. and Randić, M. Partitioning of π - Electrons in Rings of Polycyclic Benzenoid Hydrocarbons. 2. Catacondensed Coronoids. *J. Chem. Inf. Comput. Sci.***2004**, *44*, 50–59.
[11] Balaban, A. T. and Randić, M. Partitioning of p-Electrons in Rings of Polycyclic Conjugated Hydrocarbons. *New J. Chem*, **2004**, *28*, 800–806.
[12] Kiralj,R. and Ferreira,M. M. C. Predicting Bond Lengths in Planar Benzenoid Polycyclic Aromatic Hydrocarbons: A Chemometric Approach. *j. Chem. Inf. Comput. Sci.***2002**, *42*, 508–523.
[13] http://www.cambridgesoft.com/ChemDraw.
[14] Singh,J.;Singh,S.; Meer,S.; Agrawal,V. K.; KhadikarP. V. and Balaban,T. QSPR Correlations of Half-Wave Reduction Potentials of Cata-Condensed Benzenoid Hydrocarbons. *ARKAT*, **2006**, *xv*, 104–119.