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THE CALCULATIONS OF CURRENT ON PERIMETER OF SOME BENZENOIDS USING PAULING BOND ORDERS

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ABSTRACT
The bond currents on perimeter of a set of benzenoids were calculated using Pauling bond order on perimeter model *P* (1-*P*). This approach is simple and easy. The requirements are the Pauling bond orders and the number of Kekulé structures *K*. These requirements are estimated easily from the inverse of adjacency matrix A^{-1}. The results showed an agreement between the normalised and unnormalised currents of Randić with the currents on perimeter using Pauling bond orders. In addition, the correlation between the later currents and Pauling bond lengths-bond order is useful to estimate the currents, bond length and bond order that involved in the correlation.

KEYWORDS: currents, Pauling, benzenoids, Randić, perimeter.

INTRODUCTION

A polycyclic conjugated hydrocarbon is one of the most important systems to study the character of ring currents. The conjugated systems provide a good source of π-bond system[1]. Though the ring current is indirectly observable, NMR spectroscopy and Magnetic property are used to measure this property. However, theoretical methods allow visualizing the ring current directly[2].These methods are classified into two types. The first type is based on molecular orbital such as full ab initio and pseudo π. They provide interesting maps of induced intensity of ring current. They interpret the current maps according to the excitations of orbitals and bands. And consequently, it explains the character of aromaticity and anti-aromaticity.

The other type of ring current is the conjugated circuit (*CC*) methods which are based on valence bond (VB) theory. These methods consider counting the pairings of Kekulé structures *K* (perfect matchings) to calculate the intensity of bond current of Kekulean molecules[3,4] Recently, a quick and easy computational approach of Randić current on perimeter of molecule was displayed by Fowler *et al*[5]. It is called perimeter ring currents of benzenoids from Pauling bond orders. The new approach is illustrated in reference[4]. The Pauling bond orders on perimeter bonds (*P*) and the numbers of Kekulé structures are needed to calculate the Randić currents on perimeter *J* as-

$$J_{(on\,perimeter)} = P(1-P) \quad (1)$$

For benzenoids, the inverse of adjacency matrix $\boldsymbol{A}^{-1}$ is used to calculate the Pauling bond order *P*. And the Kekulé structures which are used to calculate the numbers of conjugated circuits *CC* are the eigenvalues of the adjacency matrix.[4] This VB model is based on Randić method of ring current. According to Randić[6] for a benzenoid which is have 4n+2 conjugated circuits *CC*, all contributions to currents on perimeter are reinforced and the number of conjugated circuits *CC* is equal to unnormalised currents of Randić as

$$J_{unnormalised\ Randić} = no.\,of\,CC \quad (2)$$

$$no.\,of\,CC = 2P(1-P)K^2 \quad (3)$$

$$J_{unnormalised\ Randić} = 2P(1-P)K^2 \quad (4)$$

when *J* is the maximum, then *P* is equal to a half and

$$\frac{J}{J_{max}} = 4P(1-P) = J_{unnormalised\ Randić} \quad (5)$$

Where J_{max} is the maximum value of Pauling ring current on perimeter.
The normalised bond currents of Randié on perimeter are obtained by dividing unnormalised currents by (*K*-1) as[5]

$$J_{normalised\ Randić} = 2P(1-P)K^2/(K-1) \quad (6)$$

In this paper, the bond currents of Randić on perimeter were calculated easily using Pauling bond order on perimeter $P(1\text{-}P)$. The predicted bond currents on perimeter are correlated with the Pauling bond lengths and bond orders. These correlations are efficient to calculate the current of any perimeter edge involved in the correlation.

METHODOLOGY

The Randić currents on perimeter of a set of polycyclic conjugated molecules were calculated using Pauling bond order. The geometrical structures of molecules at equilibrium were obtained using Gaussian 09 at rb3lyp/6-311g (d, p). The molecules classified into three species, straight chain, bent chain and zig-zag chain. The calculations of current using Pauling bond orders on perimeter model was described as $J_{\text{on perimeter}} = P(1\text{-}P)$. The Kekulé structures and Pauling bond orders of Kekulean benzenoids were counted computationally using the matrix of Hückel bond orders. In the next step, the obtained bond currents on perimeter were correlated with Pauling bond lengths and Pauling Bond orders to investigate the correlation among them.

RESULTS & DISCUSSION

The currents of bonds on perimeter of the set of benzenoids were calculated using Pauling bond order model. As shown, this model provides an easy and simple method of calculation of bond currents on perimeter. First, the Pauling bond orders and Kekulé structures are estimated from the adjacency matrix. Then, the Pauling currents on perimeter J were calculated and the results were listed in table 1. The normalised ring currents of Randić were calculated previously as reported in ref. 8 and listed in table 1. The maps of unnormalised induced ring current of Randić were published earlier in[8]. Interestingly, the results showed that for the linear benzenoids that have K equal to $(Q+1)$, where Q is the number of hexagons[7], the equations 5 and 6 work properly. Thus multiplying the Pauling currents $P(1\text{-}P)$ by the number of Kekulé structures K according to the equation $[2P(1-P)K^2]$ gives the unnormalized ring currents of Randić. And dividing the calculated currents by $2P(1-P)K/(K-1)$ gives the normalised ring currents of Randić. For the bent chain benzenoids with K equal to $\left[1+{}^1\!/_4\,(Q+1)^2\right]$ $\left[1+{}^1\!/_4\,Q(Q+2)\right]$ such as phenanthrene and *zig-zag* chain benzenoids with K equal to F_{Q+1} such as chrysene,[8] these equations also work accurately. The obtained currents on perimeter using Pauling bond order model agree with the Randić currents using equation 5 and 6. But for a few molecules, there is slightly difference between the currents of two models.

The calculated Pauling currents J were plotted against the predicted Pauling bond orders P and bond lengths R. As shown in Fig. 2, the relationships were twisted as curves. The curves revealed that the maximum value of the Pauling currents was (1.00) which is related to bond length R equal to (1.40) Å and a bond order P equal to a half (0.5). Both values, P and R are linked to benzene KF1. The minimum value of current was obtained at P equal to (0.00) and at R equal to (1.00).

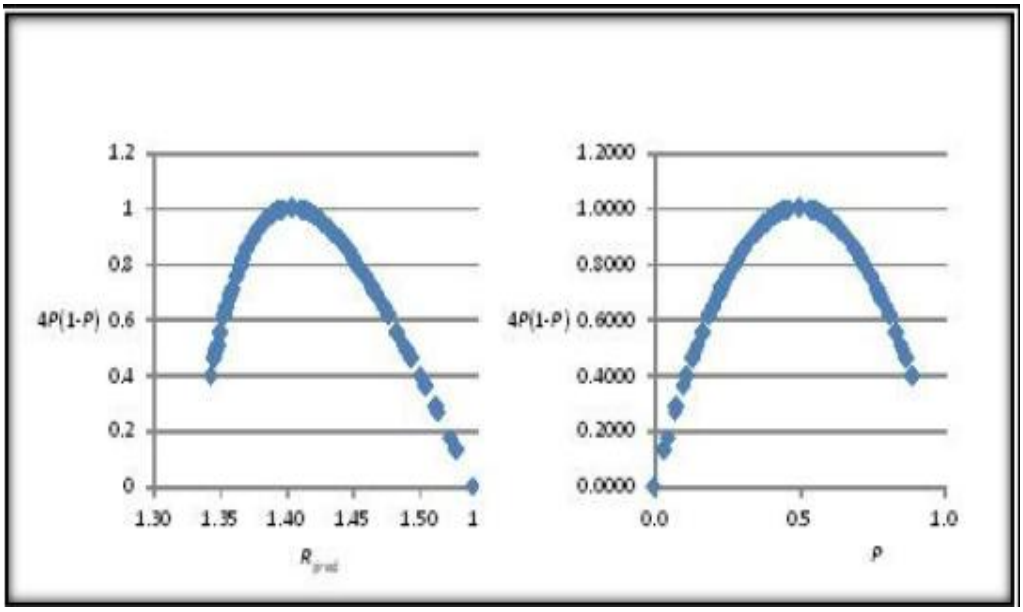

FIGURE 2: (a) the right side, the correlation between Pauling bond lengths R_{pred} and currents of Pauling bond order on perimeter $4P(1\text{-}P)$ (b) the correlation between predicted bond orders P and currents of Pauling bond order on perimeter.

TABLE 1: The predicted bond lengths *R*, Pauling bond orders *P*, Pauling bond order currents on peremiter *J*, Kekulé structure *K*, and the normalised currents of Randić of the unique bonds of the set of benzenoids with their symbols.

No.	Molecule[9]	Sym.	Bond	R^7	P^7	$J= P(1-P)$	K	Normalised Randić[7]
1	benzene	KF1	A	1.403	0.500	0.250	2	1.0000
2	napthalene	KF2	C	1.439	0.333	0.222	3	0.6667
3			B	1.375	0.667	0.222		
4			A	1.439	0.333	0.222		
5			D	1.439	0.333	0.222		
6	anthracene	KF3	C	1.460	0.250	0.188	4	0.5000
7			A	1.404	0.500	0.250		
8			D	1.362	0.750	0.188		
9			E	1.460	0.250	0.188		
10			B	1.460	0.250	0.188		
11	phenanthrene	KF4	G	1.386	0.600	0.240	5	0.6000
12			F	1.424	0.400	0.240		
13			E	1.395	0.600	0.240		
14			D	1.424	0.400	0.240		
15			B	1.474	0.200	0.160		
16			A	1.355	0.800	0.160		
17			C	1.424	0.400	0.240		
18			H	1.424	0.400	0.240		
19			I	1.474	0.200	0.160		
20	tetracene	KF5	E	1.474	0.200	0.160	5	0.6000
21			C	1.386	0.600	0.240		
22			B	1.424	0.400	0.240		
23			F	1.355	0.800	0.160		
24			G	1.474	0.200	0.160		
25			D	1.474	0.200	0.160		
26			A	1.474	0.200	0.160		
27	triphynelene	KF6	D	1.394	0.556	0.247	9	0.5556
28			C	1.415	0.444	0.247		
29			A	1.501	0.111	0.099		
30			E	1.415	0.444	0.247		
31			B	1.415	0.444	0.247		
32	chrysene	KF7	F	1.430	0.375	0.234	8	0.5357
33			D	1.460	0.250	0.188		
34			C	1.362	0.750	0.188		
35			B	1.460	0.250	0.188		
36			K	1.460	0.250	0.188		
37			J	1.430	0.375	0.234		
38			I	1.382	0.625	0.234		
39			H	1.430	0.375	0.234		
40			G	1.382	0.625	0.234		
41			E	1.430	0.375	0.234		
42			A	1.404	0.500	0.250		
43	pyrene	KF8	A	1.351	0.833	0.139	6	0.6000
44			B	1.484	0.167	0.139		
45			D	1.404	0.500	0.250		
46			E	1.404	0.500	0.250		
47			C	1.439	0.333	0.222		
48			F	1.439	0.333	0.222		
49	perylene	KF9	D	1.439	0.333	0.222	9	0.5000
50			G	1.540	0.000	0.000		
51			E	1.375	0.667	0.222		
52			C	1.375	0.667	0.222		
53			B	1.439	0.333	0.222		
54			F	1.439	0.333	0.222		
55			A	1.439	0.333	0.222		
56	1,2,5,6-dibenzoanthracene	KF10	I	1.421	0.417	0.243	10	0.5455
57			H	1.389	0.583	0.243		
58			G	1.421	0.417	0.243		
59			E	1.484	0.167	0.139		
60			D	1.351	0.833	0.139		
61			C	1.484	0.167	0.139		
62			A	1.404	0.500	0.250		
63			M	1.404	0.500	0.250		
64			L	1.484	0.167	0.139		
65			K	1.421	0.417	0.243		

66			J	1.389	0.583	0.243		
67			F	1.421	0.417	0.243		
68			B	1.439	0.333	0.222		
69	3,4-benzopyrene	KF11	N	1.375	0.667	0.222	10	0.5000
70			M	1.439	0.333	0.222		
71			L	1.375	0.667	0.222		
72			K	1.439	0.333	0.222		
73			I	1.439	0.333	0.222		
74			H	1.375	0.667	0.222		
75			F	1.501	0.111	0.099		
76			E	1.343	0.889	0.099		
77			D	1.501	0.111	0.099		
78			B	1.394	0.556	0.247		
79			A	1.415	0.444	0.247		
80			W	1.394	0.556	0.247		
81			V	1.415	0.444	0.247		
82			T	1.468	0.222	0.173		
83			S	1.358	0.778	0.173		
84			R	1.468	0.222	0.173		
85			O	1.439	0.333	0.222		
86			J	1.439	0.333	0.222		
87			P	1.439	0.333	0.222		
88			G	1.468	0.222	0.173		
89			Q	1.415	0.444	0.247		
90			C	1.439	0.333	0.222		
91			U	1.439	0.333	0.222		
92			X	1.439	0.333	0.222		
93	picene	KF12	N	1.371	0.692	0.213	13	0.5128
94			M	1.446	0.308	0.213		
95			L	1.465	0.231	0.178		
96			K	1.428	0.385	0.237		
97			J	1.383	0.615	0.237		
98			I	1.428	0.385	0.237		
99			H	1.383	0.615	0.237		
100			F	1.428	0.385	0.237		
101			G	1.428	0.385	0.237		
102			E	1.465	0.231	0.178		
103			D	1.359	0.769	0.178		
104			B	1.411	0.462	0.249		
105			C	1.465	0.231	0.178		
106			A	1.446	0.308	0.213		
107	dibenzo [a,c] anthracene	KF13	B	1.411	0.462	0.249	13	0.5385
108			C	1.397	0.538	0.249		
109			D	1.411	0.462	0.249		
110			F	1.512	0.077	0.071		
111			A	1.397	0.538	0.249		
112			E	1.411	0.462	0.249		
113			G	1.411	0.462	0.249		
114			H	1.512	0.077	0.071		
115			J	1.383	0.615	0.237		
116			K	1.428	0.385	0.237		
117			M	1.446	0.308	0.213		
118			N	1.371	0.692	0.213		
119			O	1.446	0.308	0.213		
120			L	1.446	0.308	0.213		
121			I	1.446	0.308	0.213		
122	dibenzo [fg,op] tetracene	KF14	I	1.404	0.500	0.250	20	0.5263
123			H	1.404	0.500	0.250		
124			E	1.504	0.100	0.090		
125			C	1.414	0.450	0.248		
126			B	1.395	0.550	0.248		
127			A	1.414	0.450	0.248		
128			D	1.414	0.450	0.248		
129			F	1.424	0.400	0.240		
130			G	1.474	0.200	0.160		
131	pentacene	KF15	C	1.484	0.167	0.139	6	0.6000
132			E	1.375	0.667	0.222		
133			F	1.439	0.333	0.222		
134			H	1.404	0.500	0.250		

135			B	1.351	0.833	0.139		
136			A	1.484	0.167	0.139		
137			D	1.484	0.167	0.139		
138	benzo [ghi] perylene	KF16	L	1.418	0.429	0.245	14	0.5275
139			K	1.391	0.571	0.245		
140			J	1.418	0.429	0.245		
141			G	1.470	0.214	0.168		
142			F	1.357	0.786	0.168		
142			E	1.470	0.214	0.168		
143			B	1.434	0.357	0.230		
144			A	1.379	0.643	0.230		
145			M	1.391	0.571	0.245		
145			O	1.514	0.071	0.066		
146			H	1.434	0.357	0.230		
147			N	1.434	0.357	0.230		
148			C	1.418	0.429	0.245		
149			I	1.451	0.286	0.204		
150			D	1.451	0.286	0.204		
151	coronene	KF17	C	1.447	0.300	0.210	20	0.4421
152			D	1.370	0.700	0.210		
153			B	1.424	0.400	0.240		
154			A	1.447	0.300	0.210		
155	benzo [fg,gi] phenanthro [9,10,1,2,3-pqrst] pentaphene	KF18	Q	1.395	0.550	0.248	31	0.5051
156			R	1.414	0.450	0.248		
157			S	1.504	0.100	0.090		
158			T	1.404	0.500	0.250		
159			P	1.414	0.450	0.248		
160			M	1.414	0.450	0.248		
161			N	1.414	0.450	0.248		
162			L	1.504	0.100	0.090		
163			J	1.404	0.500	0.250		
164			I	1.404	0.500	0.250		
165			H	1.404	0.500	0.250		
166			G	1.404	0.500	0.250		
167			E	1.504	0.100	0.090		
168			B	1.404	0.500	0.250		
169			A	1.404	0.500	0.250		
170			U	1.424	0.400	0.240		
171			K	1.424	0.400	0.240		
172			F	1.424	0.400	0.240		
173			V	1.474	0.200	0.160		
174			C	1.424	0.400	0.240		
175			D	1.474	0.200	0.160		
176	quatrylene	KF19	D	1.439	0.333	0.222	36	0.4500
177			C	1.375	0.667	0.222		
178			B	1.439	0.333	0.222		
179			G	1.540	0.000	0.000		
180			E	1.375	0.667	0.222		
182			I	1.375	0.667	0.222		
183			J	1.439	0.333	0.222		
184			L	1.540	0.000	0.000		
185			K	1.375	0.667	0.222		
186			A	1.439	0.333	0.222		
187			F	1.439	0.333	0.222		
188			H	1.439	0.333	0.222		
189			M	1.439	0.333	0.222		

CONCLUSION

It is concluded that Pauling bond order on perimeter provide easy method to predict Randić currents on perimeter of Kekulean benzenoids. The results showed a close correlation between currents of Pauling bond order on perimeter *J* and normalised currents of Randić. The unnormalized and normalised currents of Randić were obtained using $[2P(1-P)K^2]$ and $2P(1-P)K/(K-1)$, respectively. And the correlations between Pauling currents on perimeter and Pauling bond lengths-bond orders are useful to predict currents, bond length or bond order of any bond involved in the correlation.

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