

Numerical Determination of the Kekulé Structure Count of Some Symmetrical Polycyclic Aromatic Hydrocarbons and Their Relationship with π -Electronic Energy (A Computational Approach)

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The perfect matching (Kekulé structure count) of certain polycyclic aromatic hydrocarbons (benzenoids, i.e., PAH6) having mirror plane symmetry is obtained through a computer program. A computer operation in the form of an initial approximation (P , Q) is selected such that it extracts the quadratic factors (QFs) like $(X^2 - A_iX + B_i)$ and linear factors (LFs) like $(X - a_i)$ from the characteristic polynomials (CPs) of the different components obtained from the mirror plane fragmentation technique following an energy scale. The most minimum energy factor is extracted first, and then the next higher factor is extracted. This process of gradual extraction of the energy factor concludes after the HOMO level of the fragment is extracted. These factors contain the positive Hückel eigenvalues which are responsible for the Kekulé structure count and the π -electron energy (E_π) of the benzenoid molecules. A_i , B_i , and a_i are used to correlate $(E_\pi)_i$ and K_i of the fragments. A linear relationship between the total π -electronic energy of benzenoid hydrocarbons on the Kekulé structure count is established: $E_\pi(\text{total}) = 2[\sum_{i=1}^n (X_r)_i + \sum_{i=1}^n [1/(X_r)_i]K_i + \sum_{j=1}^n K_j]$, where K_i and K_j are the parts of the total K obtained through the quadratic and linear operations, respectively, and X_r are the positive Hückel eigenvalues extracted by the quadratic operations. Further, n refers to all of the extracted factors, and r may be 1 or 2, depicting the first or the second eigenvalue extracted by the QF.

A survey of the chemical literature reveals that many elegant procedures have been presented for the determination of the perfect matching or one-factor (Kekulé structure) count of the benzenoid and non-benzenoid hydrocarbons. This interest continues to be unabated because the structure count (Kekulé structure count, K , and algebraic structure count, ASC) information is always in qualitative agreement with experimental manifestations of stability and reactivity. Excellent reviews and books are available in chemical literature to study the enumeration problem.^{1–10} Further, Gutman and Cyvin¹¹ have pointed out that the number of Kekulé structures for the benzenoid hydrocarbons is related to the total π -electron energy, heats of formation, interatomic distances, ionization potentials, UV/visible absorption band frequencies, zero field splitting parameters, NMR ortho coupling constants, vibrational force constant, rate constants, resonance energy and aromaticity, etc. In chemical graph theory (CGT) different polynomials are used for the enumeration of the Kekulé structure count for the benzenoid molecules.¹ The most important polynomial used in CGT is the characteristic polynomial (CP).¹² It is well-known that the number of Kekulé structures (K) of the benzenoid hydrocarbons is equal to the product of the positive (non-negative) Hückel eigenvalues¹ or the last coefficient of the product of the linear factors like $(X - p_1)$, $(X - p_2)$, $(X - p_3)$..., where p_1 , p_2 , p_3 , ... are the positive Hückel eigenvalues. Further, the absolute value of the last coefficient of the CP of a benzenoid graph gives the square of the Kekulé structure count.¹ Gutman and Trinajstić¹³ and Randić¹⁴ independently have established the relationship

between the Kekulé structures of the parent conjugated molecule and of its constituent fragments. This procedure consists of three different steps. With application of the above procedure, the initial molecule has been decomposed into smaller parts and the process continues until one arrives at parts with the known number of Kekulé structures. Hence, following the above process, one gets

$$K(\text{parent conjugated molecule}) = \sum_i K_i(\text{constituting fragments})$$

Here, we shall not broach the different methods used for the determination of the K and ASC, but a less subtle computational method using a FORTRAN-77 program is proposed. A possible linear relationship between the π -electron energy of benzenoid hydrocarbons and Kekulé structures is proposed on the basis of the computer program. A computational operation (extraction technique) is applied to the CPs of the molecular graphs, and the factors responsible for the K are determined. Earlier we designed a computer program^{15–17} based on the Birge–Vieta–Bairstow method, where linear and quadratic factors (LFs and QFs) are extracted selectively from one n th order polynomial following one iteration technique.

Two long-known properties (taking eigenvalues) of the benzenoid graphs are well-cited in the chemical literature.^{2,18}

$$K = \prod_{i=1}^{n/2} X_i \quad \text{and} \quad E_\pi = 2 \sum_{i=1}^{n/2} X_i \quad (1)$$

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where X_i are the nonnegative eigenvalues. In particular, $K = 0$ if and only if the molecular graph possesses a zero eigenvalue.

OUTLINE OF THE METHOD

Large benzenoid graphs possessing a C_{2v} or D_{2h} symmetry are fragmented by applying the fragmentation technique given by McClelland.¹⁹ The CPs of the different fragments are considered. It is well-known that the multiplication of the CPs of all the fragments equals the CP of the parent conjugated molecule.¹⁹⁻²² The CP of a molecular fragment (A) is written as

$$CP(A) = X^n + a_1X^{n-1} + \dots + a_{n-1}X + a_n = 0 \quad (2)$$

where a_1, a_2, \dots, a_n are the real coefficients and may be associated with a positive or a negative sign. A quadratic factor of the type $(X^2 - AX + B)$ or $(X - a_1)(X - a_2)$ is to be extracted from (2). If polynomial 2 is divided by $(X^2 + PX + Q)$, then one obtains a quotient polynomial having degree $(n - 2)$ and a remainder $(RX + S)$. On the other hand, if polynomial 2 is divided by $(X + p_1)$, then a quotient polynomial of degree $(n - 1)$ is obtained with a remainder R . Now, the problem is to solve the following equations with some iterative principle:

$$R(p_1) = 0 \quad \text{or} \quad R(p_2) = 0 \quad (\text{linear case}) \quad (3)$$

$$R(P, Q) = 0, \quad S(P, Q) = 0 \quad (\text{quadratic case}) \quad (4)$$

By this method a deflated polynomial (DP) and a quadratic factor like $(X^2 - AX + B)$ or a linear factor like $(X - a_1)$ is obtained. To get the extracted factors correctly, one must be very sure of the proper convergence of the factor and the coefficients of the DP. Then in following the method a set of (P, Q) values are selected and are given as the initial approximations to run the program (a FORTRAN-77 program has been given in one of our earlier papers).¹⁵ All of the CPs of the different fragments of a PAH6 are subjected to the computational operation. Making use of the program QFs $(X^2 - A_iX + B_i)$ and LFs $(X - a_i)$ are extracted from the CPs of the different fragments. It may be mentioned that these QFs and LFs contain the Hückel positive eigenvalues which are responsible for the K and E_π of the molecule under consideration.^{2,18} Now, while extracting a QF, if another type of QF (which contains a negative eigenvalue) like $(X^2 + AX - B)$ or $(X^2 - AX - B)$ or $(X^2 - B^2)$ is obtained, then one has to go for one LF extraction in order to check the occurrence of the unwanted eigenvalue. Here, for the LF extraction the needed initial approximation (p_1 or p_2) is generated inside the program as $(p_1 + p_2) = P$ and $p_1p_2 = Q$. Through this extraction one must get a $(X - a_i)$ type of factor; otherwise, the (P, Q) values so chosen are to be ignored, and a fresh set of (P, Q) values are to be selected. It has been pointed out earlier that a set of (P, Q) values (initial approximations) extracts a QF and $(p_1$ or $p_2)$ extracts a LF through the iteration technique. The use of the initial approximations has been described in our earlier works.¹⁵⁻¹⁷

SELECTION OF (P, Q) VALUES

(i) Here, the (P, Q) values are selected such that they extract QFs possessing two positive eigenvalues and LFs possessing one positive eigenvalue.

(ii) Further, the (P, Q) values are chosen so that the extraction of the factors follows an energy scale; i.e., the lowest two energy levels (ground state and its next higher state) are extracted first. After the extraction of the first QF, the resultant deflated polynomial (DP) is subjected to the same (P, Q) operation, and it extracts the next two occupied energy levels. The selected (P, Q) operation goes on extracting factors until the highest occupied MO level is extracted. In a comparison of the A values obtained in different QFs, the energy scale can be noticed. If QFs and LFs are extracted in a molecular fragment, then a_i values are compared (a QF can be written as the product of two LFs).

EXAMPLE

We consider "Ovalene" (structure 21 of Table 1), a representative (PAH6) molecule which has 32 carbon atoms. Applying the fragmentation technique, we have obtained four fragments (A-D). A and B fragments contain nine carbon atoms, and C and D contain seven carbon atoms. Hence, two 9th order polynomials and two 7th order polynomials are obtained. Now with consideration of a set of $(P = -5.0, Q = 6.0)$ values, all of the above four polynomials are subjected to our computational technique (Scheme 1).

By applying our method, we are in a position to get two $(X^2 - AX + B)$ types of factors from the CP of A with $P = -5.0$ and $Q = 6.0$. From the CP of the B fragment we have obtained two QFs and one LF of the type $(X^2 - AX + B)$ and $(X - a)$ with the same (P, Q) values. When the third fragment (C) is subjected to the same kind of treatment, we obtained two $(X^2 - AX + B)$ types of factors, and finally, from the last fragment (D), we obtained one QF and one LF. After extraction of all of the factors, the total K ($K = K_A K_B K_C K_D$) is calculated, and for this molecule $K = 50$. Hence, we say that these (P, Q) values can give the factors responsible for the Kekulé structure count of the molecule under investigation.

RESULTS

Here, we have selected 27 PAH6 which have mirror plane symmetry. With application of the McClelland fragmentation technique, the large PAH6 molecules are divided into several fragments. It is well-known that Kekuléan molecules have $K > 0$.¹ Further, most of the fragmented parts of a PAH6 are weighted linear polyenes, and $K_i \neq 1$. These K_i are the parts of the original K of the PAH6 molecule under consideration. Our target is to find out factors responsible for the Kekulé structure count of the large benzenoid system. After the fragmentation, the CP of each component is subjected to our computational operation.

In order to verify that $P = -5.0$ and $Q = 6.0$ approximations can give the factors responsible for the determination of the Kekulé structures for all the molecules, we have carried out the computational operation to all the fragments of the different molecules under consideration. Tables 1 and 2 give the different components of the molecule, CPs, and their order of occurrence of the desired factors with the selected $P = -5.0$ and $Q = 6.0$ values, K_i and $(E_\pi)_i$ values of the different components, and finally the total K of the benzenoid molecule.

Table 1. PAH6 Molecules with Their Different Mirror Plane Fragments and Their Corresponding Characteristic Polynomials (CPs)^a






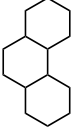








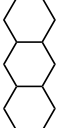





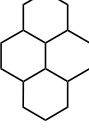




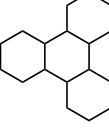
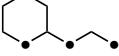
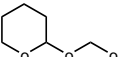








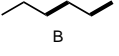


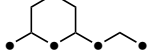
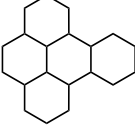
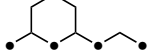
molecule	molecule	fragment	CP
1		 A  B  C  D	$X^3 + 2X^2 - 2X - 3$ $X^3 - 2X^2 - 2X + 3$ $X^2 + X - 1$ $X^2 - X - 1$
2		 A  B  C  D  E  F  G  H	$X^7 + 2X^6 - 6X^5 - 11X^4 + 9X^3 + 15X^2 - 4X - 5$ $X^7 - 2X^6 - 6X^5 + 11X^4 + 9X^3 - 15X^2 - 4X + 5$ $X^4 + 2X^3 - 3X^2 - 4X + 2$ $X^4 - 2X^3 - 3X^2 + 4X + 2$ $X^2 + X - 2$ $X^2 - X - 2$ $X^2 - 1$
3		 A  B  C  D  E	$X^5 + 2X^4 - 5X^3 - 9X^2 + 3X + 6$ $X^5 - 2X^4 - 5X^3 + 9X^2 + 3X - 6$ $X^3 + X^2 - 2X - 1$ $X^3 - X^2 - 2X + 1$
4		 A  B  C  D	$X^9 + 3X^8 - 6X^7 - 21X^6 + 9X^5 + 45X^4 - 3X^3 - 36X^2 + 9$ $X^9 - 3X^8 - 6X^7 + 21X^6 + 9X^5 - 45X^4 - 3X^3 + 36X^2 - 9$
5		 A  B  C  D  E  F  G  H	$X^5 + 3X^4 - 2X^3 - 9X^2 + 5$ $X^5 - 3X^4 - 2X^3 + 9X^2 - 5$ $X^4 + 2X^3 - 2X^2 - 3X + 1$ $X^4 - 2X^3 - 2X^2 + 3X + 1$
6		 A  B  C	$X^{10} - 13X^8 + 57X^6 - 105X^4 + 78X^2 - 16$ $X^6 - 7X^4 + 12X^2 - 4$ $X^2 - 1$
7		 A	$X^{10} + 4X^9 - 4X^8 - 30X^7 - 8X^6 + 70X^5 + 41X^4 - 62X^3 - 41X^2 + 18X + 11$
8		 A	

Table 1 (Continued)

molecule	molecule	fragment	CP
9			$X^{10} - 4X^9 - 4X^8 + 30X^7 - 8X^6 - 70X^5 + 41X^4 + 62X^3 - 41X^2 - 18X + 11$
			$X^6 + X^5 - 8X^4 - 5X^3 + 16X^2 + 4X - 9$
			$X^6 - X^5 - 8X^4 + 5X^3 + 16X^2 - 4X - 9$
			$X^4 + X^3 - 3X^2 - 2X + 1$
			$X^4 - X^3 - 3X^2 + 2X + 1$
10			$X^{11} + 2X^{10} - 11X^9 - 21X^8 + 41X^7 + 74X^6 - 66X^5 - 110X^4 + 46X^3 + 67X^2 - 12X - 13$
11			$X^{11} - 2X^{10} - 11X^9 + 21X^8 + 41X^7 - 74X^6 - 66X^5 + 110X^4 + 46X^3 - 67X^2 - 12X + 13$
			$X^{11} + 3X^{10} - 9X^9 - 30X^8 + 24X^7 + 101X^6 - 18X^5 - 142X^4 - 6X^3 + 82X^2 + 8X - 14$
12			$X^{11} - 3X^{10} - 9X^9 + 30X^8 + 24X^7 - 101X^6 - 18X^5 + 142X^4 - 6X^3 - 82X^2 + 8X + 14$
			$X^6 + 3X^5 - 3X^4 - 11X^3 + 3X^2 + 9X - 2$
			$X^6 - 3X^5 - 3X^4 + 11X^3 + 3X^2 - 9X - 2$
			$X^3 + 2X^2 - 2X - 3$
			$X^3 - 2X^2 - 2X + 3$
			$X^2 + X - 1$
13			$X^2 - X - 1$
			$X^7 + 2X^6 - 8X^5 - 14X^4 - 17X^3 + 24X^2 - 12X - 10$
			$X^7 - 2X^6 - 8X^5 + 14X^4 + 17X^3 - 24X^2 - 12X + 10$
			$X^4 + X^3 - 4X^2 - 2X + 2$
			$X^4 - X^3 - 4X^2 + 2X + 2$
			$X + 1$
14			$X - 1$
			$X^7 + 3X^6 - 5X^5 - 18X^4 + 3X^3 + 26X^2 + 2X - 10$
14			$X^7 - 3X^6 - 5X^5 + 18X^4 + 3X^3 - 26X^2 + 2X + 10$

Table 1 (Continued)

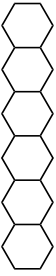


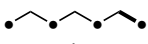
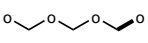


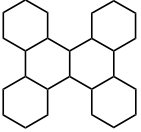






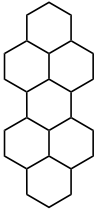




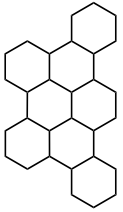
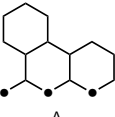
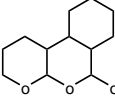
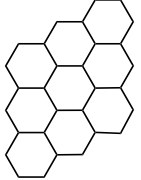
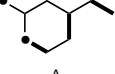
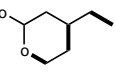

molecule	molecule	fragment	CP
15		 C	$X^5 + 2X^4 - 3X^3 - 5X^2 + 2X + 2$
		 D	$X^5 - 2X^4 - 3X^3 + 5X^2 + 2X - 2$
		 A	$X^7 + 4X^6 - X^5 - 17X^4 - 6X^3 + 21X^2 + 7X - 7$
		 B	$X^7 - 4X^6 - X^5 + 17X^4 - 6X^3 - 21X^2 + 7X + 7$
		 C	$X^6 + 3X^5 - 2X^4 - 9X^3 + X^2 + 6X - 1$
		 D	$X^6 - 3X^5 - 2X^4 + 9X^3 + X^2 - 6X - 1$
16		 A	$X^7 + 2X^6 - 7X^5 - 12X^4 + 13X^3 + 18X^2 - 7X - 6$
		 B	$X^7 - 2X^6 - 7X^5 + 12X^4 + 13X^3 - 18X^2 - 7X + 6$
		 C	$X^4 + X^3 - 5X^2 - 3X + 4$
		 F	$X^4 - X^3 - 5X^2 + 3X + 4$
		 D	$X^2 - 1$
		 E	$X^2 - 1$
17		 A	$X^8 + X^7 - 11X^6 - 8X^5 + 37X^4 + 16X^3 - 45X^2 - 9X + 18$
		 B	$X^5 + X^4 - 4X^3 - 3X^2 + 3X + 1$
		 C	$X^8 - X^7 - 11X^6 + 8X^5 + 37X^4 - 16X^3 - 45X^2 + 9X + 18$
		 D	$X^5 - X^4 - 4X^3 + 3X^2 + 3X - 1$
18		 A	$X^{15} + 3X^{14} - 14X^{13} - 45X^{12} + 71X^{11} + 257X^{10} - 162X^9 - 723X^8 + 159X^7 + 1079X^6 - 30X^5 - 849X^4 - 41X^3 + 323X^2 + 16X - 45$
		 B	$X^{15} - 3X^{14} - 14X^{13} + 45X^{12} + 71X^{11} - 257X^{10} - 162X^9 + 723X^8 + 159X^7 - 1079X^6 - 30X^5 + 849X^4 - 41X^3 - 323X^2 + 16X + 45$
19		 A	$X^9 + 2X^8 - 11X^7 - 20X^6 + 38X^5 + 60X^4 - 51X^3 - 64X^2 + 23X + 20$
		 B	$X^9 - 2X^8 - 11X^7 + 20X^6 + 38X^5 - 60X^4 - 51X^3 + 64X^2 + 23X - 20$
		 C	$X^5 + X^4 - 5X^3 - 3X^2 + 5X + 1$

Table 1 (Continued)




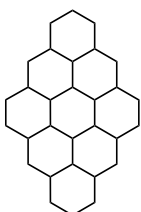


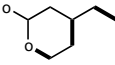

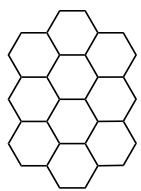




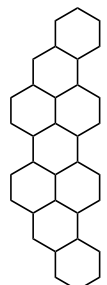
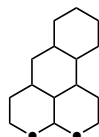
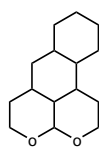
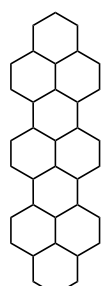
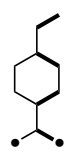

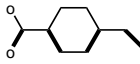

molecule	molecule	fragment	CP
			$X^5 - X^4 - 5X^3 + 3X^2 + 5X - 1$
		D	
			$X + 1$
		E	
			$X - 1$
		F	
20			$X^9 + 2X^8 - 11X^7 - 20X^6 + 38X^5 + 60X^4 - 51X^3 - 64X^2 + 23X + 20$
		A	
			$X^6 + 2X^5 - 4X^4 - 8X^3 + 2X^2 + 6X + 1$
		B	
			$X^9 - 2X^8 - 11X^7 + 20X^6 + 38X^5 - 60X^4 - 51X^3 + 64X^2 + 23X - 20$
		C	
			$X^6 - 2X^5 - 4X^4 + 8X^3 + 2X^2 - 6X + 1$
		D	
21			$X^9 + 3X^8 - 8X^7 - 27X^6 + 14X^5 + 70X^4 + 3X^3 - 59X^2 - 13X + 10$
		A	
			$X^9 - 3X^8 - 8X^7 + 27X^6 + 14X^5 - 70X^4 + 3X^3 + 59X^2 - 13X - 10$
		B	
			$X^7 - 2X^6 - 6X^5 + 11X^4 + 9X^3 - 15X^2 - 4X + 5$
		C	
			$X^7 + 2X^6 - 6X^5 - 11X^4 + 9X^3 + 15X^2 - 4X - 5$
		D	
22			$X^{17} + 2X^{16} - 19X^{15} - 36X^{14} + 145X^{13} + 256X^{12} - 583X^{11} - 936X^{10} + 1358X^9 + 1914X^8 - 1889X^7 - 2223X^6 + 1542X^5 + 1408X^4 - 679X^3 - 426X^2 + 124X + 41$
		A	
			$X^{17} - 2X^{16} - 19X^{15} + 36X^{14} + 145X^{13} - 256X^{12} - 583X^{11} + 936X^{10} + 1358X^9 - 1914X^8 - 1889X^7 + 2223X^6 + 1542X^5 - 1408X^4 - 679X^3 + 426X^2 + 124X - 41$
		B	
23			$X^{11} + 2X^{10} - 14X^9 - 27X^8 + 66X^7 + 123X^6 - 127X^5 - 233X^4 + 101X^3 + 189X^2 - 27X - 54$
		A	
			$X^7 + X^6 - 6X^5 - 5X^4 + 10X^3 + 6X^2 - 4X - 1$
		B	
			$X^{11} - 2X^{10} - 14X^9 + 27X^8 + 66X^7 - 123X^6 - 127X^5 + 233X^4 + 101X^3 - 189X^2 - 27X + 54$
		C	
			$X^7 - X^6 - 6X^5 + 5X^4 + 10X^3 - 6X^2 - 4X + 1$
		D	

Table 1 Continued

molecule	molecule	fragment	CP
24			$X^{11} + 2X^{10} - 14X^9 - 26X^8 + 68X^7 + 114X^6 - 146X^5 - 210X^4 + 141X^3 + 156X^2 - 52X - 34$
			$X^8 + X^7 - 8X^6 - 6X^5 + 19X^4 + 9X^3 - 16X^2 - 4X + 4$
			$X^{11} - 2X^{10} - 14X^9 + 26X^8 + 68X^7 - 114X^6 - 146X^5 + 210X^4 + 141X^3 - 156X^2 - 52X + 34$
			$X^8 - X^7 - 8X^6 + 6X^5 + 19X^4 - 9X^3 - 16X^2 + 4X + 4$
25			$X^{11} + 3X^{10} - 11X^9 - 35X^8 + 39X^7 + 139X^6 - 53X^5 - 233X^4 + 25X^3 + 163X^2 - X - 35$
			$X^{11} - 3X^{10} - 11X^9 + 35X^8 + 39X^7 - 139X^6 - 53X^5 + 233X^4 + 25X^3 - 163X^2 - X + 35$
			$X^9 + 3X^8 - 6X^7 - 22X^6 + 5X^5 + 45X^4 + 10X^3 - 28X^2 - 9X + 3$
			$X^9 - 3X^8 - 6X^7 + 22X^6 + 5X^5 - 45X^4 + 10X^3 + 28X^2 - 9X - 3$
26			$X^{12} + 3X^{11} - 13X^{10} - 42X^9 + 54X^8 + 205X^7 - 77X^6 - 439X^5 - 7X^4 + 411X^3 + 79X^2 - 136X - 35$
			$X^9 + 2X^8 - 8X^7 - 15X^6 + 19X^5 + 33X^4 - 16X^3 - 25X^2 + 3X + 5$
			$X^{12} - 3X^{11} - 13X^{10} + 42X^9 + 54X^8 - 205X^7 - 77X^6 + 439X^5 - 7X^4 - 411X^3 + 79X^2 + 136X - 35$
			$X^9 - 2X^8 - 8X^7 + 15X^6 + 19X^5 - 33X^4 - 16X^3 + 25X^2 + 3X - 5$
27			$X^{13} + 4X^{12} - 10X^{11} - 53X^{10} + 20X^9 + 249X^8 + 63X^7 - 516X^6 - 254X^5 + 482X^4 + 270X^3 - 174X^2 - 84X + 14$
			$X^{13} - 4X^{12} - 10X^{11} + 53X^{10} + 20X^9 - 249X^8 + 63X^7 + 516X^6 - 254X^5 - 482X^4 + 270X^3 + 174X^2 - 84X - 14$
			$X^{11} + 3X^{10} - 9X^9 - 30X^8 + 24X^7 + 101X^6 - 18X^5 - 142X^4 - 6X^3 + 82X^2 + 8X - 14$
			$X^{11} - 3X^{10} - 9X^9 + 30X^8 + 24X^7 - 101X^6 - 18X^5 + 142X^4 - 6X^3 - 82X^2 + 8X + 14$

^a ○, vertex with weight +1; ●, vertex with weight -1; (—), edge with weight 2^{1/2}; — edge without weight.

Scheme 1

Fragment A

$$CP(A) = x^9 + 3x^8 - 8x^7 - 27x^6 + 14x^5 + 70x^4 + 3x^3 - 59x^2 - 13x + 10$$

$$\begin{array}{c} \downarrow \\ P = -5.0, Q = 6.0 \\ (x^2 - 3.800008x + 3.447161) \end{array}$$

$$DP_1 = x^7 + 6.800008x^6 + 14.392919x^5 + 4.252484x^4 - 19.455250x^3 - 18.58908x^2 - 0.5732718x + 2.901114$$

$$\begin{array}{c} \downarrow \\ (P, Q) \\ (x^2 - 1.462297x + 0.3783461) \end{array}$$

$$DP_2 = x^5 + 8.262304x^4 + 26.09651x^3 + 39.2872x^2 + 28.12094x + 7.667881 \quad (\text{abandoned})$$

Note: No more $(x^2 - Ax + B)$ or $(x - a)$ type of terms are extracted from DP_2 , and also DP_2 does not contain a negative term. ($K_A = 1.3042$, and $(E_\pi)A = 5.262297\beta$.)

Fragment B

$$CP(B) = x^9 + 3x^8 - 8x^7 + 27x^6 + 14x^5 - 70x^4 + 3x^3 + 59x^2 - 13x - 10$$

$$\begin{array}{c} \downarrow \\ (P, Q) \\ (x^2 - 4.74102x + 5.4820) \end{array}$$

$$DP_1 = x^7 + 1.74102x^6 - 5.22783x^5 - 7.329586x^4 - 7.909461x^3 + 7.679988x^2 - 3.948998x - 1.824278$$

$$\begin{array}{c} \downarrow \\ (P, Q) \\ (x^2 - 2.697054x + 1.697000) \end{array}$$

$$DP_2 = x^5 + 4.438074x^4 + 5.044897x^3 - 1.254636x^2 - 4.035552x - 1.074996$$

$$\begin{array}{c} \downarrow \\ p_1 \\ (x - 0.824027) \end{array}$$

$$DP_3 = x^4 + 5.262305x^3 + 9.382254x^2 + 6.4785110x + 1.3042400 \quad (\text{abandoned})$$

$$K_B = 7.66779 \quad \text{and} \quad (E_\pi)B = 8.2623054\beta$$

Fragment C

$$CP(C) = x^7 - 2x^6 - 6x^5 + 11x^4 + 9x^3 - 15x^2 - 4x + 5$$

$$\begin{array}{c} \downarrow \\ P = -5.0, Q = 6.0 \\ (x^2 - 3.951038x + 3.691769) \end{array}$$

$$DP_1 = x^5 + 1.951038x^4 - 1.983145x^3 - 4.038262x^2 + 0.3659895x + 1.354367$$

$$\begin{array}{c} \downarrow \\ (P, Q) \\ (x^2 - 1.9110250x + 0.7903037) \end{array}$$

$$DP_2 = x^3 + 3.862063x^2 + 4.607053x + 1.713730 \quad (\text{abandoned})$$

$$K_C = 2.917616 \quad \text{and} \quad (E_\pi)C = 5.862063\beta$$

Fragment D

$$CP(D) = x^7 + 2x^6 - 6x^5 - 11x^4 + 9x^3 + 15x^2 - 4x - 5$$

$$\begin{array}{c} \downarrow \\ P = -5.0, Q = 6.0 \\ (x^2 - 3.093011x + 2.228366) \end{array}$$

$$DP_1 = x^5 + 5.093011x^4 - 7.524376x^3 - 0.9238901x^2 - 4.909459x - 2.243778$$

$$\begin{array}{c} \downarrow \\ p_1 \\ (x - 0.7690502) \end{array}$$

$$DP_3 = x^4 + 5.862061x^3 + 12.0326x^2 + 10.17756x + 2.917597 \quad (\text{abandoned})$$

$$K_D = 1.7137253 \quad \text{and} \quad (E_\pi)D = 3.8620612\beta$$

Since, (P, Q) values give the desired factors, we are apt to say that $P = -5.0$ and $Q = 6.0$ values give the Kekulé structure count for the studied PAH6 molecules. It is true that a number of analytical methods are available for the determination of the Kekulé structures. But, if the computational method is applied, then one has to go for the construction of the CP of a large benzenoid molecule and to

compute all the eigenvalues of the molecular graph. It is well-known that CP construction requires high precision arithmetically,^{23,24} which is not a demerit of the computational method but requires a mainframe type computer having the facilities of a quadruple precision. But, in this method smaller components are used for the determination of the Kekulé structure and easily factors like $(X^2 - AX + B)$ and

Table 2. Approximation with $P = -5.0$, $Q = 6$, $p_1 = -3.0$, and $p_2 = -2.0$

order of occurrence of the factors CP \rightarrow DP ₁ (I), DP ₁ \rightarrow DP ₂ (II), DP ₂ ... \rightarrow DP _n					
molecule	fragment		$(E\pi)_i$	K_i	K
1	A	$X - 1.30278$ (I, p_1)	1.302 78	1.302 78	3
	B	$X - 2.30278$ (I, p_2)	3.302 80	2.302 78	
	C	$X - 0.61803$ (I, p_1)	0.618 03	0.618 03	
	D	$X - 1.61803$ (I, p_1)	1.618 03	1.618 03	
2	A	$X^2 - 3.09301X + 2.22837$ (I, QF) $X - 0.76905$ (II, p_1)	3.862 06	1.713 728	5
	B	$X^2 - 3.95104X + 3.69177$ (I, QF) $X^2 - 1.91103X + 0.79030$ (II, QF)	5.862 06	2.917 62	
3	A	$X^2 - 1.82843X + 0.58578$ (I, QF)	1.828 43	0.585 78	4
	B	$X^2 - 3.82843X + 3.41421$ (I, QF)	3.828 43	3.414 21	
	C	$X - 1$ (I, p_1)	1	1	
	D	$X - 2$ (I, p_1)	2	2	
4	E	$X - 1$ (I, p_1)	1	1	6
	A	$X^2 - 2.87938X + 1.75877$ (I, QF)	2.879 38	1.758 77	
	B	$X^2 - 3.87939X + 3.41147$ (I, QF)	4.879 38	3.411 46	
	C	$X - 1.00000$ (II, p_1)			
5	D	$X - 1.24698$ (I, p_1)	1.246 98	1.246 98	9
	A	$X^2 - 2.24698X + 0.80194$ (I, QF)	2.246 98	0.801 94	
	B	$X^2 - 3.25519X + 2.53209$ (I, QF)	4.818 61	1.532 11	
	C	$X^2 - 1.56342X + 0.60153$ (II, QF)			
6	D	$X^2 - 4.50170X + 4.98724$ (I, QF)			5
	A	$X^2 - 2.63288X + 1.73207$ (II, QF)	7.818 62	5.908 90	
	B	$X - 0.6840242$ (III, p_1)			
	C	$X^2 - 2.24422X + 1.14036$ (I, QF)	2.244 22	1.140 361	
7	D	$X^2 - 4.24422X + 4.38458$ (I, QF)	5.244 21	4.384 57	8
	A	$X - 1.00000$ (II, p_1)			
	B	$X^2 - 1.48849X + 0.35205$ (I, QF)	1.488 49	0.352 05	
	C	$X^2 - 3.48849X + 2.84054$ (I, QF)	3.488 49	2.840 54	
8	D	$X^2 - 4.27641X + 4.43591$ (I, QF)	7.381 60	4	11
	A	$X^2 - 2.53759X + 1.58869$ (II, QF)			
	B	$X - 0.56761$ (III, p_1)			
	C	$X^2 - 3.55000X + 3.02045$ (I, QF)	4.212 15	2	
9	D	$X - 0.66215$ (II, p_1)			9
	A	$X - 1$ (I, QF)	1	1	
	B	$X^2 - 3.36593X + 2.72208$ (I, QF)	5.084 01	1.954 67	
	C	$X^2 - 1.71808X + 0.71808$ (II, QF)			
10	D	$X^2 - 4.69717X + 5.45586$ (I, QF)	9.083 95	5.627 08	13
	A	$X^2 - 2.88998X + 2.07570$ (II, QF)			
	B	$X^2 - 1.49688X + 0.49696$ (III, QF)			
	C	$X^2 - 3.18191X + 2.18187$ (I, QF)	4.181 98	2.181 76	
11	D	$X - 1.00000$ (II, p_1)			14
	A	$X^2 - 4.18194X + 4.12476$ (I, QF)	5.181 94	4.124 76	
	B	$X - 1$ (II, p_1)			
	C	$X^2 - 1.87939X + 0.53209$ (I, QF)	1.879 39	0.532 09	
12	D	$X^2 - 2.87939X + 1.87939$ (I, QF)	2.879 39	1.879 39	13
	A	$X^2 - 3.83045X + 3.52310$ (I, QF)	6.735 80	2.813 03	
	B	$X^2 - 2.22493X + 1.17350$ (II, QF)			
	C	$X - 0.6804535$ (III, p_1)			
13	D	$X^2 - 4.47113X + 4.90822$ (I, QF)	8.735 80	4.621 31	14
	A	$X^2 - 2.76270X + 1.87581$ (II, QF)			
	B	$X^2 - 1.50196X + 0.50193$ (III, QF)			
	C	$X^2 - 3.81202X + 3.54699$ (I, QF)	6.356 29	1.721 67	
14	D	$X^2 - 2.10503X + 1.10503$ (II, QF)			14
	A	$X - 0.43923$ (III, p_1)			
	B	$X^2 - 4.71866X + 5.48845$ (I, QF)	9.356 27	8.132 59	
	C	$X^2 - 2.95352X + 2.16568$ (II, QF)			
15	D	$X^2 - 1.68413X + 0.68427$ (III, QF)			6
	A	$X^2 - 2.49551X + 1.49551$ (I, QF)	2.715 19	0.328 54	
	B	$X - 0.21969$ (II, p_1)			
	C	$X^2 - 4.49551X + 4.99102$ (I, QF)	5.715 195	6.087 47	
16	D	$X - 1.21969$ (II, p_1)			20
	A	$X - 1.30278$ (I, p_1)	1.302 78	1.302 78	
	B	$X^2 - 3.30278X + 2.30278$	3.302 78	2.302 78	
	C	$X - 0.61803$ (I, p_1)	0.618 03	0.618 03	
17	D	$X - 0.61803$ (I, p_2)	1.618 03	1.618 03	36
	A	$X^2 - 3.42864X + 2.68889$ (I, QF)	4.428 64	2.688 89	
	B	$X - 1.0000$ (II, p_1)			
	C	$X^2 - 4.35026X + 4.48119$ (I, QF)	6.428 64	3.719 00	
18	D	$X^2 - 2.07838X + 0.82991$ (II, QF)			7
	A	$X^2 - 2.21432X + 0.90321$ (I, QF)	2.214 32	0.903 21	
	B	$X^2 - 3.21432X + 2.21432$ (I, QF)	3.214 32	2.214 32	
	C	$X^2 - 3.15165X + 2.27800$ (I, QF)	3.824 94	1.533 76	
19	D	$X - 0.67329$ (II, p_1)			36
	A	$X^2 - 4.49427X + 4.89970$ (I, QF)	6.824 95	6.519 91	
	B	$X^2 - 2.33068X + 1.33068$ (II, QF)			
	C	$X^2 - 2.21615X + 1.13411$ (I, QF)	2.216 15	1.134 11	
20	D	$X^2 - 3.66120X + 3.177710$ (I, QF)	3.661 19	3.177 71	7
	A	$X^2 - 2.65460X + 1.72726$ (I, QF)	3.156 11	0.866 24	
	B	$X - 0.5015083$ (II, p_1)			
	C				

Table 2 (Continued)

molecule	fragment	order of occurrence of the factors CP \rightarrow DP ₁ (I), DP ₁ \rightarrow DP ₂ (II), DP ₂ ... \rightarrow DP _n	$(E_n)_i$	K_i	K
16	B	$X^2 - 4.65460X + 5.38186$ (I, QF)	7.156 11	8.080 93	24
	C	$X^2 - 2.50151X + 1.501514$ (II, QF)	2.382 88	0.195 73	
	D	$X^2 - 2.21351X + 1.55596$ (I, QF)	5.387 94	5.120 02	
	A	$X - 0.16937$ (II, p_1)	4.102 98	2.058 58	
	B	$X^2 - 4.21351X + 4.36910$ (I, QF)	6.103 07	2.914 63	
	C	$X - 1.16937$ (II, p_1)	2.595 84	1.322 60	
17	A	$X^2 - 3.31035X + 2.59715$ (I, QF)	1	1	18
	B	$X - 0.79263$ (II, p_1)	1	1	
	C	$X^2 - 4.28340X + 4.35636$ (I, QF)	3.595 84	3	
	D	$X^2 - 1.81959X + 0.66905$ (II, QF)	5.759 07	3.051 32	
	E	$X^2 - 2.59584X + 1.3326$ (I, QF)	2.513 34	1.397 88	
	F	$X - 1$ (I, p_1)	6.759 07	5.899 07	
18	A	$X^2 - 3.59584X + 3.00165$ (I, QF)	3.228 71	0.715 37	45
	B	$X^2 - 3.93108X + 3.68524$ (I, QF)	9.266 35	3.181 72	
	C	$X^2 - 1.82799X + 0.82799$ (II, QF)	12.254 25	13.982 86	
	D	$X^2 - 2.51334X + 1.39788$ (I, QF)	6.005 31	3.763 65	
	E	$X^2 - 4.64315X + 5.2863$ (I, QF)	8.005 31	5.313 93	
	F	$X^2 - 2.11591X + 1.1159$ (II, QF)	2.774 62	1.774 62	
19	A	$X^2 - 3.22871X + 2.51334$ (I, QF)	4.774 62	0.563 50	20
	B	$X - 0.28463$ (II, p_1)	4.774 62	0.563 50	
	C	$X^2 - 4.26578X + 4.48351$ (I, QF)	6.005 31	3.763 65	
	D	$X^2 - 2.74410X + 1.86998$ (II, QF)	2.774 62	1.774 62	
	E	$X^2 - 1.75933X + 0.76147$ (III, QF)	8.005 31	5.313 93	
	F	$X - 0.49593$ (IV, p_2)	4.774 62	0.563 50	
20	A	$X^2 - 4.64713X + 5.26453$ (I, QF)	4.774 62	0.563 50	50
	B	$X^2 - 2.76279X + 1.29639$ (II, QF)	5.262 30	1.304 220	
	C	$X^2 - 2.85791X + 2.04251$ (III, QF)	8.262 31	7.667 79	
	D	$X^2 - 1.99631X + 1.00665$ (IV, QF)	5.862 063	2.917 616	
	E	$X^2 - 3.99803X + 3.83202$ (I, QF)	3.862 061	1.713 725	
	F	$X^2 - 2.00728X + 0.98215$ (II, QF)	11.134 66	6.705 26	
21	A	$X^2 - 4.75389X + 5.53474$ (I, QF)	13.134 415	6.129 297	54
	B	$X^2 - 2.71250X + 1.78160$ (II, QF)	7.638 74	5.286 51	
	C	$X - 0.53894$ (III, p_2)	3.783 39	1.511 18	
	D	$X^2 - 2.77462X + 1.77462$ (I, QF)	9.638 76	10.214 77	
	E	$X^2 - 3.58874X + 3.03144$ (I, QF)	4.783 39	0.661 73	
	F	$X^2 - 3.99803X + 3.83202$ (I, QF)	6.566 11	5.171 70	
22	A	$X^2 - 2.00728X + 0.98215$ (II, QF)	4.811 68	1.284 39	136
	B	$X^2 - 2.77462X + 1.77462$ (I, QF)			
	C	$X^2 - 4.75389X + 5.53475$ (I, QF)			
	D	$X^2 - 2.71250X + 1.78160$ (II, QF)			
	E	$X - 0.53894$ (III, p_1)			
	F	$X^2 - 3.58874X + 3.03144$ (I, QF)			
23	A	$X^2 - 1.18589X + 0.18588$ (II, QF)			
	B	$X^2 - 3.80000X + 3.44716$ (I, QF)			
	C	$X^2 - 1.46230X + 0.37835$ (II, QF)			
	D	$X^2 - 4.74102X + 5.48204$ (I, QF)			
	E	$X^2 - 2.69777X + 1.69720$ (II, QF)			
	F	$X - 0.82410$ (III, p_1)			
24	A	$X^2 - 3.95104X + 3.69177$ (I, QF)			
	B	$X^2 - 1.91103X + 0.79030$ (II, QF)			
	C	$X^2 - 3.09301X + 2.22837$ (I, QF)			
	D	$X - 0.76905$ (II, p_1)			
	E	$X - 2.48622$ (I, p_1)			
	F	$X - 1.99128$ (II, p_2)			
25	A	$X - 1.70959$ (III, p_1)			
	B	$X - 1.32471$ (IV, p_2)			
	C	$X - 1.21511$ (V, p_1)			
	D	$X^2 - 1.53042X + 0.84855$ (VI, QF)			
	E	$X - 0.57485$ (VII, p_1)			
	F	$X^2 - 4.91382X + 5.99289$ (I, QF)			
26	A	$X^2 - 3.61285X + 3.24868$ (II, QF)			
	B	$X^2 - 2.57656X + 1.64945$ (III, QF)			
	C	$X^2 - 1.80204X + 0.81864$ (IV, QF)			
	D	$X - 0.22534$ (V, p_2)			
	E	$X^2 - 4.53587X + 5.07174$ (I, QF)			
	F	$X^2 - 2.30280X + 1.30282$ (II, QF)			
27	A	$X - 0.80007$ (III, p_1)			
	B	$X^2 - 3.16535X + 2.44513$ (I, QF)			
	C	$X - 0.61804$ (II, p_1)			
	D	$X^2 - 4.98499X + 6.17653$ (I, QF)			
	E	$X^2 - 2.61458X + 1.58891$ (II, QF)			
	F	$X^2 - 2.03915X + 1.04068$ (III, QF)			
28	A	$X^2 - 3.57433X + 3.16535$ (I, QF)			
	B	$X^2 - 1.209056X + 0.20905$ (II, QF)			
	C	$X^2 - 4.3007X + 4.47701$ (I, QF)			
	D	$X^2 - 2.61492X + 1.68697$ (II, QF)			
	E	$X - 0.52003$ (III, p_1)			
	F	$X^2 - 3.30999X + 2.56012$ (I, QF)			
29	A	$X^2 - 1.50169X + 0.50169$ (II, QF)			
	B				

Table 2 (Continued)

molecule	fragment	order of occurrence of the factors CP \rightarrow DP ₁ (I), DP ₁ \rightarrow DP ₂ (II), DP ₂ ... \rightarrow DP _n	$(E_{\pi})_i$	K_i	K
25	C	$X^2 - 4.94797X + 6.03497$ (I, QF) $X^2 - 3.05823X + 2.30944$ (II, QF) $X^2 - 1.55995X + 0.47176$ (III, QF)	9.566 11	6.574 22	105
	D	$X^2 - 4.02199X + 3.94375$ (I, QF) $X^2 - 1.78969X + 0.78969$ (II, QF)	5.811 68	3.114 32	
	A	$X^2 - 4.10235X + 4.11932$ (I, QF) $X^2 - 2.27567X + 1.29217$ (II, QF) $X - 0.58112$ (III, p_1)	6.959 20	3.093 74	
	B	$X^2 - 5.01239X + 6.20818$ (I, QF) $X^2 - 3.16987X + 2.48462$ (II, QF) $X^2 - 1.77690X + 0.73331$ (III, QF)	9.959 21	11.312 93	
	C	$X^2 - 3.48991X + 2.91417$ (I, QF) $X^2 - 1.14470X + 0.19854$ (II, QF)	4.634 66	0.578 56	
	D	$X^2 - 4.40690X + 4.72730$ (I, QF) $X^2 - 2.49321X + 1.49318$ (II, QF) $X - 0.73458$ (III, p_1)	7.634 68	5.185 01	
	A	$X^2 - 4.33714X + 4.56524$ (I, QF) $X^2 - 2.63447X + 1.67879$ (II, QF) $X - 0.84815$ (III, p_1)	7.819 58	6.498 32	
	B	$X^2 - 3.44716X + 2.82130$ (I, QF) $X^2 - 1.62852X + 0.58888$ (II, QF)	5.075 67	1.661 39	
26	C	$X^2 - 4.78478X + 5.55961$ (I, QF) $X^2 - 3.59037X + 3.04972$ (II, QF) $X^2 - 2.17339X + 1.17286$ (III, QF) $X - 0.27124$ (IV, p_1)	10.819 589	5.386 19	162
	D	$X^2 - 4.22188X + 4.33145$ (I, QF) $X^2 - 2.25298X + 1.15644$ (II, QF) $X - 0.60081$ (III, p_1)	7.075 67	3.009 52	
	A	$X^2 - 4.30526X + 4.58532$ (I, QF) $X^2 - 2.50165X + 1.56088$ (II, QF) $X^2 - 0.89739X + 0.10532$ (III, QF)	7.703 58	0.747 998	
	B	$X - 2.79676$ (I, p_1) $X^2 - 4.17829X + 4.27296$ (II, QF) $X^2 - 3.03916X + 2.27020$ (III, QF) $X^2 - 1.68950X + 0.69024$ (IV, QF)	11.703 57	18.717 42	
	C	$X^2 - 3.81202X + 3.54699$ (I, QF) $X^2 - 2.10503X + 1.10503$ (II, QF) $X - 0.43923$ (III, p_1)	6.356 29	1.722 65	
	D	$X^2 - 4.71866X + 5.48845$ (I, QF) $X^2 - 2.95352X + 2.16568$ (II, QF) $X^2 - 1.68414X + 0.68427$ (III, QF)	9.356 277	8.132 59	
27	A				196
	B				
	C				
	D				

$(X - a)$ are obtained, which eventually give the desired result.

RELATIONSHIP BETWEEN E_{π} (TOTAL) AND K OF THE PAH6 MOLECULES OBTAINED THROUGH THE PROGRAM

Following the Hückel theory, the total π -electronic energy is defined as twice the sum of the positive eigenvalues of the adjacency matrix, and this is taken over simply as the definition of the graph theory.²⁵ The dependence of E_{π} on the structure of the conjugated molecules was first addressed by Coulson and Rushbrooke.²⁶ Many workers^{18,27–30} have investigated the relationship between the E_{π} and K of the benzenoid hydrocarbons. Gutman and Hall, while advocating the linear dependence of E_{π} on K over the nonlinear one for the benzenoid hydrocarbons, proposed that the highest occupied molecular orbitals (HOMOs) are nondegenerate and well-separated from the second highest MOs.²⁷ Here, in this study an attempt has been made to study the linear relationship between E_{π} and K , taking different fragments into consideration. Now making use of the program, we have extracted two types of factors like $(X^2 - A_iX + B_i)$ and $(X - a_i)$ with $P = -5.0$ and $Q = 6.0$. When the fragments of

a molecule are subjected to our computational technique, we observed the following two important points.

(i) Factors are extracted following one energetic scale; i.e., the most minimum energy factor is extracted first, then the second one, and so on, concluding with the HOMO level extraction as the last factor (here the HOMO level does not depict the HOMO of the molecule, rather the HOMO of the fragment). This can be observed by comparing the A values obtained from the different QFs. If in a particular fragment one QF and two LFs are obtained, then the QF is converted back to its linear form and the a_i are compared to show the extraction of the factors to corroborate the proposed energy scale.

(ii) When the last QF factor (energetic one) is extracted containing the HOMO level of a fragment, the nondegeneracy of the HOMO level can be tested through the following simple relation as

$$B^{1/2} \neq A/2 \quad (5)$$

It may be mentioned that in some fragments $B^{1/2}$ may be equal to $A/2$. But, if the (a_i) of all the last extracted factors of all the fragments (which contain the HOMO level) are

compared, then at least one lowest positive nonrepeated eigenvalue is there in one of the fragments. This level refers to the nondegenerate HOMO level of the molecule.

Now following a particular QF, one can write

$$(E_{\pi})_i/2 = X_r + 1/X_r(K_i) \quad (6)$$

Here, $r = 1$ or 2 (first or the second eigenvalue), $(E_{\pi})_i$ is the π -electron energy of the i th fragment, and K_i is the fraction of the total K of the molecule.

On the other hand when one LF is extracted, then

$$(E_{\pi})_i/2 = K_j \quad (7)$$

where K_j is also a fraction of the total K . Then $E_{\pi}(\text{total})$ of the molecule can be written as

$$E_{\pi}(\text{total}) = 2\left[\sum_{i=1}^n (X_r)_i + \sum_{i=1}^n (1/X_r)_i K_i + \sum_{j=1}^n K_j\right]$$

Here, the last term is obtained from the LFs, the first and second terms are obtained from the QFs, n refers to all the extracted factors, and K_i and K_j are the fractions of K associated with the QFs and LFs, respectively.

CONCLUSION

In this study we have established a linear relationship between E_{π} and K by fragmenting a PAH6 into different components. The initial approximations in the form of $P = -5.0$ and $Q = 6.0$ not only gives the K of the PAH6 but also extracts the factors following an energy scale; i.e., the lowest energy factor is extracted first, and the process continues until the HOMO is extracted. Also, the nondegeneracy of the HOMO of the molecule is tested through this computer program.

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