

THE LOCAL TOPOLOGICAL DEPENDENCE OF RING CURRENT
IN POLYCYCLIC AROMATIC HYDROCARBONS

Noriyuki MIZOGUCHI

Department of Physics, Meiji College of Pharmacy
Nozawa, Setagaya-ku, Tokyo 154

Ring currents in individual hexagons of many catacondensed hydrocarbons were calculated systematically. It was found that the values of ring currents are distributed within the four different ranges corresponding to the four classes of hexagon which are classified by the local topological structure.

It is known that London (ring current) diamagnetic susceptibility of a kind of hexagon in a benzenoid hydrocarbon is very small.¹⁾ This suggests that London diamagnetic susceptibilities of individual hexagons are dependent on the local topological (geometric) structure around them. Recently Aida and Hosoya²⁾ showed that the aromatic sextet character of a given benzenoid ring in a polycyclic aromatic hydrocarbon is determined by the local topological structure around it.

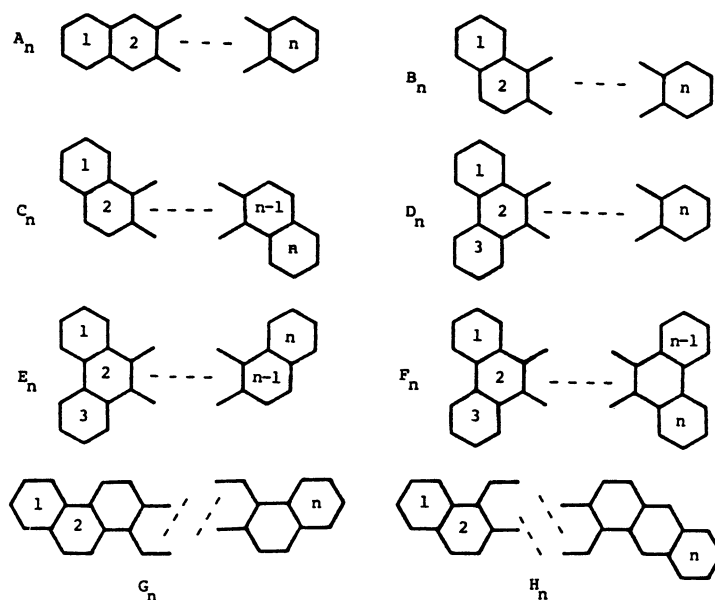


Fig.1 The shapes and sizes of molecules considered

In order to examine the dependence of ring current on the local topological structure, ring currents in the component hexagon of many catacondensed hydrocarbons are calculated from the London-McWeeny method³⁾ which is an extension of the simple Huckel molecular orbital method. The molecules whose ring currents are calculated are shown in Fig.1, where tentative symbols representing the shape and size of the molecule are shown. They are expressed relative to the ring current in benzene. After Aida and Hosoya,²⁾ the component hexagons of catacondensed hydrocarbons are classified into the four classes (primary, linear, kink and tertiary) as shown in Fig.2, depending on the local topological structure around them. Hereafter let the symbols C_P , C_L , C_K and C_T represent the ring current in the primary, linear, kink and tertiary hexagons, respectively.

The values of ring current of molecules F_7 and F_9 are plotted in Fig.3(a). As shown in this figure, these values in molecules of the same shape resemble closely in appearance. Ring currents for each shape of molecule with 7 hexagons are shown in Table 1. From this table it can be seen that the following inequality is obtained for a molecule of any shape except the molecule G_9 ;

$$C_L > C_P > C_K > C_T.$$

Table 1 Ring currents in individual hexagons of each type of molecule with 7 hexagons

	The site of hexagon						
	1	2	3	4	5	6	7
A_7	1.044 (P) ^{a)}	1.284 (L)	1.348 (L)	1.361 (L)			
B_7	1.096 (P)	0.814 (K)	1.228 (L)	1.352 (L)	1.369 (L)	1.308 (L)	1.059 (P)
C_7	1.108 (P)	0.842 (K)	1.272 (L)	1.371 (L)			
D_7	1.052 (P)	0.584 (T)	1.052 (P)	1.170 (L)	1.338 (L)	1.320 (L)	1.074 (P)
E_7	1.072 (P)	0.629 (T)	1.071 (P)	1.233 (L)	1.294 (L)	0.889 (K)	1.123 (P)
F_7	1.102 (P)	0.721 (T)	1.102 (P)	1.124 (L)			
G_7	1.159 (P)	1.067 (K)	1.158 (K)	1.140 (K)			
H_7	1.158 (P)	1.068 (K)	1.137 (K)	1.154 (K)	0.986 (K)	1.304 (L)	1.126 (P)

a) The letters in the parentheses represent the classes of hexagons.

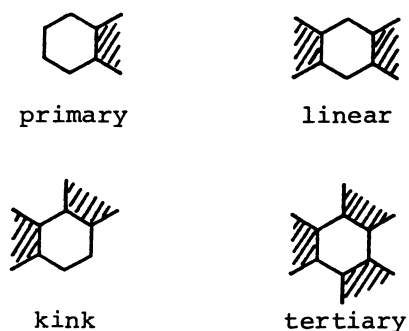


Fig.2 The classification of hexagon in a catacondensed hydrocarbon.

Next we consider the changes of ring current in individual hexagons for a few typical shapes of molecule in detail. For polyacenes A_n the values of ring current sharply increase at the second hexagon, and slightly increase towards the center hexagon. They become the largest at the center hexagon as shown in Fig.3(b). The values C_P and C_L in polyacenes $A_2 - A_9$ are distributed within the following ranges, respectively;

$$\begin{array}{ll} C_P & 1.040 - 1.093 \\ C_L & 1.280 - 1.357 \end{array}$$

For molecules B_n the values of ring current drastically decrease at the second hexagon and increase at the third hexagon. They increase monotonically towards the center of series of linear hexagons and become the largest at the center hexagon. The values C_P, C_L and C_K in molecules $B_3 - B_9$ are distributed within the following ranges, respectively;

$$\begin{array}{ll} C_P & 1.046 - 1.137 \\ C_L & 1.137 - 1.371 \\ C_K & 0.806 - 0.975 \end{array}$$

The results for molecules G_7 and G_9 are given in Table 1 and Fig.3(b), respectively. The values of ring current in molecules G_n sharply decrease at the second hexagon, change zig-zag with small differences and become the largest at the center hexagon. Table 2 shows the ranges of distribution of the values C_P, C_L, C_K and C_T for each shape of molecule. The values C_P, C_L, C_K and C_T for all the molecules calculated are

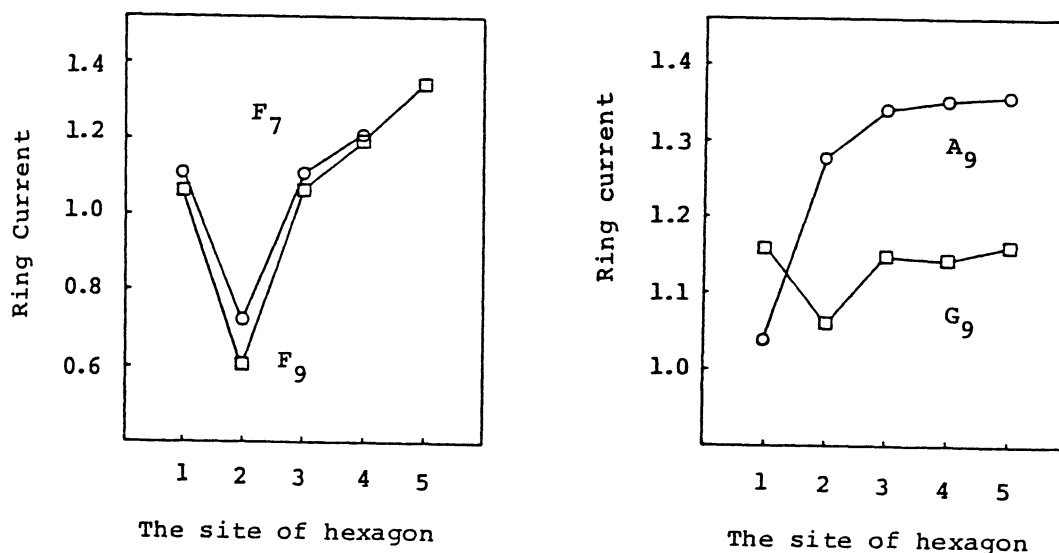


Fig.3 The plots of values of ring current of (a) molecules F_7 and F_9 ; (b) molecules A_9 and G_9 .

Table 2. The ranges of distribution of the values C_P, C_L, C_K and C_T for each shape of molecule

	$n^a)$	C_P	C_L	C_K	C_T
A_n	2 - 9	1.040 - 1.093	1.280 - 1.357		
B_n	3 - 9	1.046 - 1.137	1.212 - 1.371	0.806 - 0.975	
C_n	4 - 9	1.096 - 1.152	1.231 - 1.388	0.814 - 1.086	
D_n	4 - 9	1.046 - 1.116	1.114 - 1.368		0.571 - 0.748
E_n	6 - 9	1.051 - 1.140	1.172 - 1.371	0.827 - 0.962	0.582 - 0.698
F_n	6 - 9	1.060 - 1.142	1.203 - 1.342		0.602 - 0.904
G_n	3 - 9	1.137 - 1.160		0.975 - 1.161	
H_n	5 - 9	1.122 - 1.159	1.300 - 1.305	0.973 - 1.163	

a) The n means the size of molecule calculated.

distributed within the following four almost distinct ranges, respectively;

C_P	1.040 - 1.160
C_L	1.114 - 1.388
C_K	0.806 - 1.163
C_T	0.571 - 0.904

One can conclude from the above result that the values of ring current in individual hexagons of catacondensed hydrocarbons are almost determined by the local topological structure around them. Further analysis of ring current is being under way.

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