

CHAPTER-8

Application of Budan-Fourier theorem for analysis of characteristic polynomials of some π -systems

8.1. Introduction : Many interesting properties of π -conjugated molecules can be obtained by analysing their characteristic polynomials (CP). The application of Descartes's rule of signs to the CP of a molecular graph has been shown to yield results related to the energy of the highest occupied molecular orbital (HOMO)¹ and validity or nonvalidity of Hückel's $(4n+2)$ rule^{2,3}. However, there are many other well known theorems in polynomial algebra which have not been exploited much in the study of CP's. The aim of the present work is to use one such theorem — the Budan-Fourier theorem⁴ — for obtaining chemically interesting results related to the energy level patterns and donor properties of aniline, phenol, p-phenylenediamine and p-quinol. Although a good number of methods⁵⁻⁹ are available for constructing CP's, the process may be simplified by employing graph-theoretical symmetry factorisation technique developed in Chapter-5.

8.2. Some graph-spectral features of the systems under study : Some chemically relevant graph-spectral features ($F_1 - F_6$) of the conjugated molecules under study (figs. 8.1 and 8.2) are summarised below :

F_1 : For $0 < h < 1$ and $0 < k < 1$, aniline-like systems have exactly one eigenvalue in each of the ranges $(0,1)$ and $(1,2)$ and exactly one positive eigenvalue above 2. The same is also true when $1 < h \leq 2$ and $1 \leq k \leq \sqrt{2}$.

F_2 : With a given value of k , the eigenvalue of the highest occupied molecular orbital (HOMO) of an aniline-like system (G_1) should increase with increase in h ; with a given $h > 0$, the HOMO eigenvalue should decrease with increase in k .

F_3 : If $h = 1$, a p-phenylenediamine-like system (G_2) will have a doubly degenerate π -MO with eigenvalue = 1, whatever be the value of k .

F_4 : For $2h = k^2$, G_2 has a non-bonding π -MO.

F_5 : For $2h > k^2$, G_2 has five positive and three negative eigenvalues. When $2h < k^2$, G_2 has four positive and four negative eigenvalues.

F_6 : When $2h > k^2$ and $1 < h < 5$, there is exactly one eigenvalue in the range $(0,1)$ for systems having G_2 -type graphs. For a fixed k , this eigenvalue increases with increase in h and for a fixed h , it decreases with increase in k .

8.3. Explanation of the above features :

Case (a) : aniline-like systems

The factorisation of aniline-like graphs according to schemes described in Chapter-5 is shown in Fig.8.1. It shows that the CP of the aniline-like graph (G_1) has the form,

$$P(G_1; x) = (x^2 - 1) f(x) \quad \dots (8.1)$$

where

$$f(x) = x^5 - hx^4 - (5+k^2)x^3 + 5hx^2 + (4+3k^2)x - 4h \quad \dots (8.2)$$

is the CP of the third factor graph in fig.8.1. Thus, ± 1 must be two zeros of $P(G_1; x)$ whatever be the values of h and k .

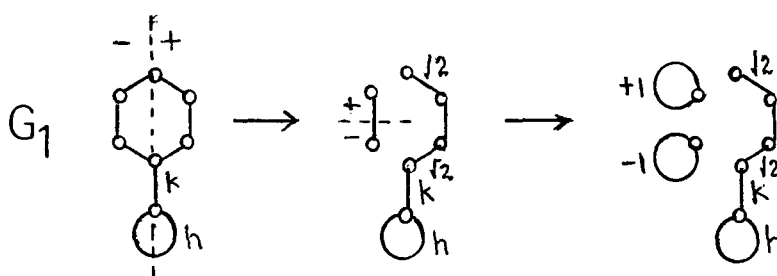


Fig.8.1. Factorisation of aniline-like graphs

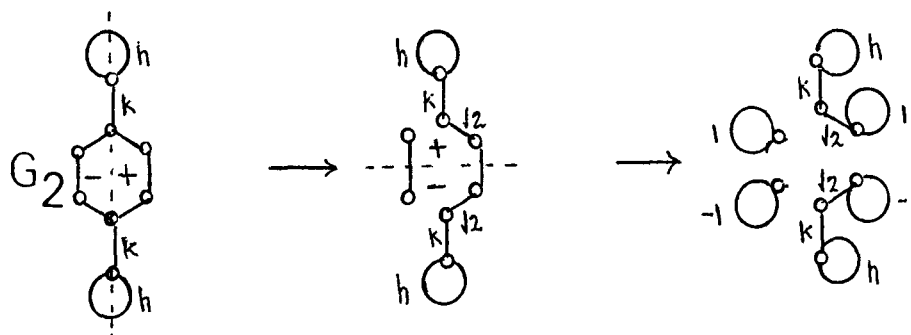


Fig.8.2. Factorisation of p-phenylenediamine-like graphs

Eqn.(8.2) gives $f(0) = -4h$, $f(1) = 2k^2$ and $f(2) = -2k^2$. Thus, according to Rolle's theorem⁴ $f(x)$ should have zeros in the range $(0,1)$ and $(1,2)$ for $h > 0$. To ascertain the position of the HOMO of G_1 , one must find the exact number of zeros of $f(x)$ in these ranges; we have done this by using Budan-Fourier theorem⁴ which states that for a polynomial $P(x)$ of degree n , the zeros of which are real, the exact number of zeros in the range (a,b) is $N(a) - N(b)$ where $N(a)$ is the number of changes of sign in the sequence,

$$P(a), P^1(a), P^2(a), \dots, P^n(a)$$

The superscripts on P indicate the orders of the derivatives of $P(x)$ with respect to x ; $N(b)$ has a similar meaning.

The values of the zeroeth to fifth order derivatives of $f(x)$ at $x = 0, 1$

and 2 are shown in table 1. From this table it is evident that if $0 < h < 1$ and $0 < k < 1$, $N(0) = 3$, $N(1) = 2$ and $N(2) = 1$. Thus, according to Budan-Fourier⁴ theorem there is exactly one zero of $f(x)$ in the ranges $(0,1)$ and $(1,2)$ for the above mentioned values of h and k .

Table 1. Derivatives of $f(x)$ at $x = 0, 1$ and 2

Order of derivatives	Value of derivative at		
	$x = 0$	$x = 1$	$x = 2$
0	$-4h$	$2k^2$	$-2k^2$
1	$4+3k^2$	$-6+6h$	$24-12h-9k^2$
2	$10h$	$-10-2h-6k^2$	$100-38h-12k^2$
3	$-6(5+k^2)$	$30-24h-6k^2$	$210-48h-6k^2$
4	$-24h$	$120-24h$	$240-24h$
5	120	120	120

When $1 < h \leq 2$, $N(0) = 3$ whatever be the value of k . For $x = 1$, signs of the aforesaid sequence of derivatives must have one of the following three patterns if $1 < h \leq 2$, whatever be the value of k .

+	+	-	+	+	+
+	+	-	-	+	+
+	+	-	0	+	+

Sign sequence 1

The signs of the derivatives have been arranged row-wise. The blocked portion indicates that only the third order derivative may have different signs (or zero value) depending on k . Therefore, $N(1) = 2$. For $x = 2$, one obtains from table-1 the following three sign-change patterns of the derivative sequence with $1 < h \leq 2$ and $1 < k \leq \sqrt{2}$:

-	+	+	+	+	+
-	-	+	+	+	+
-	0	+	+	+	+

Sign sequence 2

Here the first order derivative may have any sign depending on h and k as shown in the block. This gives $N(2) = 1$ and thus by Budan-Fourier theorem $f(x)$ has exactly one zero in each of the ranges $(0,1)$ and $(1,2)$ when $1 < h \leq 2$ and $1 < k \leq \sqrt{2}$.

Now, for $h > 0$, $f(x)$ has three changes of sign and so by Descartes's rule of signs $f(x)$ has three positive zeros (the adjacency matrix being hermitian, complex roots do not appear). Thus, one positive zero of $f(x)$ should be above 2. This explains the feature F_1 .

If the positive eigenvalues x_i ($i=1$ to 4) of G_1 are arranged as $x_1 < x_2 < x_3 < x_4$, the above analysis shows that $0 < x_1 < 1$, $x_2 = 1$, $1 < x_3 < 2$ and $x_4 > 2$, for $0 \leq h \leq 2$ and $1 \leq k \leq \sqrt{2}$. Recalling that x_i 's are expressed in β unit (which is negative), we find that x_1 is the energy of the HOMO of an aniline-like system. In the following discussion we have determined the mode of variation of x_1 in an approximate manner (table-2).

Table 2 - Mode of variation of HOMO energy with h and k for aniline-like systems

Value of h	Value of k	HOMO energy (in β unit)
0.0	1.0	0.0
0.5	1.0	0.2767160
1.0	1.0	0.5042842
0.5	0.5	0.4091893
0.5	1.0	0.2767160
0.5	1.5	0.1824341

x_1 satisfies $f(x) = 0$ and for $h > 0$, $x_1 \neq 0$. When $0 < h < 1$ and $1 \leq k \leq \sqrt{2}$, we have already proved that $0 < x_1 < 1$. So from Eqn.(8.2), we can approximately write,

$$5hx_1^2 + (4+3k^2)x_1 - 4h = 0 \quad \dots (8.3a)$$

which yields

$$x_1 = [-(4+3k^2) + \sqrt{\{(4+3k^2)^2 + 80h^2\}}]/10h \quad \dots (8.3b)$$

We get from (8.3b)

$$\begin{aligned} (\partial x_1 / \partial k)_k &= (4+3k^2) [\sqrt{\{(4+3k^2)^2 + 80h^2\}} - (4+3k^2)] / [10h^2 \sqrt{\{(4+3k^2)^2 + 80h^2\}}] \\ &= (+) ve \quad \dots (8.4a) \end{aligned}$$

$$\text{and } (\delta x_1 / \delta k)_h = (3k/5h) [(4+3k^2) / \sqrt{(4+3k^2)^2 + 80h^2}] - 1] \\ = (-)ve \quad \dots (8.4b)$$

This explains the feature F₂.

Case (b) : p-phenylenediamine-like systems

The factorisation of such graphs (G₂) has been shown in fig.8.2. It shows that the CP of such a graph is given by,

$$P(G_2; x) = (x^2 - 1) \phi(x) \Psi(x) \quad \dots (8.5)$$

where $\phi(x) = x^3 - (h+1)x^2 - (k^2+2-h)x + (2h+k^2) \quad \dots (8.6)$

and $\Psi(x) = x^3 - (h-1)x^2 - (k^2+2+h)x + (2h-k^2) \quad \dots (8.7)$

when h = 1, $\Psi(1) = -2k^2$ and $\phi(1) = 0$.

Thus, whatever be the value of k, 1 is a doubly degenerate eigenvalue of G₂ — one value coming from the factor (x²-1) and the other from the factor $\phi(x)$ of Eqn.(8.5). This explains the feature F₃.

Table 3. Derivatives of $\phi(x)$ at x = 0, 1 and 2

Order of derivative	Value of derivative at		
	x = 0	x = 1	x = 2
0	2h+k ²	2(h-1)	-k ²
1	-(k ² +2-h)	-(1+h+k ²)	6-3h-k ²
2	-2(h+1)	4-2h	10-2h
3	6	6	6

Table 4. Derivatives of $\Psi(x)$ at x = 0 and 1

Order of derivative	Value of derivative at	
	x = 0	x = 1
0	2h-k ²	-2k ²
1	-(k ² +2+h)	-3(h-1)-k ²
2	-2(h-1)	8-2h
3	6	6

When $2h = k^2$, the factor $\phi(x)$ gives $x=0$ as one eigenvalue of G_2 . This explains the feature F_4 .

If $2h < k^2$, there are two changes of sign in both $\phi(x)$ and $\psi(x)$, irrespective of whether h is greater than, equal to or less than 1. Hence, including the eigenvalue $+1$ obtainable from the first factor in eqn.(8.5), G_2 should have five positive (and so three negative) eigenvalues. Again, if $2h < k^2$, $\phi(x)$ has two and $\psi(x)$ has one change of sign. Thus G_2 has four positive (and so four negative) eigenvalues when $2h < k^2$. This explains the feature F_5 .

The values of the zeroeth to the third order derivatives of $\phi(x)$ and $\psi(x)$ are given in tables 3 and 4 respectively. For $1 < h < 5$, one finds from these tables that for $x = 0$ the signs of the sequence $\{\phi^{(i)}(0)\}$, $i = 1$ to 3, will be like any one of the following rows.

+	+	-	+
+	-	-	+
+	0	-	+

Sign sequence 3

There is uncertainty in the sign of the first order derivative only, as shown in the block. In any case, $N(0) = 2$. In the same way one can verify that $\{\phi^{(i)}(1)\}$, and $\{\phi^{(i)}(2)\}$ have the following sign sequences (with $1 < h < 5$):

+	-	+	+	-	+	+	+
+	-	0	+	-	0	+	+
+	-	-	+	-	-	+	+
$\{\phi^{(i)}(1)\}$			$\{\phi^{(i)}(2)\}$				

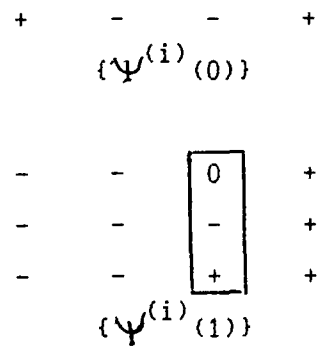
Sign sequence 4

Thus, $N(1) = 2$ and $N(2) = 1$. Hence, for $1 < h < 5$, there is no zero of $\phi(x)$ in $(0, 1)$ and exactly one zero in $(1, 2)$, whatever be the value of k .

Next we consider $\psi(x)$ under the condition

$$2h > k^2 \text{ and } 1 < h < 5 \quad \dots (A)$$

The following sign-sequences can be obtained from table 4.



Sign sequence 5.

Thus, $N(0) = 2$ and $N(1) = 1$ so that $\Psi(x)$ has exactly one zero in $(0,1)$ under the condition (A). And we have already proved that $\phi(x)$ has no zero in $(0,1)$ under condition (A). Thus, $P(G_2;x)$ has only one zero in $(0,1)$ when condition (A) is satisfied. Moreover, since it is a zero of the factor $\Psi(x)$ we can approximately examine its mode of variation with h and k as follows :

Neglecting x^3 from $\Psi(x)$ and writing x_j for the root in $(0,1)$, we have

$$(h-1)x_j^2 + (k^2+2+h)x_j - (2h-k^2) = 0 \quad \dots (8.8)$$

$$(\delta x_j / \delta h)_k = (2-x_j^2-x_j) / [2x_j(h-1)+k^2+2+h] = (+) \text{ ve} \quad \dots (8.9a)$$

$$(\delta x_j / \delta k)_h = -2k(x_j+1) / [2x_j(h-1)+k^2+2+h] = (-) \text{ ve} \quad \dots (8.9b)$$

This explains the feature F_6 .

Table 5. Mode of variation of the eigenvalue x_j between 0 and 1 with change in h and k for the graph G_2 under the condition $2h > k^2$ and $1 < h < 5$.

Value of h	Value of k	x_j
1	0.5	0.6074191
2	0.5	0.8577246
1	1.0	0.2541017
2	1.0	0.5719933
1	0.5	0.6074191
1	1.0	0.2541017
2	1.0	0.5719933
2	1.5	0.2714127

8.4. Conclusion: That the energy of the highest occupied molecular orbital (HOMO) in β unit for most chemically interesting conjugated systems lie in the range (0,1) has been assumed by many workers¹⁰ for estimating HOMO-LUMO separation graph-theoretically. We have proved this for aniline-like systems.

The node of variation of the HOMO energy as described in the feature F_2 and proved in eqns. (8.4a) & (8.4b) can be verified from Coulson's dictionary of π -electron calculations¹¹. For a ready reference we have shown some HOMO eigenvalues in table-2, where the feature F_2 is obvious. Increase in h means increase in electronegativity of the heteroatom in G_1 . With a fixed k , if the electronegativity of the heteroatom increases, π -electrons from the ring are drawn towards the heteroatom and the π -electron density in the ring decreases. Thus the energy of the HOMO should decrease with increase in h . Remembering that β is negative, we get a qualitative explanation for the trend predicted by eqn. (8.4a) and reflected in the first part of table-2.

There are experimental evidences also for this trend. For example, the CT transition energies of complexes of tetracyanoethylene with aniline and *N*-methylaniline in CHCl_3 are 2.097 eV and 1.946 eV respectively¹² which show that *N*-methylaniline is the better donor. The inductive effect of CH_3 reduces the h value of *N*-atom and thus makes the HOMO energy of *N*-methylaniline greater than that of aniline. With a given h , increase in k means increase in the resonance integral between the heteroatom and the ring C-atom attached to it. Thus, with increase in k , more and more π -electrons are drawn towards the ring from the heteroatom which increases the electron density in the ring and thus increases the HOMO energy. In β unit, therefore, the HOMO eigenvalue should decrease with increase in k at a fixed h . This is predicted by eqn. (8.4b) and reflected in the second part of table-2.

The results stated in the features F_3 to F_6 as regards the number of bonding, antibonding and non-bonding π -MO's for *p*-phenylenediamine-like systems can be verified from Coulson's compilation¹¹. From Streitwieser's list¹³ we find for oxygen atom, $h_O = 2$ and $k_{C-O} = 1$, which are applicable to *p*-quinol and $h_O = 1$ and $k_{C-O} = 1$ which are applicable to *p*-benzoquinone. In both cases $2h > k^2$, so that both these systems (with graph G_2) should have five bonding MO's. In *p*-benzoquinone there are 8 π -electrons, so that one bonding MO remains vacant which makes it a π -electron acceptor. Again, *p*-quinol has 10 π -electrons and all its bonding MO's are filled up; thus it behaves as a π -donor. The existence of well known CT complexes of the quinhydrone type^{14,15} (in the solid state) is in agreement with these facts. For

p-quinol and p-phenylenediamine, Streitwieser's list¹³ also shows that the necessary heteroatom parameters satisfy condition (A). The physical reason for the variation of x_j (which is presumably the HOMO of p-quinol and p-phenylenediamine), as proved in eqn.(8.9a) and (8.9b), can be interpreted as done in the case of aniline above; such trends are shown in table-5.

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