

Triads of Fibonacci graphs in MO calculations: Some applications to charge-transfer complexes

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Abstract. El-Basil's Fibonacci triad (FT) method has been utilised to construct the characteristic polynomials of a series of aromatic hydrocarbon radicals. These, in turn, have been used to calculate graph-theoretically the HOMO energies of a series of methylbenzenes in a hyperconjugative model. From a correlation of the calculated energies with the charge-transfer bands of their π -type molecular complexes, reasonable values of the hyperconjugative Hückel parameters of the methyl group have been found. The convenience resulting from the regressive use of FT's has been focussed on.

Keywords. Fibonacci triads; Ulam subgraphs; characteristic polynomials.

1. Introduction

There exist quite a good number of methods (Hosoya 1972; Aihara 1976; Gutman and Polansky 1981) for construction of various graphic polynomials. Computation of such polynomials for conjugated molecules becomes more and more difficult as the graphs representing such systems increase in size and number. However, the method developed by El-Basil (1984), which uses Fibonacci Triads (FT) for counting $p(k)$ numbers and constructing characteristic polynomials (CP) has a special advantage – it can be applied regressively to obtain the CP's of a large series of graphs by a simple paper-and-pencil method.

The $p(k)$ number (Hosoya 1972) of a graph G is the number of k collections of non-adjacent K_2 -subgraphs of G . If G contains no ring, its CP is given by

$$P(G; x) = \sum_{k=0}^m (-1)^k p(k) x^{n-2k}, \quad (1)$$

where m is the maximum possible value of k in G and n is the total number of vertices of G . If G contains rings, its CP is given by

$$P(G; x) = \sum_{k=0}^m (-1)^k p(k) x^{n-2k} + \sum_{s \in S} (-2)^{c(s)} x^{n-q}, \quad (2)$$

where S is a collection of disjoint rings with q vertices, s represents each member of

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this set and $c(s)$ is the number of components (i.e. rings) in s (Sachs 1962). A triad of graphs (G_1, G_2, G_3) is said to be a Fibonacci Triad (FT) if the set $(G_3 - G_2, G_3 - G_1, G_2 - G_1)$ consists only of the paths L_1 and L_2 (i.e. a single vertex and a path with two vertices). $G_i - G_j$ means a graph resulting from pruning G_j out of G_i (Hosoya 1972; El-Basil 1984). The following recurrence relation exists among the members of an FT:

$$p(G_1, k) + p(G_2, k + 1) = p(G_3, k + 1), \quad (3)$$

where $p(G, k)$ is the $p(k)$ number of the graph G .

Literature survey shows that after El-Basil's (1984) papers showing the method of construction of CP on the basis of relations (1) to (3), no work has been done to show its application in real chemical problems. The object of the present work is to demonstrate the application of the FT method in obtaining the CP's of a fairly large series of graphs (corresponding to aromatic radicals) and to show how these CP's can be used regressively to get the HOMO energies of a series of methylbenzenes graph-theoretically.

The organisation of the paper is as follows. In §2 the necessary graphs forming FT's have been explained. In §3 the CP's of the required graphs have been constructed by El-Basil's method. In §4 the HOMO energies of methylbenzenes have been calculated graph-theoretically in terms of the hyperconjugative Hückel parameters h_{Me} and k_{C-Me} of the methyl group. In these calculations the CP's obtained in §3 have been used regressively. In §5 a correlation of the HOMO energies with CT absorption maxima of methylbenzene-ICl complexes has been shown. This has led to suitable values of h_{Me} and k_{C-Me} .

2. Fibonacci triads of graphs representing the necessary aromatic radicals

The systems under the present study are methylbenzenes. Their π -MO energies have been calculated graph-theoretically on the basis of Coulson and Longuet-Higgins

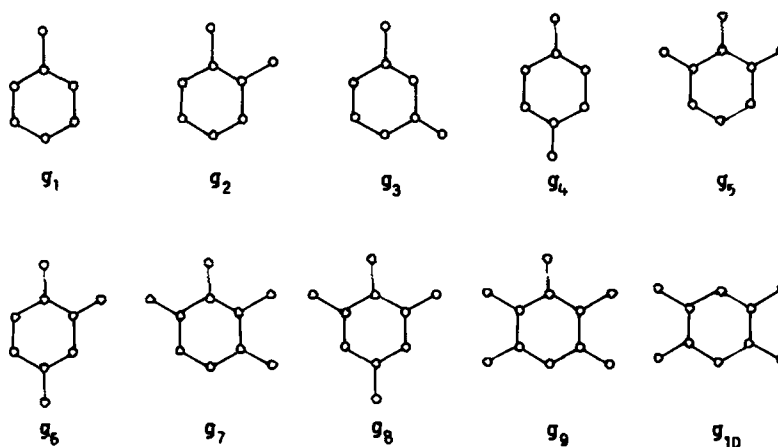


Figure 1. Graphs representing aromatic hydrocarbon radicals required for the present analysis.

(1947) perturbation technique. The unperturbed systems corresponding to them form a series of aromatic radicals obtained by replacing each $-\text{CH}_3$ by a $-\text{CH}_2$. The graphs representing their sp^2 -C atom connectivities are shown in figure 1. For example, g_1 represents the benzyl radical, the unperturbed system for toluene. The eigenvalues of the adjacency matrices of these graphs are the π -MO energies, (E_i^0) , of the aromatic hydrocarbon radicals in β units (Graovac *et al* 1972) where β is the C-C resonance integral in benzene.

Each graph in figure 1 is a member of an FT as shown in figure 2. In the triad FT (1), $G_3^{(1)} = g_1$; $G_3^{(1)} - G_1^{(1)} = L_2$, $G_2^{(1)} - G_1^{(1)} = L_1$ and $G_2^{(1)} - G_1^{(1)} = L_1$. Similarly in FT (2), $G_3^{(2)} = g_2$; $G_3^{(2)} - G_1^{(2)} = L_2$, $G_2^{(2)} - G_1^{(2)} = L_1$ and $G_2^{(2)} - G_1^{(2)} = L_1$. Thus FT(1), FT(2) etc. all satisfy the requirement of an FT.

3. Construction of CP's from the FT's

For the triad FT(1), the $p(k)$ numbers are as listed below. The $p(k)$ numbers of $G_1^{(1)}$ and $G_2^{(1)}$ have been obtained by simple counting and for $G_3^{(1)}$ the numbers have been obtained by the recursion formula (3).

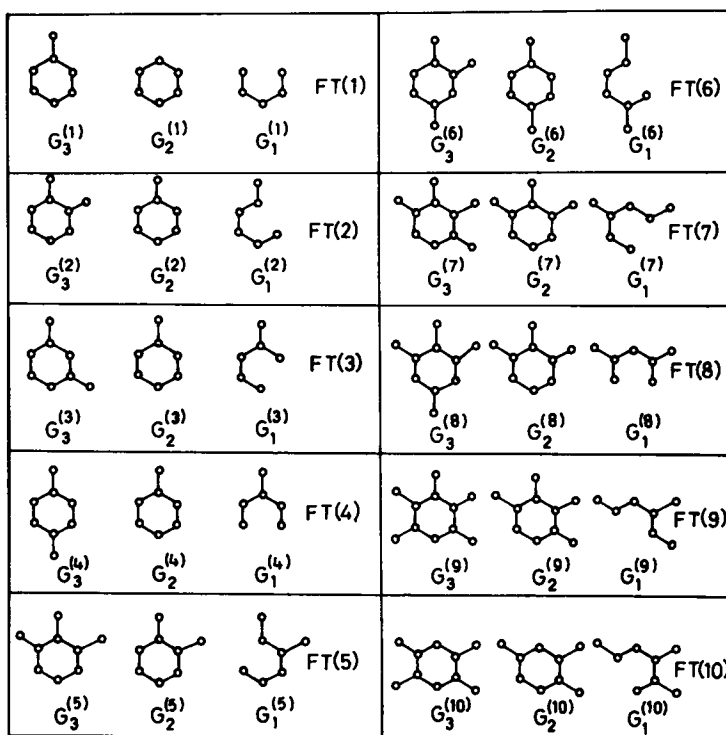


Figure 2. Fibonacci triads for the graphs in figure 1.

Triad FT(1):

	$p(0)$	$p(1)$	$p(2)$	$p(3)$
$G_1^{(1)}$	1	4	3	0
$G_2^{(1)}$	1	6	9	2
		↓	↓	↓
$G_3^{(1)}$	1	7	13	5

Considering the fact that the ring of $G_3^{(1)}$ contributes -2 to the coefficient of x^{7-6} according to (2), the CP of $G_3^{(1)}$ can be written down immediately from the third row:

$$P(G_3^{(1)}; x) = P(g_1; x) = x^7 - 7x^5 + 13x^2 - (5 + 2)x.$$

Triad FT(2): In this and all the subsequent triads great convenience is achieved through the fact that

$$G_2^{(2)} = G_2^{(3)} = G_2^{(4)} = G_3^{(1)},$$

$$G_2^{(5)} = G_3^{(2)}, \quad G_2^{(6)} = G_3^{(4)} \text{ etc.}$$

	$p(0)$	$p(1)$	$p(2)$	$p(3)$	$p(4)$
$G_1^{(2)}$	1	5	6	1	0
$G_2^{(2)} = G_3^{(1)}$	1	7	13	5	0
		↓	↓	↓	↓
$G_3^{(2)}$	1	8	18	11	1

The $p(k)$ numbers of the other triads are listed in table 1. The CP's of the last members of the triads are given in table 2, where the contribution -2 of the ring has been considered at the appropriate places.

4. Graph-theoretical calculation of HOMO energies of methylbenzenes in the hyperconjugative model

For calculation of π -MO energies the effect of CH_3 -groups attached to an aromatic ring can be treated in two models. In the first, the CH_3 exerts an inductive effect and changes the Coulomb integral of the conjugated C atom to which it is attached. Using such a model, trends in CT absorption bands have been analysed and the inductive effect Hückel parameter has been determined by a number of workers (Lepley 1964; Keyser 1974; Seal and Mukherjee 1984; Mukherjee and Seal 1986; Mukherjee and Das 1993a). In the second model the hyperconjugative effect of the methyl group is considered (Mulliken and Rieke 1941; Mulliken *et al* 1941; Matsen 1950). The π -MO's of a methylbenzene are regarded as the perturbed MO's of an "extended" conjugated system obtained by replacing each CH_3 by a CH_2 group (with the C atom sp^2 -hybridised). Now according to Coulson and Longuet-Higgins' (1947)

Table 1. $p(k)$ numbers of the triads FT(3)–FT(10).

Triad	Graph	$p(0)$	$p(1)$	$p(2)$	$p(3)$	$p(4)$	$p(5)$
FT(3)	$G_1^{(3)}$	1	5	5	0		
	$G_2^{(3)}$	1	7	13	5	0	
	$G_3^{(3)}$	1	8	18	10	0	
FT(4)	$G_1^{(4)}$	1	5	5	1	0	
	$G_2^{(4)}$	1	7	13	5	0	
	$G_3^{(4)}$	1	8	18	10	1	
FT(5)	$G_1^{(5)}$	1	6	9	3	0	
	$G_2^{(5)}$	1	8	18	11	1	
	$G_3^{(5)}$	1	9	24	20	4	
FT(6)	$G_1^{(6)}$	1	6	9	2	0	
	$G_2^{(6)}$	1	8	18	10	1	
	$G_3^{(6)}$	1	9	24	19	3	
FT(7)	$G_1^{(7)}$	1	7	13	7	1	
	$G_2^{(7)}$	1	9	24	20	4	0
	$G_3^{(7)}$	1	10	31	33	11	1
FT(8)	$G_1^{(8)}$	1	7	12	4	0	
	$G_2^{(8)}$	1	9	24	20	4	0
	$G_3^{(8)}$	1	10	31	32	8	0
FT(9)	$G_1^{(9)}$	1	8	18	12	2	
	$G_2^{(9)}$	1	10	31	33	11	1
	$G_3^{(9)}$	1	11	39	51	23	3
FT(10)	$G_1^{(10)}$	1	7	13	6	0	
	$G_2^{(10)}$	1	9	24	19	3	0
	$G_3^{(10)}$	1	10	31	32	9	0

Taking these $p(k)$ numbers and considering the contributions of rings at appropriate places, the CP's of the graphs in figure 1 are found to be as in table 2.

Table 2. CP's of the graphs in figure 1.

Graph	CP
g_1	$x^7 - 7x^5 + 13x^2 - 7x$
g_2	$x^8 - 8x^6 + 18x^4 - 13x^2 + 1$
g_3	$x^8 - 8x^6 + 18x^4 - 12x^2$
g_4	$x^8 - 8x^6 + 18x^4 - 12x^2 + 1$
g_5	$x^9 - 9x^7 + 24x^5 - 22x^3 + 4x$
g_6	$x^9 - 9x^7 + 24x^5 - 21x^3 + 3x$
g_7	$x^{10} - 10x^8 + 31x^6 - 35x^4 + 11x^2 - 1$
g_8	$x^{10} - 10x^8 + 31x^6 - 34x^4 + 8x^2$
g_9	$x^{11} - 11x^9 + 39x^7 - 53x^5 + 23x^3 - 3x$
g_{10}	$x^{10} - 10x^8 + 31x^6 - 34x^4 + 9x^2$

perturbation method, the energy of the j th MO of a methylbenzene is given by

$$E_j = E_j^0 + h_{\text{Me}}\beta \sum_r C_{rj}^2 + 2(k_{\text{C-Me}} - 1)\beta \sum_{r < s} C_{rj} C_{sj}, \quad (4)$$

where E_j^0 is energy of the j th MO of the corresponding unperturbed system (i.e. methylbenzene radical), r is the location of the methyl group, s is the location adjacent to r and C_{rj} and C_{sj} are the atomic orbital coefficients of the r th and s th atoms in the j th LCAO wave functions of the unperturbed system. The perturbational parameters h_{Me} and $k_{\text{C-Me}}$ are defined as follows:

$$\alpha' = \alpha + \delta\alpha = \alpha + h_{\text{Me}}\beta \text{ and } \beta' = k_{\text{C-Me}}\beta, \quad (5)$$

where $\delta\alpha$ is the change in Coulomb integral of the C-atom of the CH_2 group when it is converted into CH_3 and $\delta\beta = \beta' - \beta$ is the change in the resonance integral due to such a perturbation.

The quantity C_{rj}^2 can be calculated by the following graph theoretical formula (Mukherjee and Datta 1989).

$$C_{rj}^2 = [P(g - v_r; x)]/[d(P(g; x)/dx)], \text{ at } x = x_j. \quad (6)$$

Here g is the graph representing the unperturbed system (i.e. the aromatic hydrocarbon radical) which corresponds to the methylbenzene under consideration and $g - v_r$ is the Ulam subgraph (Ulam 1960) obtained by deleting the r th vertex from g . The most important advantage of using this formula in the present set of graphs (g_i) (figure 1) is that the necessary Ulam subgraphs all belong to the same set and hence (6) and the CP's of table 2 can be used regressively for all the methylbenzenes.

Thus, referring to the labelling scheme of g_5 as shown in figure 3, we have $g_5 - v_7 = g_5 - v_9 = g_2$ and $g_5 - v_8 = g_3$. The only exception is g_1 , but its Ulam subgraph $g_1 - v_1$ is a six-membered cycle C_6 whose CP is well known:

$$P(g_1 - v_1; x) = P(C_6; x) = x^6 - 6x^4 + 9x^2 - 4.$$

The quantities $C_{rj}C_{sj}$ (r, s adjacent) can be obtained graph-theoretically by the formula (Mukherjee and Das 1993b),

$$C_{rj}C_{sj} = [P(g - e_{rs}; x)]/[dP(g; x)/dx], \text{ at } x = x_j, \quad (7)$$

where $g - e_{rs}$ is the subgraph of g obtained by deleting the edge joining the vertices

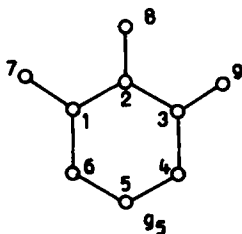


Figure 3. Graph representing the unperturbed system for 1,2,3-trimethylbenzene.

r and s . Here also we get the same advantage – the necessary subgraphs all belong to $\{g_i\}$ in figure 1. Thus

$$P(g_5 - e_{71}; x) = P(g_5 - e_{93}; x) = xP(g_2; x)$$

and

$$P(g_5 - e_{82}; x) = xP(g_3; x).$$

The CP's in table 2 are, therefore, self-contained for the purpose of calculation of the perturbational quantities in (4).

5. Correlation of the HOMO energies with the CT absorption maxima

In table 3 are given the energies of the HOMO and the calculated perturbational coefficients ΣC_r^2 and $\Sigma C_{rj}C_{sj}$ for the unperturbed systems corresponding to the polymethylbenzenes (PMB) under study. The CT transition energies of the π -type molecular complexes of these PMB's as donors with ICI as acceptor in CCl_4 medium are also given in table 3. Experimental data for the CT transition energies have been taken from the work of Farrel and Newton (1965).

The energy ($h\nu_{\text{CT}}$) of CT transition observed in a molecular complex is related to the vertical ionisation potential (I_D) of the donor and the vertical electron affinity (E_A) of the acceptor by the well-known equation (McConnell *et al* 1953; Mulliken and Person 1961),

$$h\nu_{\text{CT}} = I_D - E_A - C, \quad (8)$$

where C is a term which sums the contributions from nonbonding species, polarisation and solvation. The main part of C comes from the electrostatic attraction between the negatively charged acceptor and the positively charged donor in the excited state (Mulliken and Person 1969). Working with a common acceptor and a series of structurally related donors in a common solvent, we may use (8) in the form

$$h\nu_{\text{CT}} = -E_j + \text{const}, \quad (9)$$

Table 3. CT transition energies and calculated perturbational coefficients of PMB-ICI complexes in CCl_4 .

Donor	$h\nu_{\text{CT}}(\text{eV})$	Energy of HOMO (β)	$\sum_r C^2$	$\sum_{r>s} C_{rj}C_{sj}$
Toluene	4.3090	0	0.5714301	0
<i>p</i> -Xylene	4.2500	-0.3111078	0.6645892	-0.206761
<i>o</i> -Xylene	4.1645	-0.2949629	0.550935	-0.1680779
1,2,4-Trimethylbenzene	4.1505	-0.4194626	0.6305286	-0.2644823
1,2,3-Trimethylbenzene	4.0556	-0.488306	0.7502814	-0.3663668
1,2,3,4-Tetramethylbenzene	3.9776	-0.5062872	0.7832763	-0.3965627
1,2,3,5-Tetramethylbenzene	3.9776	-0.564508	0.7445881	-0.4203259
Pentamethylbenzene	3.8540	-0.6180339	0.7236066	-0.4472134

where E_j is the HOMO energy of the donor. Using (4) we now have

$$(h\nu_{CT} + E_j^0) = -h_{Me}\beta \sum_r C_{rj}^2 - 2(k_{C-Me} - 1)\beta \sum_{r < s} C_{rj} C_{sj} + \text{const.} \quad (10)$$

A linear regression analysis of the data in table 3 according to (10) yields $h_{Me} = 1.35$ and $k_{C-Me} = 0.98$ which are close to the previously reported values, $h_{Me} = 1.4-3.3$ and $k_{C-Me} = 0.8$, obtained from other types of experimental data (Matsen 1950; Streitwieser and Nair 1959). The value of β in this analysis has been taken to be -3.1 eV as obtained from the first four singlet-singlet transitions in benzene.

6. Concluding remarks

So far the use of FT's has been restricted to the calculation of CP only. In the present work it has been shown that application of such triads can also be extended to the calculation of eigenvector components and that the method is particularly useful when the systems (molecules/radicals) under study form a large series because the graphs involved can be used regressively after identifying them as components of suitable FT's. The same PMB's as used in this paper were considered in a previous work (Mukherjee and Datta 1989) but some group-theoretic methods were used there in conjunction with graph-theoretic techniques. In the present work, pure graph-theoretic methods have been applied and are found to be much less laborious.

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