Theor Chim Acta (1989) 75: 279-297

Theoretica Chimica Acta

Stability and reactivities based on moment analysis

Y. Jiang* **and H. Zhang**

Institute of Theoretical Chemistry, Jilin University, Changchun, People's Republic of China

(Received January 4, revised April 18/Accepted June 20, 1988)

The truncated expansion of a function $|x|$ is used to obtain the total Hückel π-electron energy partitioned into various sums, in terms of moments as well as molecular fragments. The additivity is in general satisfactory for acyclic and cyclic systems, which exhibit a regularity called the generalized Hückel rule which indicates whether a fragment plays the role of stabilization or of destabilization. A unified treatment based on the energy partitioning is proposed for rationalizing aromaticity, reactivities and bond lengths of conjugated hydrocarbons. The relationships between molecular properties and topology can be deduced from inspecting, enumerating or summing the relative contributions of various fragments.

Key words: Hückel theory — Moments — Molecular topology — Aromaticity — Reactivity

1. Introduction

Extensive experimental results indicate that chemical reactions usually begin at a localized position in the reactants. A local interaction view has been the starting point for the empirical understanding and interpretation of molecular behaviour for chemists. However, MO (molecular orbital) theory displays a delocalized picture for the movement of electrons [1]. In order to conform with chemical usage, in MO theory, quantities defined in terms of the coefficients of occupied MO's such as charge density, bond order, free valence and others were introduced [2]. On the other hand, local MO schemes have been successfully proposed by suitable linear transformations of the SCF(self consistent field)-MO's [3, 4].

---

* *Also known as*: Yuan-sun Kiang

In MO theory, one first solves the secular equations to obtain energy levels and MO coefficients. Alternative approaches exist: for example, the use of moments enables the solution of the secular equation to be by-passed and molecular information determined directly. Haydock [5], Burdett [6-8] and their coworkers obtained the DOS (density of state), stabilized energy and other results for solids by means of the continued fraction [9]. On the other hand, Whitehead [10] discussed the distribution of energy levels in nuclear physics by analyzing the triangular matrice of moments. Of course, they all simplified the original theory to a certain degree, but even so the results seem far from clarifying the intuitive relationships which exist between molecular behaviour and structure. Very recently, Hall [11] suggested that an analysis of moments in terms of graphical invariants could be of prime importance in understanding these molecules.

Following our previous paper [12], we intend to develop an approach, which can be handled easily, to obtain MO information using molecular topology. We choose to use Hückel MO theory for this discussion. In this paper, a scheme based on moment analysis and energy partitioning is proposed for determining the stability and reactivity of conjugated hydrocarbons without referring to the usual manipulation of MO theory. We start with a truncated expansion of a function $|x|$ and a set of relations holding between moments and molecular fragments. The total π-electron energy is partitioned into various sums characterized by local structures whose arguments are moments as well as molecular fragments. Their contributions satisfy the generalized Hückel rule which gives an insight into the role played by various fragments. These fragments can be categorized as $4n$- and $(4n+2)$-species, they destabilize and stabilize the molecule and its local sites respectively. A unified energy scheme is then proposed in which the total resonance energy, point-energy, edge-energy and ring resonance energy are used for rationalizing the aromaticity, reactivities and bond lengths of conjugated hydrocarbons. The procedure can be manipulated by simply enumerating various fragments or comparing their relative contributions.

2. Moments and molecular fragments

Generally, in MO calculations, secular equations are solved by computing both the energy levels and MO's simultaneously. However, if moments are used instead, it is possible to utilize only the energy sequence without referring to the MO's [5-8, 10]. Moments are related to the topological connectivity [12] of a molecule and are able to give chemists explicit intuitive results.

Let us start with Hückel secular equation

$$|xI-A|=0 \tag{1}$$

where, A and I signify the adjacency and unit matrices respectively. If the x_i $(i=1,2,\dots,N)$ represent the energy levels, then the lth moment, u_l, equals the sum of the lth powers of the x_i^ls

$$u_l=\sum_{i=1}^{N} x_i^l \tag{2}$$

An alternative definition, which is equivalent to Eq. (2) is given by

$$u_l = \text{trace}\,(A^l) = \sum_{i=1}^{N} \sum_{\alpha,\beta,\ldots,\gamma} A_{i\alpha}A_{\alpha\beta}\cdots A_{\gamma i}. \tag{3}$$

Since the entries of the adjacency matrix A satisfying

$$A_{ij} = \begin{cases} 1 \text{ when points } i \text{ and } j \text{ are connected} \\ 0 \text{ otherwise} \end{cases} \tag{4}$$

each term in the summation of Eq. (3) is a self-adjoint walk of length l starting from point i and passing through points $\alpha, \beta, \ldots, \gamma$, without or with repetition, before returning to point i. The count of such walks with respect to each point gives the value of u_l. Obviously, there are only $2l$-moments for alternant hydrocarbons.

u_{2l} is in any case well expressed as the sum of acyclic and cyclic components symbolized by u'_{2l} and u''_{2l} respectively:

$$u_{2l} = u'_{2l} + u''_{2l} \tag{5}$$

walks enumerated in u'_{2l} and u''_{2l} are spanned by acyclic and cyclic fragments respectively, namely

$$u'_{2l} = \sum_{G'} C_{2l}^{G'}\{G'\} \tag{6}$$

$$u''_{2l} = \sum_{G''} C_{2l}^{G''}\{G''\} \tag{7}$$

in which $\{G'\}$ and $\{G''\}$ represent the number of acyclic and cyclic fragments, $C_{2l}^{G'}$ and $C_{2l}^{G''}$ denote the number of self-adjoint walks of length $2l$ spanned by G' and G'', respectively. The acyclic fragments $\{G'\}$ and corresponding coefficients $C_{2l}^{G'}$ in Eq. (6) have been tabulated previously [12], thus we review them partially up to u'_{12} as follows

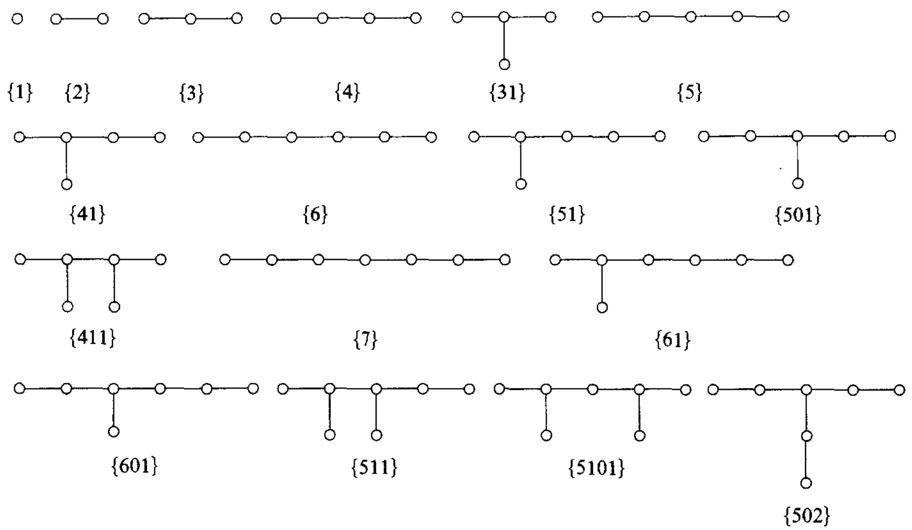
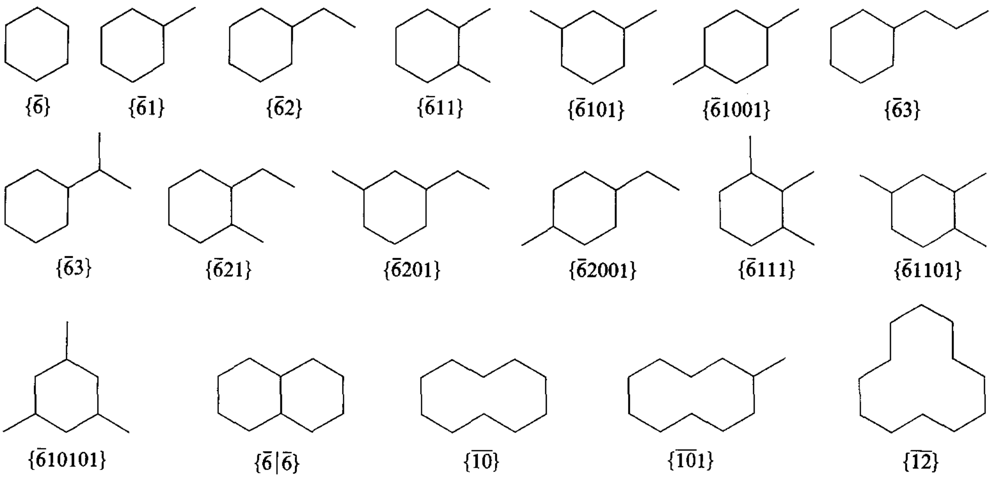


Fig. 1

$$
\begin{aligned}
u'_0 &= \{1\} \\
u'_2 &= 2\{2\} \\
u'_4 &= 2\{2\}+4\{3\} \\
u'_6 &= 2\{2\}+12\{3\}+6\{4\}+12\{31\} \\
u'_8 &= 2\{2\}+28\{3\}+32\{4\}+72\{31\}+8\{5\}+16\{41\} \\
u'_{10} &= 2\{2\}+60\{3\}+120\{4\}+300\{31\}+60\{5\}+140\{41\} \\
&\quad +10\{6\}+20\{51\}+20\{501\}+40\{411\} \\
u'_{12} &= 2\{2\}+124\{3\}+390\{4\}+1080\{31\}+300\{5\}+804\{41\} \\
&\quad +96\{6\}+216\{51\}+228\{501\}+504\{411\} \\
&\quad +12\{7\}+24\{61\}+24\{601\}+48\{511\}+48\{5101\}+24\{502\}.
\end{aligned} \tag{8}
$$

A similar procedure can be utilized for obtaining the cyclic component u''_{2l}, but in this paper only the benzenoid fragments are illustrated. The symbol $\{\bar{n}a^{\alpha}b^{\beta}c^{\gamma}\cdots\}$ is used for characterizing a cyclic member $\{G''\}$ in which an n-membered ring links with side chains $a, b, c, \ldots$ at their points $\alpha, \beta, \gamma, \ldots$ respectively. A vertical line signifies that the two rings share an edge. The lower members encountered in the benzenoid case are compiled in Fig. 2. In the following, formulas up to u''_{12} are listed.


$\{\bar{6}\}$ $\{\bar{6}1\}$ $\{\bar{6}2\}$ $\{\bar{6}11\}$ $\{\bar{6}101\}$ $\{\bar{6}1001\}$ $\{\bar{6}3\}$

$\{\bar{6}3\}$ $\{\bar{6}21\}$ $\{\bar{6}201\}$ $\{\bar{6}2001\}$ $\{\bar{6}111\}$ $\{\bar{6}1101\}$

$\{\bar{6}10101\}$ $\{\bar{6}|\bar{6}\}$ $\{\overline{10}\}$ $\{\overline{10}1\}$ $\{\overline{12}\}$

Fig. 2

$$
\begin{aligned}
u''_6 &= 12\{\bar{6}\} \\
u''_8 &= 96\{\bar{6}\}+16\{\bar{6}1\} \\
u''_{10} &= 540\{\bar{6}\}+180\{\bar{6}1\}+20\{\bar{6}2\}+20\{\bar{6}11\}+20\{\bar{6}101\} \\
&\quad +20\{\bar{6}1001\}+20\{\overline{10}\}
\end{aligned}
$$

$$\begin{aligned} u''_{12} = {} & 2724\{\bar{6}\}+1344\{\bar{6}1\}+264\{\bar{6}2\}+312\{\bar{6}11\}+288\{\bar{6}101\} \\ & +288\{\bar{6}1001\}+240\{\overline{10}\}+24\{\bar{6}3^1\}+48\{\bar{6}3^2\}+24\{\bar{6}21\} \\ & +24\{\bar{6}201\}+24\{\bar{6}2001\}+24\{\bar{6}111\}+24\{\bar{6}1101\}+24\{\bar{6}10101\} \\ & +72\{\bar{6}|\bar{6}\}+24\{\overline{10}1\}+24\{\overline{12}\}. \end{aligned} \tag{9}$$

3. Expansion of function $|x|$

The function $|x|$ means the absolute value of the variable x. Since it is an even function, in principle it can be expanded in terms of a complete set of even bases functioning under certain conditions [13-15]. Unfortunately, $|x|$ is singular at $x=0$. However, if x varies within a definite interval (not closed to zero), a truncated expansion of $|x|$ is a reasonable approximation. Thus one can write

$$|x| = \alpha_0 + \alpha_2 x^2 + \alpha_4 x^4 + \cdots + \alpha_{2L} x^{2L} = \sum_{l=0}^{L} \alpha_{2l} x^{2l}. \tag{10}$$

When $0.10 \le x \le 3.00$, which is most probable for Hückel levels of conjugated molecules, parametrization of Eq. (10) is easily carried out by means of least square computations. In this way, numerical values of α's in Eq. (10) are determined and tabulated for three cases where L is equal to 2, 4 and 6 (see Table 1).

A fundamental trend in Table 1 is that the coefficients in different rows differ somewhat in magnitude but tend to converge and change sign steadily. This implies that the regularity inherent in the expansion of $|x|$ is not changed if the tuncation scheme is varied. Such evidence is essential for the later developments.

4. Total π-electron energy

It is well known that the total π-electron energy of the ground state, E_π, for alternant hydrocarbons can be written as the sum of absolute values of x_i spanning the entire orbital set.

$$E_\pi = \sum_{i=1}^{N} |x_i|. \tag{11}$$

Table 1. Numerical values of α's in the three truncations

L	α_0	α_2	α_4	α_6	α_8	α_{10}	α_{12}
2	0.3904	0.5262	−0.0283				
4	0.2393	0.9253	−0.2105	0.02733	−0.00130		
6	0.1783	1.2955	−0.6277	0.2042	−0.03565	0.00310	−0.000105

On substituting Eq. (10) into Eq. (11) and utilizing the definition of moments expressed by Eq. (2), one can obtain an additive formula for E_π

$$E_\pi = \alpha_0 u_0 + \alpha_2 u_2 + \cdots + \alpha_{2L} u_{2L} = \sum_{l=0}^{L} \alpha_{2l} u_{2l} \tag{12}$$

where α's have been tabulated. Since the moments are the combinations of various fragments indicated by Eqs. (6)-(9), it is straightforward to transform Eq. (12) into another form in which the molecular fragments are variables

$$E_\pi = \sum_{G'} \beta_{G'}\{G'\} + \sum_{G''} \beta_{G''}\{G''\} \tag{13}$$

where $\beta_{G'}$ and $\beta_{G''}$ are

$$\beta_G = \sum_{l=0}^{L} C_{2l}^{G} \alpha_{2l} \qquad (G = G' \text{ or } G''). \tag{14}$$

Numerical values of β_G have been computed and listed in Table 2 for $L = 2$, 4 and 6, respectively.

Equation (13) exhibits the intuitive meaning of additivity, namely that the coefficient β_G signifies the contribution of fragment G. That, the absolute magnitude of β_G shown in Table 2 increases in inverse proportion to the extension of G reveals the principal role played by the smaller fragments. The regular alternation of signs for β_G satisfies the generalized Hückel rule. This rule is based on classifying all fragments into two categories, namely the $(4n+2)$- and $4n$-species specified by a count of edges in which chain edges are doubly enumerated but those in rings are singly enumerated. Whether β_G is positive or negative depends on whether such a count equals $4n+2$ or $4n$ since $4n+2$ and $4n$ demonstrate bonding effects of opposite topology. For example, the counts of fragments {4} and $\{\bar{6}\}$ are equal to 6 and their β_G's are positive, thus both of them stabilize the molecule. By way of contrast, fragments {3} and $\{\bar{6}1\}$ give counts equalling 4 and 8 respectively with the negative β_G's, thus destabilize the molecule.

For a thorough understanding of the above results, let us review the famous

Table 2. Numerical values of β_G in various truncations

$L = 2$	{1}	{2}	{3}						
	0.3904	0.9959	−0.1131						
$L = 4$	{1}	{2}	{3}	{4}	{31}	{5}	{41}	$\{\bar{6}\}$	$\{\bar{6}1\}$
	0.2393	1.4815	−0.5505	0.1225	0.2347	−0.01036	−0.02072	0.2036	−0.02072
$L = 6$	{1}	{2}	{3}	{4}	{31}	{5}	{41}	$\{\bar{6}\}$	$\{\bar{6}1\}$
	0.1783	1.6786	−0.8886	0.4156	0.7006	−0.1307	−0.2208	0.4164	−0.1535
	{6}	{51}	{501}	{411}	{7}	{61}	{601}	{511}	{5101}
	0.02092	0.03932	0.03806	0.07108	−0.00126	−0.00252	−0.00252	−0.00504	−0.00504
	{502}	$\{\bar{6}2\}$	$\{\bar{6}11\}$	$\{\bar{6}101\}$	$\{\bar{6}1001\}$	$\{\bar{6}3^1\}$	$\{\bar{6}3^2\}$	$\{\bar{6}21\}$	$\{\bar{6}201\}$
	−0.00252	0.03428	0.02924	0.03176	0.03176	−0.00252	−0.00504	−0.00252	−0.00252
	$\{\bar{6}2001\}$	$\{\bar{6}111\}$	$\{\bar{1}101\}$	$\{\bar{6}10101\}$	$\{\bar{6}\|\bar{6}\}$	$\{\overline{10}\}$	$\{\overline{10}1\}$	$\{\overline{12}\}$	
	−0.00252	−0.00252	−0.00252	−0.00252	−0.00756	0.03680	−0.00252	−0.00252	

Coulson formula [16]

$$E_\pi = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\ln|H_G(x)|}{x^2}\,dx \tag{15}$$

where $H_G(x)$ is a variant of the characteristic polynomial $P_G(x)$ in which all the coefficients are positive, i.e. if

$$P_G(x) = (\pm)(x^N - a_2x^{N-2} + a_4x^{N-4} - \cdots \pm a_N) \tag{16}$$

with $a_2, a_4, \ldots, a_N$ being positive, then

$$H_G(x) = x^1 + a_2x^2 + a_4x^4 + \cdots + a_Nx^N. \tag{17}$$

Equation (15) reveals that the relationship between E_π and molecular topology is concealed in the coefficients of $P_G(x)$. These coefficients have recently been expressed in terms of molecular fragments as follows [17, 18]

$$\begin{aligned} a_2 &= \binom{\{2\}}{1} \\ a_4 &= \binom{\{2\}}{2} - \binom{\{3\}}{1} \\ a_6 &= \binom{\{2\}}{3} - \binom{\{3\}}{1}\binom{\{2\}-2}{1} + \binom{\{4\}}{1} + 2\binom{\{31\}}{1} + 2\binom{\{\bar{6}\}}{1} \\ &\cdots \end{aligned} \tag{18}$$

where brackets represent binomial factors. One could easily find that terms involving fragment {3} are negative while others are positive. We can conclude from Eq. (15) that fragment {3} destabilizes, but fragments {2}, {4}, {31} and $\{\bar{6}\}$ stabilize molecules. The omitted formulas of a_8, a_{10}, $a_{12}, \ldots$ induce similar qualitative information for the larger fragments in agreement with Table 2.

Of course, Eq. (10) is only valid provided the $x = 0$ is not involved. The reason is that the parametrization is carried out on the basis of a truncated approximation with a nonvanishing constant α_0 inadequate for modeling the function $|x|$ at $x = 0$. In order that Eq. (10) also holds for the zero point, α_0 must be properly eliminated. Thus we propose to modify Eq. (10) as follows

$$|x| = \alpha_0 + \alpha_2x^2 + \alpha_4x^4 + \cdots + \alpha_{2L}x^{2L} - \alpha_0\,\delta_{x,0} \tag{19}$$

where $\delta_{x,0}$ signifying Kronecker's symbol. As corollaries, E_π's in Eqs. (12) and (13) are changed into

$$E_\pi = \sum_{l=0}^{L} \alpha_{2l}u_{2l} - z\alpha_0 \tag{20}$$

$$E_\pi = \sum_{G'} \beta_{G'}\{G'\} + \sum_{G''} \beta_{G''}\{G''\} - z\alpha_0 \tag{21}$$

where z represents the number of zero levels involved. These additive formulas have been utilized for calculating 187 acyclic and 52 cyclic hydrocarbons where

63% contain zero levels. The numerical values of E_π's agree well with those exactly computed. For example, when parameters of $L=2$, 4 and 6 are adopted, the coefficients of correlation are −0.9982, −0.9995 and −0.9998 respectively.

5. Aromaticity

There has been considerable research on aromaticity as defined by Dewar's criterion [1]:

$$\mathrm{REPE} = (E_\pi - E_{\mathrm{ref}})/N \tag{22}$$

where E_{ref} representing the total energy of reference molecule is hypothetically additive in terms of the acyclic fragments involved [12, 19, 20, 21]. In the present treatment, E_{ref} is obviously equal to the first term of Eq. (21), namely

$$E_{\mathrm{ref}} = \sum_{G'} \beta_{G'}\{G'\} \tag{23}$$

Therefore, the REPE is either evaluated by the difference

$$\mathrm{REPE} = \left(E_\pi - \sum_{G'} \beta_{G'}\{G'\}\right)\Big/ N \tag{24}$$

or straightforwards as follows

$$\mathrm{REPE} = \left(\sum_{G''} \beta_{G''}\{G''\} - z\alpha_0\right)\Big/ N. \tag{25}$$

Equation (25) indicates that the aromaticity of a molecule depends on the behaviour of its cyclic fragments, which is governed by the generalized Hückel rule. Zero levels are solely associated with anti-aromaticity. We can easily compute REPE's according to Eqs. (24) or (25) by utilizing Table 2 and counting the various fragments. (β_G's for fragments involving 3-, 4-, 5-, 7- and 8-membered rings have been obtained and will be published elsewhere.) In the following Fig. 3, a number of molecules are chosen and their REPE's are listed in Table 3 together with those from other sources for comparison.

From Table 3, we can see that REPE's or TRE [25, 26] from different sources show similar qualitative trends, but the result of this paper are quantitatively close to TRE for larger molecules. In other words, values calculated from Eqs. (24) or (25) are comparable to those calculated in the TRE scheme. This also implies that the characteristic polynomial of a reference molecule obtained from Eq. (23) via enumerating acyclic fragments might approach the matching polynomial introduced in the TRE scheme.

Gutman [27] and Heilbronner [28] have shown the failure of TRE scheme for some nonclassical systems. It seems that the reference entities must not contain zero levels as indicated by Eq. (23). This suggests that an extremely active species is an inadequate standard for characterizing aromaticity. For example, consider the molecules in Fig. 4 [27], it is easy to verify that the acyclic or matching polynomials of these molecules contain zero levels.

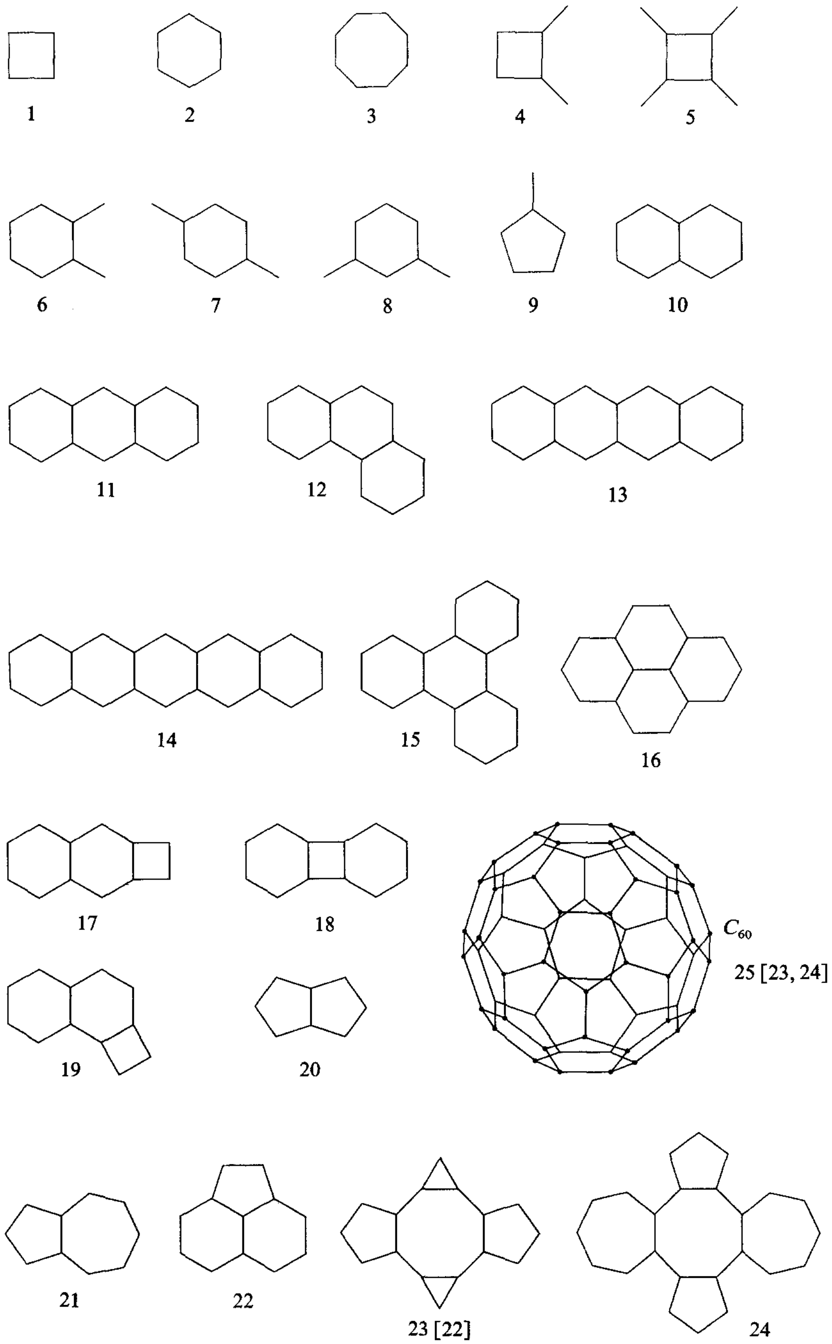

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
C_{60}
25 [23, 24]
19
20
21
22
23 [22]
24

Fig. 3

Table 3. Values of REPE (or TRE)

Mols.	This paper ($L=6$)	JTH [12]	H-S [19]	TRE [25, 26]
1	−0.385	−0.296	−0.268	−0.307
2	0.069	0.064	0.065	0.046
3	−0.068	−0.062	−0.060	−0.060
4	−0.046	−0.030	−0.038	−0.027
5	0.006	−0.011	−0.010	0.009
6	0.017	0.004	0.005	0.007
7	0.018	0.003		
8	−0.027	−0.058		
9	0.016	−0.004	−0.002	0.003
10	0.042	0.052	0.055	0.039
11	0.036	0.042	0.047	0.034
12	0.040	0.050	0.055	0.039
13	0.033	0.036	0.042	0.038
14	0.031	0.032	0.038	
15	0.044	0.051	0.056	0.041
16	0.038	0.045	0.051	0.037
17	−0.023	0.002	0.007	−0.010
18	0.012	0.023	0.027	0.010
19	−0.029	−0.017	−0.012	−0.032
20	−0.019	−0.021	−0.018	−0.027
21	0.013	0.020	0.023	0.015
22	0.033	0.034	0.039	0.030
23	0.068	0.029	0.036	
24	0.007			
25	0.032	0.020	0.021	

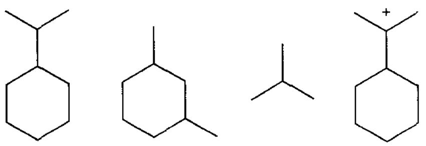


Fig. 4

6. Point-energy and site reactivity

For alternants, the equal charge density at each atom gives little information about site reactivity [2]. Therefore, free valence [2], delocalization energy [29] and other concepts have been introduced. These quantities are all defined in terms of occupied MO coefficients, so do not indicate the dependence of reactivity on the local energy and molecular topology. Indeed, equal charge densities may behave with unequal reactivity in agreement with their different average energy. In general, site reactivity will be specifically dependent on the local energy appropriately defined. Such an index named point-energy is described below.

Now, u_{2l} equals the sum of self-adjoint walks of length $2l$ (W_{2l}^{i}) starting from point i:

$$u_{2l}=\sum_{i=1}^{N} W_{2l}^{i} \tag{26}$$

In order to count W_{2l}^{i} in terms of connectivities, it is necessary to divide each fragment into sub-species according to the topology of points involved, because W_{2l}^{i} depends on the environment of point i. For this purpose, symbols α, β, $\gamma, \ldots$ are used for specifying inequivalent points of a fragment respectively as shown in Fig. 5. Similarly, edges are classified into $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}, \ldots$ species in the same sense for later usage.

As a result, for any fragment the number $\{G\}$ is equal to the sum of $\{G\}^{v}$ multiplied by the number of v, where v denotes the discriminating inequivalent points. For example, there are two subspecies for $\{3\}^{v}$, $\{4\}^{v}$ and $\{31\}^{v}$ with $v=\alpha$ and β. With this specification, W_{2l}^{i} can be written as

$$W_{2l}^{i}=\sum_{v}\sum_{G} C_{2l}^{Gv}\{G\}^{v}\,\delta_{vi} \tag{27}$$

where C_{2l}^{Gv} enumerates self-adjoint walks of length $2l$ starting from point v spanned by the fragment G. Lower members are easily carried as illustrated below:

$$\begin{aligned}
W_{2}^{i}&=\{2\}^{\alpha}\delta_{\alpha i}\\
W_{4}^{i}&=\{2\}^{\alpha}\delta_{\alpha i}+\{3\}^{\alpha}\delta_{\alpha i}+2\{3\}^{\beta}\delta_{\beta i}\\
W_{6}^{i}&=\{2\}^{\alpha}\delta_{\alpha i}+3\{3\}^{\alpha}\delta_{\alpha i}+6\{3\}^{\beta}\delta_{\beta i}+\{4\}^{\alpha}\delta_{\alpha i}+2\{4\}^{\beta}\delta_{\beta i}\\
&\quad+2\{31\}^{\alpha}\delta_{\alpha i}+6\{31\}^{\beta}\delta_{\beta i}+2\{\bar{6}\}^{\alpha}\delta_{\alpha i}\\
W_{8}^{i}&=\{2\}^{\alpha}\delta_{\alpha i}+7\{3\}^{\alpha}\delta_{\alpha i}+13\{3\}^{\beta}\delta_{\beta i}+5\{4\}^{\alpha}\delta_{\alpha i}+11\{4\}^{\beta}\delta_{\beta i}\\
&\quad+12\{31\}^{\alpha}\delta_{\alpha i}+36\{31\}^{\beta}\delta_{\beta i}+16\{\bar{6}\}^{\alpha}\delta_{\alpha i}+\{5\}^{\alpha}\delta_{\alpha i}+2\{5\}^{\beta}\delta_{\beta i}\\
&\quad+2\{5\}^{\alpha}\delta_{\alpha i}+2\{41\}^{\alpha}\delta_{\alpha i}+6\{41\}^{\beta}\delta_{\beta i}+4\{41\}^{\gamma}\delta_{\gamma i}+2\{41\}^{\zeta}\delta_{\zeta i}\\
&\quad+2\{\bar{6}1\}^{\alpha}\delta_{\alpha i}4\{\bar{6}1\}^{\beta}\delta_{\beta i}+2\{\bar{6}1\}^{\gamma}\delta_{\gamma i}+2\{\bar{6}1\}^{\zeta}\delta_{\zeta i}+2\{\bar{6}1\}^{\eta}\delta_{\eta i}\\
&\quad\ldots\ldots
\end{aligned} \tag{28}$$

By substituting the results of Eqs. (26) and (27) into Eq. (12), the total π-electron energy can be rearranged into a sum with a current index running through each

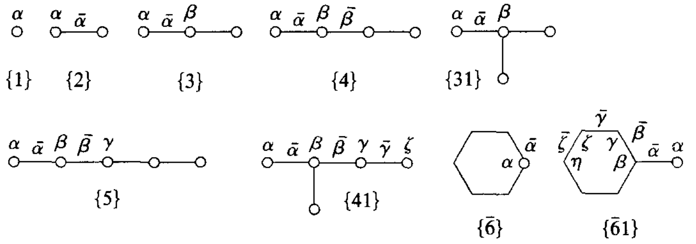


Fig. 5

point(atom) of the skeleton

$$E_\pi = \sum_{i=1}^{N} E_i \tag{29}$$

where

$$E_i = \alpha_0 + \sum_v \sum_G d_{Gv}\{G\}^v \delta_{vi}. \tag{30}$$

Therefore, E_i, being the point-energy with respect to the ith atom, can be interpreted as the average energy of the π-electron density around point(atom) i. Values of E_i at various points provide information about site reactivities towards substitution reactions, e.g. the smaller the value at the point(atom), the higher its reactivity. As indicated by Eq. (30), E_i is computed by summing the contributions of fragments connected to point i, where d_{Gv} signifies the energy for a single fragment of species $\{G\}^v$ which can be evaluated according to the following relation

$$d_{Gv} = \sum_{l=1}^{L} C_{2l}^{Gv} \alpha_{2l}. \tag{31}$$

Along with the known C_{2l}^{Gv} in Eq. (28) as well as the α_{2l} in Table 1, numerical values of d_{Gv} can be readily calculated. Some of them are given in Table 4 for $L=2$ and $L=4$

The evidence that d_{Gv} behaves similarly to β_G should be noted: it decreases when the fragment becomes larger and changes sign alternatively in accord with the generalized Hückel rule. This seems fundamental for universally applying the fragment analysis to various conjugated hydrocarbons.

For some qualitative purpose, it is instructive to omit the trivial term α_0 in E_i, because it is common to every point. Thus, the primary role is played by the

Table 4. Values of d_{Gv}

$L=2$	$\{1\}^\alpha$	$\{2\}^\alpha$	$\{3\}^\alpha$	$\{3\}^\beta$
	0.3904	0.4980	−0.02827	−0.05653
$L=4$	$\{1\}^\alpha$	$\{2\}^\alpha$	$\{3\}^\alpha$	$\{3\}^\beta$
	0.2393	0.7408	−0.1376	−0.2752
	$\{4\}^\alpha$	$\{4\}^\beta$	$\{31\}^\alpha$	$\{31\}^\beta$
	0.02085	0.01956	0.03911	0.1175
	$\{\bar{6}\}^\alpha$	$\{5\}^\alpha$	$\{5\}^\beta$	$\{5\}^\gamma$
	0.03394	−0.00130	−0.00259	−0.00259
	$\{41\}^\alpha$	$\{41\}^\beta$	$\{41\}^\gamma$	$\{41\}^\zeta$
	−0.00259	−0.00777	−0.00518	−0.00259
	$\{\bar{6}1\}^\alpha$	$\{\bar{6}1\}^\beta$	$\{\bar{6}1\}^\gamma = \{\bar{6}1]^\zeta = [\bar{6}1]^\eta$	
	−0.00259	−0.00518	−0.00259	−0.00259

fragment $\{2\}^\alpha$ multiplied by a positive coefficient $d_{2\alpha}$ which stabilizes the point(atom). This means that the site reactivity varies in inverse proportion to the valency (or degree) of the point considered, namely mono-valent atoms will be the most reactive while tri-valent ones will be the most inert. We would like to summarize this familiar evidence as follows:

Rule 1. Site reactivity decreases as the point degree increases.

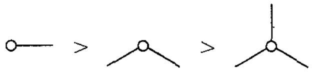


Fig. 6

When a set of points have equal valency, attention should be paid to the decisive term $d_{3\alpha}\{3\}^\alpha$ in Eq. (30), because the terms $d_{2\alpha}\{2\}^\alpha$ and $d_{3\beta}\{3\}^\beta$ both become trivial. Since $d_{3\alpha}$ is negative and $\{3\}^\alpha$ increases in proportion to the valencies of adjacent points, E_i varies in inverse proportion to the valencies of adjacent points, so we have the following rule:

Rule 2. The site reactivities of atoms with equal valency are proportional to the valencies of their adjacent atoms.

This can best be illustrated diagrammatically below

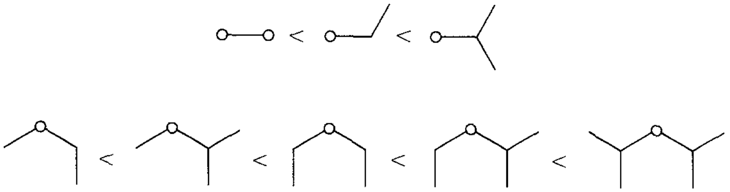


Fig. 7

For an acyclic chain, points can be divided into even or odd, with respect to the point whose site reactivity is being considered, according to whether their distances are even or odd. In general, even points reinforce, but odd points weaken the site reactivity. The following diagram shows how site reactivity of an atom (solid one) is affected by connectivities.

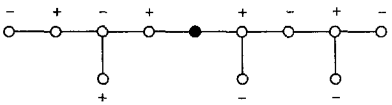


Fig. 8

The situation becomes more complicated for benzenoid systems, since the contribution of cyclic fragments is also significant. As a result, one often needs to compute E_i in detail using Eq. (30) and the parameters listed in Table 4, based on counting the various fragments.

The foregoing arguments and results are easily handled and the site reactivities for a compound can be determined by inspection or calculated with the help of Table 4. For examples, in Fig. 9, reactivity sequences are written below for each compound, provided E_i of phenanthrene has been calculated in detail by means of Eq. (30) with d_{Gv} as $L=6$ (unpublished). Dozens of benzenoid hydrocarbons

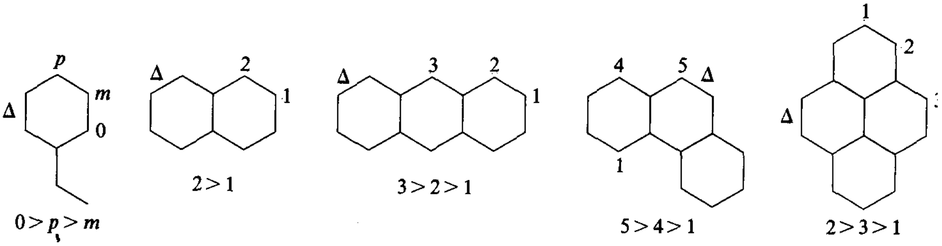


Fig. 9

which exhibit linear relationship between E_i and free valence (symbolized by F_i), have been examined

$$F_i = b + aE_i \tag{32}$$

where, $a=-0.9955$, $b=1.7195$ for $L=4$, and $a=-0.9732$, $b=1.6966$ for $L=6$. We are therefore encouraged by the fact that point energy E_i is additive in fragments, to satisfy the generalized Hückel rule, and presents a versatile intuitive picture for chemists.

7. Edge-energy and bond lengths

Owing to the fact that every walk first crosses an edge the moment u_{2l} can be alternatively viewed as the sum of self-adjoint walks of length $2l$ initiating from each edge (W_{2l}^e) in a molecule.

$$u_{2l} = \sum_e W_{2l}^e. \tag{33}$$

In reference to the classification of fragments with respect to individual edges as shown in Fig. 5, a formula analogous to Eq. (27) can readily be derived

$$W_{2l}^e = \sum_{\bar{e}} \sum_{G} C_{2l}^{G\bar{e}} \{G\}^{\bar{e}} \delta_{\bar{e}e} \tag{34}$$

where $\{G\}^{\bar{e}}$ represents the number of fragment G characterized with edge $\bar{e}$ and $C_{2l}^{G\bar{e}}$ enumerates walks of length $2l$ initiating from edge $\bar{e}$ spanned by G. Lower members of W_{2l}^e are given as follows

$$W_2^e = 2\{2\}^{\bar{\alpha}} \delta_{\bar{\alpha}e}$$

$$W_4^e = 2\{2\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 2\{3\}^{\bar{\alpha}} \delta_{\bar{\alpha}e}$$

$$W_6^e = 2\{2\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 6\{3\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 2\{4\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 2\{4\}^{\bar{\beta}} \delta_{\bar{\beta}e} + 4\{31\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 2\{\bar{6}\}^{\bar{\alpha}} \delta_{\bar{\alpha}e}$$

$$W_8^e = 2\{2\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 14\{3\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 11\{4\}^{\bar{\alpha}} \delta_{\bar{\alpha}e} + 10\{4\}^{\bar{\beta}} \delta_{\bar{\beta}e}$$

Table 5. Numerical values of $S_{G\bar{e}}$

$L=2$	$\{2\}^{\bar{\alpha}}$	$\{3\}^{\bar{\alpha}}$			
	0.9955	−0.05653			
$L=4$	$\{2\}^{\bar{\alpha}}$	$\{3\}^{\bar{\alpha}}$	$\{4\}^{\bar{\alpha}}$	$\{4\}^{\bar{\beta}}$	$\{31\}^{\bar{\alpha}}$
	1.4815	−0.2752	0.04041	0.04171	0.07823
	$\{\bar{6}\}^{\bar{\alpha}}$	$\{5\}^{\bar{\alpha}}$	$\{5\}^{\bar{\beta}}$	$\{41\}^{\bar{\alpha}}$	$\{41\}^{\bar{\beta}}$
	0.3394	−0.00259	−0.00259	−0.00518	−0.00518
	$\{41\}^{\bar{\gamma}}$	$\{\bar{6}1\}^{\bar{\alpha}}$	$\{\bar{6}1\}^{\bar{\beta}}$	$\{\bar{6}1\}^{\bar{\gamma}}$	$\{\bar{6}1\}^{\bar{\zeta}}$
	−0.00518	−0.00518	−0.00259	−0.00259	−0.00259

$$
\begin{aligned}
&+24\{31\}^{\bar{\alpha}}\delta_{\bar{\alpha}e}+16\{\bar{6}\}^{\bar{\alpha}}\delta_{\bar{\alpha}e}+2\{5\}^{\bar{\alpha}}\delta_{\bar{\alpha}e}+2\{5\}^{\bar{\beta}}\delta_{\bar{\beta}e}\\
&+4\{41\}^{\bar{\alpha}}\delta_{\bar{\alpha}e}+4\{41\}^{\bar{\beta}}\delta_{\bar{\beta}e}+4\{41\}^{\bar{\alpha}}\delta_{\bar{\alpha}e}+4\{\bar{6}1\}^{\bar{\alpha}}\delta_{\bar{\alpha}e}\\
&+2\{\bar{6}1\}^{\bar{\beta}}\delta_{\bar{\beta}e}+2\{\bar{6}1\}^{\bar{\gamma}}\delta_{\bar{\gamma}e}+2\{\bar{6}1\}^{\bar{\zeta}}\delta_{\bar{\zeta}e}\\
&\ldots\ldots \qquad (35)
\end{aligned}
$$

As a consequence, the total π-electron energy is partitioned into the sum of edge-energies E_e with respect to each edge

$$E_\pi = N\alpha_0+\sum_e E_e \tag{36}$$

where

$$E_e=\sum_{\bar{e}}\sum_f S_{G\bar{e}}\{f\}^{\bar{e}}\delta_{\bar{e}e} \tag{37}$$

and the coefficient $S_{G\bar{e}}$ means the energy contributed from a single fragment of species $\{G\}^{\bar{e}}$ and satisfies

$$S_{G\bar{e}}=\sum_{l=1}^{L} C_{2l}^{f\bar{e}}\alpha_{2l}. \tag{38}$$

Numerical values of $S_{G\bar{e}}$ for $L=2$ and 4 are tabulated in Table 5. They display a qualitative trend quite similar to those of d_{Gv}.

Values of E_e provide information about bond lengths, as well as about reactivities toward 1,2-addition reactions. Either the bond lengths or the addition reactivity for an arbitrary conjugated bond will be inversely proportional to the value of E_e. By comparison with the discussion of point-energies similar qualitative conclusions about how the bond lengths depend on edge degrees[1] can be obtained.

Rule 3. The bond length of an edge varies in proportion to its degree, namely

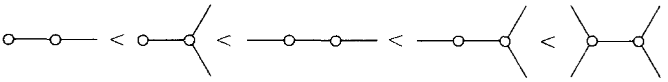


Fig. 10

---

[1] The degree of an edge is specified by the sum of degrees of its connected points

Rule 4. For edges with identical degree, bond lengths vary in inverse proportion to degrees of their adjacent points,

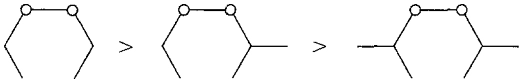


Fig. 11

By these rules, the shortest edges in benzenoid hydrocarbons can readily be designated. Examples are given in Fig. 9 marked with Δ. These edges are those at which 1,2-addition reactions take place [30].

8. Local aromaticity

The reactivity towards addition and other reactions in a polycyclic hydrocarbon of a given hexagon is often related to local aromaticity. As a result of Clar's postulate of the "aromatic sextet" [31], several empirical investigations have been published which can afford fairly reliable predictions of the behaviour of an individual ring in a molecule [32-35]. According to Eq. (25), the REPE is usually the value of the cyclic component of total energy per electron. Thus the resonance energy, RE, can be written as

$$\mathrm{RE}=\sum_{G''} \beta_{G''}\{G''\} \tag{39}$$

where $\{G''\}$ represents the count of the cyclic fragment G'' and the numerical value of $\beta_{G''}$ has been tabulated in Table 2. Obviously,

$$\{G''\}=\sum_{r}\{G''\}_r \tag{40}$$

where r runs through all rings, and $\{G''\}_r$ signifies the count of fragment G'' involving the rth ring. Substituting Eq. (40) into Eq. (39), the following additive formula can be deduced

$$\mathrm{RE}=\sum_{r}(\mathrm{RE})_r \tag{41}$$

with

$$(\mathrm{RE})_r=\sum_{G''} \beta_{G''}\{G''\}_r \tag{42}$$

where $(\mathrm{RE})_r$ represents resonance energy of the rth ring.

In the treatment of benzenoid hydrocarbons, only hexagons are emphasized. As a result, it is reasonable to distribute an average of the $(\mathrm{RE})_r$'s of larger rings to each hexagon involved. In this way, the resonance energy for a particular hexagon is redefined as

$$(\mathrm{RE})_h=\sum_{r}(\mathrm{RE})_r/n_r \tag{43}$$

in which h is used instead of r on the left side to signify the hexagon, r on the right-hand side runs through all rings involving the hexagon considered. and the denominator n_r represents the number of hexagons that the rth ring accommodates.

According to Eqs. (42) and (43), it is easy to calculate the value of $(\mathrm{RE})_h$ for an arbitrary hexagon in a molecule by means of counting fragments $\{G''\}_r$ and utilizing Table 2. Dozens of benzenoid hydrocarbons have been investigated and several typical results are listed below.

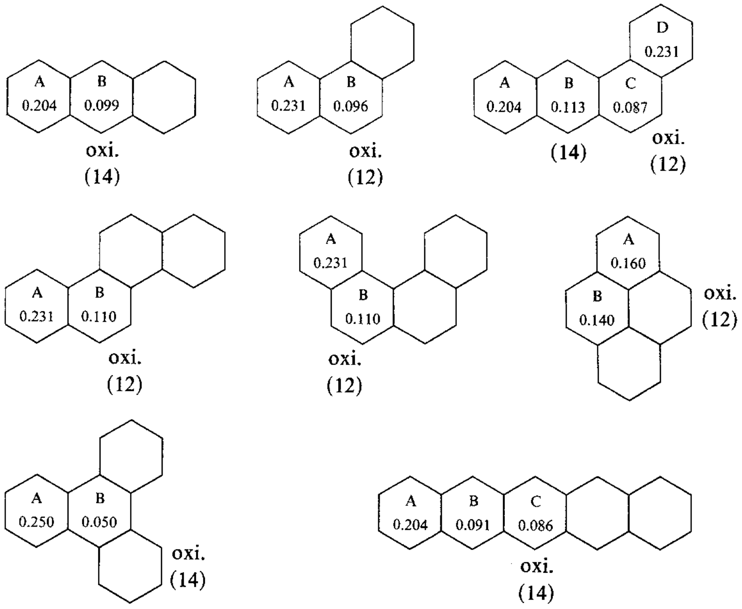
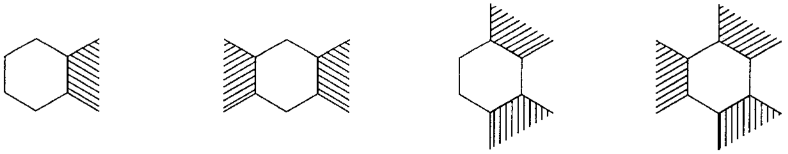


Fig. 12

Where the calculated $(\mathrm{RE})_h$'s are recorded for each hexagon. Symbols (12), (14) and oxi. on the side of some rings mean that 1,2-, 1,4-addition reactions and oxidations, respectively, are known to take place there experimentally. These illustrate the predictive power of $(\mathrm{RE})_h$ as defined above, namely: the smaller the value of $(\mathrm{RE})_h$, the easier it is for additional reactions and oxidations to occur on ring h. One exception is that the inner ring B in triphenylene has lower $(\mathrm{RE})_h$ than the three outer ones. Obviously, the inertness of the inner ring originates from the saturation of its connectivities, which means that a reaction taking place on the ring might simultaneously destroy its adjacent rings.

A general trend for hexagon aromaticity can be seen from values of $(\mathrm{RE})_h$ as tabulated above. Upon classifying them into four categories below [33] one can make the following summary:



primary (P) linear (L) kink (K) tertiary (T)

Fig. 13

Table 6. $\{G''\}_r$ for various hexagons in catahexes

$\{G''\}$	$\{G''\}_r$			
	P	L	K	T
$\{\bar{6}1\}$	2	4	4	6
$\{\bar{6}11\}$	1	2	3	6
$\{\bar{6}101\}$	0	2	2	6
$\{\bar{6}1001\}$	0	2	1	3

$$P > L > K > T$$

This will generally be true as can be seen from a comparison of $\{G''\}_r$ in Eq. (42) with their contributions governed by generalized Hückel rule. (See Table 6.)

By comparing $\{\bar{6}1\}$, we have

$$P > L, \qquad K > uT$$

since $\beta_{\bar{6}1} < 0$. Furthermore, owing to

$$(\mathrm{RE})_k - (\mathrm{RE})_L = \beta_{\bar{6}11} - \beta_{\bar{6}1001} < 0 \qquad \text{(see Table 2)}$$

we obtain

$$(\mathrm{RE})_P > (\mathrm{RE})_L > (\mathrm{RE})_K > (\mathrm{RE})_T.$$

This trend was also discussed by Hosoya who used the Pariser–Parr–Pople approach [33].

References

1. See, for example, Dewar MJS (1969) The molecular orbital theory of organic chemistry. McGraw-Hill, New York
2. Coulson CA (1946) Proc Roy Soc (London) A169; 413 (1939); Trans Faraday Soc 42:256 (1946)
3. Foster JM, Boys SF (1960) Rev Mod Phys 32:300
4. Edmiston G, Ruedenberg K (1963) Rev Mod Phys 35:457; (1965) J Chem Phys 43:S97
5. Haydock R, Meine V, Kelly MJ (1972) J Phys C: Solid State Phys 5:2845; (1975) 8:2591
6. Burdett JK, Lee S, Sha WC (1984) Croat Chem Acta 57:1193
7. Burdett JK, Lee S (1985) J Am Chem Soc 107:3050, 3063
8. Burdett JK, Lee S, McLarnan TJ (1985) J Am Chem Soc 107:3083
9. Wall HS (1948) Analytic theory of continued fractions. Van Nostrand, New York
10. Whitehead RR, Watt A (1978) J Phys G Nucl Phys 4:835
11. Hall GG (1986) Theor Chim Acta 70:323 and the references therein
12. Jiang Y, Tang A, Hoffmann R (1984) Theor Chim Acta 66:183
13. Gutman I, Trinajstic N (1972) Chem Phys Lett 17:535; (1973) 20:257
14. Tang AC, Kiang YS, Yan GS, Dai SS (1986) Graph theoretical molecular orbitals. Science Press, Beijing
15. Coislowski J (1985) Chem Phys Lett 112:243
16. Coulson CA (1940) Proc Cambridge Phil 36:201
17. Kiang YS, Tang AC (1986) Int J Quantum Chem 22:229
18. Jiang Y, Zhang H: to be submitted to Theor Chim Acta
19. Hess Jr BA, Schaad LT (1971) J Am Chem Soc 93:305

20. Cao W, Jiang Y (1982) Acta Chim Sin 40:880
21. Schmalz TG, Zivkovic T, Klein DJ: to be published in Proceedings of Math/Chem/Comp 87, Yugoslavia, Elsevier
22. Yoneda S, Shibata M, Kida S, Yoshida Z, Kai Y, Miki K, Kasai N (1984) Angew Chem Int Ed Engl 23:63
23. Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE (1985) Nature 318:162
24. Klein DJ, Schmalz TG, Seitz WA, Hite GE (1986) J Am Chem Soc 108:1301; and the references therein
25. Gutman I, Trinajstic N, Millan M (1977) J Am Chem Soc 99:1962
26. Gutman I, Petrovic S, Mohar B (1982) In: "ZBORNIK RADOVA, Prirodno-Matematickog Fakulteta 3", Kragujevac: Univerzitet "Svetozar Markovic" U Kragujevcu, 1982; and the references therein
27. Gutman I (1980) Theor Chim Acta 56:89
28. Heilbronner E (1982) Chem Phys Lett 85:377
29. Fukui K, Yonezawa T, Nagata C (1957) J Chem Phys 27:1274
30. Clar E (1964) Polycyclic hydrocarbons. Academic Press, New York
31. Clar E (1972) The aromatic sextet. Wiley, London
32. Polansky OE, Derflinger G (1967) Int J Quantum Chem 1:379
33. Aida M, Hosoya H (1980) Tetrahedron 36:1317
34. Randic M (1980) Pure Appl Chem 52:1587
35. Sakurai K, Kitaura K, Nishimoto K (1986) Theor Chim Acta 69:23