

## Graph-theoretical calculation of products of eigen coefficients: Some application to charge-transfer complexes

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MS received 27 March 1992; revised 8 October 1992

**Abstract.** A graph-theoretical formula for computation of products of eigen coefficients  $C_{r_j}C_{s_j}$  ( $r \neq s$ ) of a graph has been derived. A general formula for the characteristic polynomial of a linear chain having a branch with a weighted pendant vertex has been given. These have been utilised, together with the Ulam subgraph method for obtaining squares of eigen coefficients, to take into account the perturbations in Coulomb and resonance integrals due to introduction of heteroatoms in a conjugated system or due to attachment of Me groups to conjugated atoms. Heteroatom Hückel parameters  $h$  and  $k$  of N and Me groups have been estimated and some structural information about a number of electron donors have been extracted by applying the results to the trends in the charge-transfer bands of their  $\pi$ -type molecular complexes.

**Keywords.** Graphs; eigen coefficients; charge-transfer complexes.

### 1. Introduction

The correlation between Hückel molecular orbital (HMO) theory and graph theory (GT) is well known. Molecules of conjugated hydrocarbons are represented by graphs (Graovac *et al* 1972) and those of heteroconjugated systems by vertex- and edge-weighted graphs (Gutman and Polansky 1986) such that with proper scaling of energy, the Hückel Hamiltonian matrix becomes the adjacency matrix of the graph.

Quite a large number of papers have appeared on construction of characteristic polynomials (CP) (Sachs 1962, Hosoya 1972, Mallion *et al* 1974, Aihara 1976 and Gutman and Polansky 1981, to mention a few). Many interesting chemical properties can be deduced by analysing the CP only, without actually evaluating the eigenvalues and eigenvectors (Rouvray 1976; Mukherjee 1986; Gutman and Mukherjee 1988; Mukherjee and Datta 1989; Gutman 1990). But so far no graph theoretical expression is known for evaluation of the product  $C_{r_j}C_{s_j}$  where  $r$  and  $s$  denote two adjacent conjugated atoms (i.e., two adjacent vertices of the graph) and  $C_{ij}$  means the  $i$ th component of the eigenvector corresponding to the  $j$ th eigenvalue,  $x_j$  ( $i = r, s$ ). The aim of the present communication is to find GT expressions for products of the type  $C_{r_j}C_{s_j}$  and use them for analysing the trends in the charge-transfer bands of a series of  $\pi$ -type molecular complexes having a common acceptor and a series of structurally similar donors.

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**2. Derivation of a graph-theoretical formula for  $C_{rj}C_{sj}$  and its verification**

For a graph  $G$  with adjacency matrix  $A$ , the secular equation

$$P(G; x) = \det(xI - A) = 0 \tag{1}$$

is a necessary condition for existence of solutions to the system of equations,

$$\begin{aligned} C_1(x - \omega_1) + C_2(-\omega_{12}) + C_3(-\omega_{13}) + \dots + C_n(-\omega_{1n}) &= 0 \\ C_1(-\omega_{21}) + C_2(x - \omega_2) + C_3(-\omega_{23}) + \dots + C_n(-\omega_{2n}) &= 0 \\ \vdots & \\ C_1(-\omega_{n1}) + C_2(-\omega_{n2}) + C_3(-\omega_{n3}) + \dots + C_n(x - \omega_n) &= 0 \end{aligned}, \tag{2}$$

where  $\omega_i$  and  $\omega_{ij}$  ( $= \omega_{ji}$ ) are, respectively, the weights of the vertex  $i$  and the edge  $(i, j)$ . In (1),  $P(G; x)$  is the characteristic polynomial (CP) of  $G$  and  $I$  is the unit matrix of the size of  $A$ . The coefficient vector  $[C_1 C_2 C_3 \dots C_n]^T$  is the eigenvector corresponding to eigenvalue  $x$  (superscript  $T$  denotes transpose). Since (1) has  $n$  roots  $x_j, j = 1$  to  $n$ , the eigenvector corresponding to the eigenvalue  $x_j$  is  $[C_{1j} C_{2j} C_{3j} \dots C_{nj}]^T$ , normalised to the condition

$$\sum_r C_{rj}^2 = 1. \tag{3}$$

Let us consider the change in  $x_j$  when a vertex-weight is changed from  $\omega_r$  to  $\omega_r + h_r$ , and an edge-weight is changed from  $\omega_{rs}$  to  $\omega_{rs} + \Delta\omega_{rs}$ .

Multiplying the first member of (2) by  $C_1$ , the second by  $C_2$  and so on, adding the results and rearranging, we have

$$x = \sum_r C_r^2 \omega_r + \sum_{r \neq s} C_r C_s \omega_{rs}, \tag{4}$$

where condition (3) has been utilised. Our desired change in  $x$  is

$$\delta x = \left( \frac{\partial x}{\partial \omega_r} \right) h_r + \left( \frac{\partial x}{\partial \omega_{rs}} \right) \Delta\omega_{rs} + \sum_r \left( \frac{\partial x}{\partial C_r} \right) \delta C_r. \tag{5}$$

The coefficients  $\{C_r\}$  in the set of equations (2) have been obtained by minimising  $x$  w.r.t. small arbitrary variations in  $\{C_r\}$  so that the last term of (5) vanishes. Hence from (4) and (5) we have after putting  $x = x_j$ ,

$$\delta x_j = \sum_r C_{rj}^2 h_r + \sum_{r \neq s} C_{rj} C_{sj} \Delta\omega_{rs}. \tag{6}$$

The squares of the eigen coefficients,  $C_{rj}^2$ , can be determined by employing the Ulam subgraph technique (Mukherjee and Datta 1989). The value of  $C_{rj}C_{sj}$  can be obtained graph-theoretically by the formula

$$C_{rj}C_{sj} = \frac{P(G - e_{rs}; x)}{P'(G; x)} \Big|_{x=x_j}, \tag{7}$$

where the numerator is the CP of the subgraph obtained from  $G$  by deleting the  $(r, s)$  edge (denoted by  $e_{rs}$ ) and  $P'(G; x)$  is the first-order derivative with respect to  $x$  of the CP of  $G$ . This formula can be derived as follows:

With fixed values of  $\{\omega_r\}$  of a graph  $G$ ,

$$f(P, x, \omega_{rs}) = 0,$$

where the symbol  $P$  has been used for  $P(G; x)$ . Hence

$$\left(\frac{\partial P}{\partial x}\right)_{\omega_{rs}} \left(\frac{\partial x}{\partial \omega_{rs}}\right)_P \left(\frac{\partial \omega_{rs}}{\partial P}\right)_x = -1,$$

or

$$\begin{aligned} \left(\frac{\partial P}{\partial \omega_{rs}}\right)_x &= -\left(\frac{\partial P}{\partial x}\right)_{\omega_{rs}} \left(\frac{\partial x}{\partial \omega_{rs}}\right)_P \\ &= -C_r C_s P'(G; x), \text{ using (6).} \end{aligned} \tag{8}$$

If the edge-weight  $\omega_{rs}$  is increased by an amount  $\Delta\omega_{rs}$ , the resulting change in  $P(G; x)$  is,

$$\Delta P = \left(\frac{\partial P}{\partial \omega_{rs}}\right) \Delta\omega_{rs} = -C_r C_s P'(G; x) \Delta\omega_{rs}. \tag{9}$$

If  $G$  is initially unweighted and we construct a new graph  $G'$  by deleting the  $(r, s)$  edge of  $G$ , then

$$\Delta\omega_{rs} = (0 - 1) = -1,$$

so that the CP of  $G'$  is

$$P(G'; x) = P(G; x) + \Delta P = P(G; x) + C_r C_s P'(G; x),$$

and putting  $x = x_j$  we have

$$P(G'; x_j) = C_r C_s P'(G; x_j), \tag{10}$$

which gives the formula, (7):

$$C_r C_s = \frac{P(G - e_{rs}; x)}{P'(G; x)} \Big|_{x=x_j}.$$

**Example 1. Propene:** Its molecular graph  $\bar{G}_1$  is shown in figure 1 together with the subgraph required for computation of  $C_{2j}C_{3j}$  corresponding to  $x_j = \sqrt{2}$ .

Here  $P(\bar{G}_1) = x^3 - 2x$  and  $P(\bar{G}_1 - e_{23}; x) = x(x^2 - 1)$ . Thus, for  $x_j = \sqrt{2}$ ,  $C_{2j}C_{3j} = x(x^2 - 1)/(3x^2 - 2) = \frac{1}{2}\sqrt{2}$ , at  $x = \sqrt{2}$ .

**Example 2. p-Xylyl radical:** The molecular graph and subgraph required for computation of  $C_{1j}C_{7j}$  with  $x_j = -2.1700865$  are  $\bar{G}_2$  and  $\bar{G}_2 - e_{17}$  as shown in figure 2.

Here  $P(\bar{G}_2; x) = x^8 - 8x^6 + 18x^4 - 12x^2 + 1$  with eigenspectrum  $(\pm 2.1700865, \pm 1.4811943, \pm 1, \pm 0.3111078)$  and  $P(\bar{G}_2 - e_{17}; x) = x(x^7 - 7x^5 + 13x^3 - 7x)$ . Thus for  $x_j = -2.1700865$ ,  $C_{1j}C_{7j} = P(\bar{G}_2 - e_{17}; x_j)/P(\bar{G}_2; x_j) = -0.0861922$ .

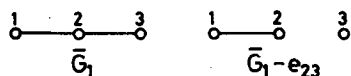


Figure 1. Construction of subgraph for  $C_{2j3j}$  of propene.

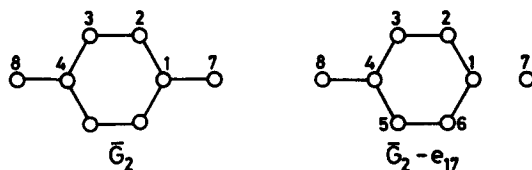


Figure 2. Construction of subgraph for  $C_{1j7j}$  of *p*-xylyl radical.

### 3. Trends in charge-transfer absorption maxima of some molecular complexes

The energy of electronic charge-transfer (CT) absorption,  $h\nu_{CT}$ , of the molecular complexes of some aromatic amines and methylated anilines with tetracyanoethylene (TCNE) in chloroform are given in tables 1 and 2. Such transition energies obey the well-known McConnell–Ham–Platt (1953) equation,

$$h\nu_{CT} = I_D - E_A - C, \quad (11)$$

where  $I_D$  is the vertical ionisation potential of the donor,  $E_A$  is the vertical electron affinity of the acceptor and  $C$  is a term which takes into account the interaction between the nonbonding species, solvation, coulombic attraction etc. The main part of  $C$  comes from coulombic attraction between the positively charged donor and the negatively charged acceptor in the excited state (Mulliken and Person 1969). Working with a common acceptor and a series of structurally similar donors in a common solvent, one may write (11) as,

$$h\nu_{CT} = -I_D + \text{constant}. \quad (12)$$

If  $E_D$  denotes the energy of the highest occupied molecular orbital (HOMO) of the donor, then (12) can be written as

$$h\nu_{CT} = -E_D + \text{constant}. \quad (13)$$

The apparently scattered values of  $h\nu_{CT}$  shown in tables 1 and 4 (below) can be shown by (13) to follow a regular trend if  $E_D$  can be calculated. From such trends, some structural features/parameters of the donors can be derived. In order to determine a regularity in the observed  $h\nu_{CT}$  values, we shall calculate  $E_D$  by HMO formalism using Coulson–Longuet-Higgins (1947) perturbation formula. The kind of perturbation we are going to consider is, for example, that caused by replacement of an  $sp^2$ -carbon atom by N or by attachment of methyl group(s) to one (or several)  $sp^2$  carbon atom(s) of a  $\pi$ -conjugated system. According to Coulson and Longuet-Higgins (1947)

$$E_D = E_j^0 + \alpha_r \sum_r C_{rj}^2 + 2\delta\beta_{rs} \sum_{r<s} \sum C_{rj} C_{sj} = E_j^0 + h_r \beta \sum_r C_{rj}^2 + 2(k_{rs} - 1)\beta \sum_{r<s} \sum C_{rj} C_{sj} \quad (14)$$

**Table 1.** Some aromatic amines, characteristic polynomials (CP) of the unperturbed systems corresponding to these amines, and CT transition energies of the amine-TCNE complexes.

Amine	CP of the unperturbed system	Graph	$h\nu_{CT}$ (eV)
Aniline	$x^7 - 7x^5 + 13x^3 - 7x$	$G_1$	2.097
2-Amino-naphthalene	$x^{11} - 12x^9 + 50x^7 - 90x^5 + 69x^3 - 17x$	$G_2$	1.763
1-Amino-naphthalene	$x^{11} - 12x^9 + 50x^7 - 91x^5 + 72x^3 - 20x$	$G_3$	1.676
2-Aminopyrene	$x^{17} - 20x^{15} + 160x^{13} - 666x^{11} + 1567x^9 - 2112x^7 + 1563x^5 - 556x^3 + 63x$	$G_4$	1.813
1-Aminopyrene	$x^{17} - 20x^{15} + 160x^{13} - 667x^{11} + 1579x^9 - 2165x^7 + 1670x^5 - 657x^3 + 99x$	$G_5$	1.316
6-Aminochrysen	$x^{19} - 22x^{17} + 199x^{15} - 969x^{13} + 2793x^{11} - 4928x^9 + 5307x^7 - 3357x^5 + 1133x^3 - 156x$	$G_6$	1.453

**Table 2.** Eigenspectra of the graphs in table 1.

Graph	Eigenspectra
$G_1$	$0, \pm 1, \pm 1.259280, \pm 2.101003$
$G_2$	$0, \pm 0.67573, \pm 1.12321, \pm 1.32776, \pm 1.75351, \pm 2.33324$
$G_3$	$0, \pm 1, \pm 2.351365, \pm 0.7990816, \pm 1.414214, \pm 1.683018$
$G_4$	$0, \pm 0.4450419, \pm 1, \pm 1, \pm 1.2469796, \pm 1.5166977, \pm 1.8019377, \pm 2.0589131, \pm 2.5417523$
$G_5$	$0, \pm 0.6124157, \pm 0.9145267, \pm 1, \pm 1.2819131, \pm 1.453648, \pm 1.8179311, \pm 2.058713, \pm 2.54742$
$G_6$	$0, \pm 0.6831541, \pm 2.5199198, \pm 2.18650479, \pm 0.793859, \pm 0.8999696, \pm 1.2181659, \pm 1.346575, \pm 1.658398, \pm 1.707299$

and from (13)

$$h\nu_{CT} = -E_j^0 - h_r \beta \sum_r C_{rj}^2 - 2(k_{rs} - 1) \beta \sum_{r < s} C_{rj} C_{sj} + \text{constant}, \quad (15)$$

where  $j$  is the index of the HOMO,  $E_j^0$  is the energy,  $C_{rj}$  and  $C_{sj}$  are the coefficients of the  $r$ th and  $s$ th atoms respectively in the  $j$ th MO of the corresponding unperturbed system obtained on replacing the  $r$ th atom (where perturbation has occurred) by an  $sp^2$ -hybridised C atom and  $s$  is the location adjacent to  $r$ . The Hückel parameters  $h_r$  and  $k_{rs}$  are defined as

$$\alpha_r = \alpha + \delta\alpha_r = \alpha + h_r \beta, \quad (16a)$$

$$\beta_{rs} = k_{rs} \beta, \quad (16b)$$

to take into account the changes in Coulomb and bond (or resonance) integrals caused by perturbation. In (16),  $\alpha$  is the standard Coulomb integral of the  $sp^2$ -C atom in benzene and  $\beta$  is the standard bond (or resonance) integral between two adjacent  $sp^2$ -C atoms in benzene. In the HMO energy scale,  $\alpha$  and  $\beta$  are regarded respectively as zero and the unit of energy. With such a scaling of  $\pi$ -MO energy, the molecular structure, representing only the connectivities of the conjugated atoms of the molecule, is the molecular graph.  $sp^2$ -C atoms which are not perturbed (in the sense mentioned

earlier) are vertices with no self-loops and those ( $r$ ) which are perturbed are vertices with self-loops of weight  $h_r$ . Similarly the bond between two unperturbed  $sp^2$ -C atoms is an edge of weight 1 but if a bond between two adjacent atoms  $r$  and  $s$  is perturbed, it is represented in the graph by an edge  $e_{rs}$  of weight  $k_{rs}$ . From now on the HMO energy  $E_j$  and the graph eigenvalue  $x_j$  will be taken to be synonymous.

We now consider two sets of charge-transfer complexes A and B separately.

*Case A. Complexes of some aromatic amines with TCNE in  $CHCl_3$ :* The unperturbed systems corresponding to the amines appearing in table 1 are graphically represented in figure 3. The characteristic polynomials of these graphs are given in table 1 together with the CT transition energies of the amine-TCNE complexes. Eigenspectra of the graphs in figure 3, obtained by solving the equation  $CP = 0$  numerically (using the Newton-Raphson method), are shown in table 2. From these it will be evident that in each case the HOMO of the unperturbed system is a nonbonding MO (recalling that the  $-NH_2$  group contributes two  $\pi$ -electrons to conjugation). If we denote the location of the N atom by 1 and the HOMO by index  $j$ , then for the second term in (15) we require the value of  $C_{1j}^2$ , which can be calculated by the Ulam subgraph method (Mukherjee and Datta 1989) as

$$C_{1j}^2 = P(G - v_1; x) / P'(G; x) \text{ at } x = x_j = 0. \quad (17)$$

For the time-being we neglect the third term of (15) and so we have

$$h\nu_{CT} = -h_N \beta C_{1j}^2 + \text{constant}. \quad (18)$$

The values of  $C_{1j}^2$  computed according to (17) are shown in table 3. As shown in figure 4, the plot of  $h\nu_{CT}$  against  $C_{1j}^2$  is linear (dotted line), as expected from (18), but the slope of the straight line ( $= 2.9306$ ) gives  $h_N = 0.945$  (taking  $\beta = -3.1 \text{ eV}$  as obtained from the first four singlet-singlet transitions in benzene). The linear

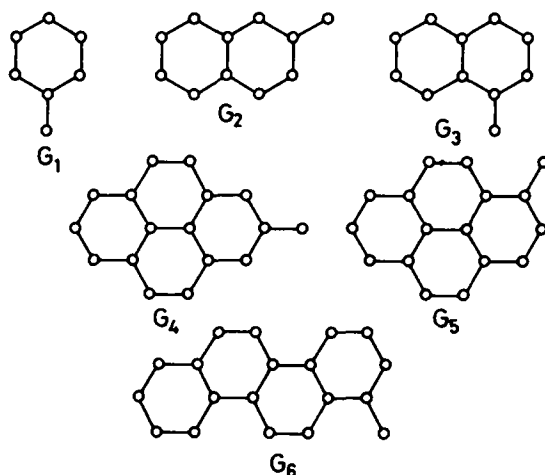
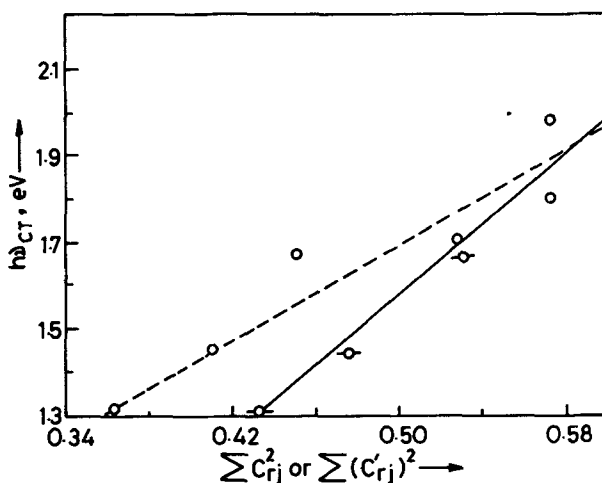


Figure 3. Graphs of the unperturbed systems corresponding to the aromatic amines of table 1.  $G_1$  = aniline,  $G_2$  = 2-aminonaphthalene,  $G_3$  = 1-aminonaphthalene,  $G_4$  = 2-amino-pyrene,  $G_5$  = 1-amino-pyrene and  $G_6$  = 6-amino-chrysene.

**Table 3.** Perturbational coefficients for the amines considered in case A

Amine (donor)	$C_{1j}^2$	$C_{1j}^2(1 + 0.15 \sum_{i \neq j}^{occ} 2C_{1i}C_{2i}/x_i)^2$
Aniline	0.57143	No steric hindrance
2-Amino-naphthalene	0.52940	No steric hindrance
1-Amino-naphthalene	0.45000	0.52730
1-Aminopyrene	0.36364	0.43540
6-Aminochrysen	0.41026	0.47556

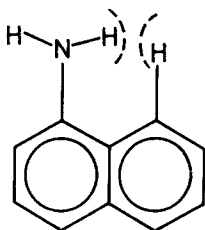
**Figure 4.** Plots of transition energy against calculated perturbational coefficients for complexes of aromatic amines with TCNE.  $\circ$  = cases considering no steric hindrance;  $\circ$ — = considering steric hindrance where it arises.

correlation is,

$$h\nu_{CT} = 2.9306 C_{1j}^2 + 0.2717, \quad (19)$$

with a correlation coefficient of 0.93. The value of  $h\nu_{CT}$  thus obtained is far away from Streitwieser's (1961) recommended value, 1.5. The value is improved when it is recognised that the  $-\text{NH}_2$  groups in 1-aminonaphthalene, 1-aminopyrene and 6-aminochrysen are sterically hindered as shown in figure 5; this causes rotation about the C-N bond through some angle and thus prevents the nitrogen  $2p_z$  orbital from being parallel to the  $2p_z$  orbitals of the C-atoms in the ring. (For the sake of simplicity we assume the N atom of  $-\text{NH}_2$  to be in a state of  $sp^2$  hybridization with the unhybridised  $2p_z$  orbital, parallel to those of the ring carbon atoms, when there is no steric hindrance.) Let us consider the change in  $C_{1j}$  as a result of the above kind of twisting of the  $-\text{CH}_2$  group in the hydrocarbon radical analogous to the respective amine. Let  $\theta$  be the angle between the  $2p_z$  orbital of the  $-\text{CH}_2$  group and that of the attached C atom of the ring. The change in  $\beta$  resulting from this is given by (Streitwieser 1961):

$$\delta\beta = \beta' - \beta = \beta \cos \theta - \beta. \quad (20)$$



**Figure 5.** Steric effect in 1-aminonaphthalene; the  $-\text{NH}_2$  group rotates about the C-N bond to increase the distance of one H-atom of  $-\text{NH}_2$  from the nearest H-atom of the adjacent ring.

The nonbonding MO in the respective hydrocarbon radical is changed by such a perturbation (Murrell 1963) according to the following expression:

$$\psi'_j = \psi_j + \sum_{i \neq j}^{\text{occ}} (H_{ij} / -E_i) \cdot \psi_i, \quad (21)$$

where  $j$  is the index of the HOMO (i.e. the index of the nonbonding MO as already mentioned) and  $i$  is the index for all the other occupied MO's.  $H_{ij}$  is the matrix element of the perturbation operator corresponding to the twisting of the  $2p_z$  orbital of the  $-\text{CH}_2$  group by an angle  $\theta$  and  $E_i$  is the energy of the  $i$ th occupied MO in units of  $\beta$ . The value of the eigen coefficient of the C atom of the  $-\text{CH}_2$  group after the above kind of twisting (perturbation) becomes

$$C'_{1j} = C_{1j} + 2C_{1j} \delta\beta \sum_{i \neq j}^{\text{occ}} C_{1i} C_{2i} / (-x_i). \quad (22)$$

For the quantity  $C_{1i} C_{2i}$  we can use the graph-theoretical formula, (7). We tentatively assume  $\delta\beta = -0.15\beta$ , which corresponds to  $\cos \theta = 0.85$  i.e.,  $\theta = 31.7^\circ$  and we have from (22),

$$(C'_{1j})^2 = (C_{1j})^2 \left[ 1 + 0.15 \left( \sum_{i \neq j}^{\text{occ}} 2C_{1i} C_{2i} / x_i \right) \right]^2. \quad (23)$$

These are calculated by using (7) and (23) and are given in table 3. When these, together with the other three non-hindered cases, are linearly correlated, we get the straight line (depicted in figure 4 by a solid line)

$$h\nu_{\text{CT}} = 4.8105(C_{1j})^2 - 0.8075, \quad (24)$$

with a better correlation coefficient of 0.94. In (24)  $C_{1j}^2$  should be read as  $(C'_{1j})^2$  for the sterically hindered cases. The slope gives  $h_{\text{N}} = 1.55$ , a value almost identical with that recommended by Streitwieser (1961). The linearity also suggests that  $(k_{\text{C-N}} - 1)$  of (15) = 0, i.e.  $k_{\text{C-N}} = 1$  (Streitwieser's recommended value is 0.8).

*Case B. Complexes of methylated anilines and N,N-dimethyl anilines with TCNE in  $\text{CHCl}_3$ :* Experimental data for these systems, taken from the work of Farrel and Newton (1965, 1966) are presented in tables 4 and 5. In order to estimate the inductive



**Table 4.** Complexes of methylated anilines with TCNE in chloroform.

Donor	$h\nu_{CT}$ (eV)	$\sum_r C_{r4}^2$
<i>o</i> -Toluidine	1.940	0.14676
<i>p</i> -Toluidine	1.925	0.23974
<i>m</i> -Toluidine	2.019	0.02608
3-Amino-1,5-dimethylbenzene	1.961	0.05216
2-Amino-1,3-dimethylbenzene	1.839	0.29352
3-Amino-1,2-dimethylbenzene	1.881	0.17284
2-Amino-1,4-dimethylbenzene	1.867	0.17284
4-Amino-1,3-dimethylbenzene	1.786	0.38651

**Table 5.** Complexes of methyl substituted N,N-dimethylanilines with TCNE in chloroform.

Donor	$h\nu_{CT}$ (eV)	$\sum_r C_{r4}^2$	$h\nu_{CT} - 0.3\beta C_{14} C_{74}$	$\sum_r (C_{r4}^2)^2$
N,N-dimethylaniline	1.839	0.48597	1.649	0.47424
2-Methyl-N,N-dimethylaniline	1.774	0.63273	1.584	0.60725
4-Methyl-N,N-dimethylaniline	1.749	0.72572	1.559	0.71573
2,6-Dimethyl-N,N-dimethylaniline	1.655	0.77950	1.465	0.74025
2,4-Dimethyl-N,N-dimethylaniline	1.612	0.87253	1.422	0.84873

effect of the  $\text{CH}_3$ -group the unperturbed system has been taken to be aniline and the perturbation formula,

$$E_D = E_j^0 + h_{Me} \beta \sum C_{rj}^2, \quad (25)$$

was first attempted; here  $r$  is the location of the methyl group and  $j$  is the index of the HOMO of aniline. As aniline is the unperturbed system for all donors in tables 4 and 5,  $E_j^0$  is a constant in the series and (13) and (24) can be combined as

$$h\nu_{CT} = -h_{Me} \beta \sum C_{rj}^2 + \text{constant}. \quad (26)$$

With  $h_N = 1.5$  and  $k_{C-N} = 1$  as obtained in case A, the graph of aniline,  $G_7$  (figure 6), has the CP,

$$P(G_7; x) = x^7 - 1.5x^6 - 7x^5 + 9x^4 + 13x^3 - 13.5x^2 - 7x + 6, \quad (27)$$

with eigenspectrum (2.35426, 1.66781, 1, 0.65968, -1, -1.12777, -2.05398). The HOMO eigenvalue is  $x_4 = 0.65968$  (in  $\beta$  unit). Now, to calculate  $C_{rj}^2$  for aniline, we shall often require the CP of a graph of the type  $G_8$  as shown in figure 7. We shall denote such a graph by  $L_n^{(i)}(h, k)$  to indicate that it is a linear chain with  $(n+1)$  vertices having a weighted pendant vertex attached to the  $i$ th vertex of the chain by an edge of weight  $k$ . CP of such a graph can be written as

$$P[L_n^{(i)}(h, k)] = (x-h)L_n - k^2 L_{(i-1)} L_{(n-i)}, \quad (28)$$

with  $L_0 = 1$  and  $i \geq 1$  where  $L_r$  is the CP of a path graph with  $r$  vertices and no self-loops or edge-weights:

$$L_r = \sum_{p=0}^{\lfloor r/2 \rfloor} (-1)^p \binom{r-p}{p} x^{r-2p} \tag{29}$$

Here  $\lfloor r/2 \rfloor$  is the greatest integer not exceeding  $r/2$ . As some sample calculations, we take the following cases.

(a) *p-Toluidine*: Referring to the vertex labels shown in figure 6, the perturbational coefficient required for computing the inductive effect of  $-\text{CH}_3$  is

$$\begin{aligned} C_{44}^2 &= P(G_7 - v_4; x)/P'(G_7; x), \text{ at } x = x_4, \\ &= P[L_5^{(3)}(h, k); x]/P'(G_7; x), \text{ at } x = x_4, \\ &= [(x - h) L_5 - k^2 L_2 L_2]/P'(G_7; x), \text{ at } x = x_4, \end{aligned} \tag{30}$$

which on simplification gives

$$C_{44}^2 = 0.23974. \tag{31}$$

(b) *m-Toluidine*:

$$\begin{aligned} C_{34}^2 &= P(G_7 - v_3; x)/P'(G_7; x), \text{ at } x = x_4, \\ &= P[L_5^{(2)}(h, k); x]/P'(G_7; x) \text{ at } x = x_4, \\ &= 0.02608. \end{aligned} \tag{32}$$

(c) *o-Toluidine*:

$$\begin{aligned} C_{24}^2 &= P(G_7 - v_2; x)/P'(G_7; x), \text{ at } x = x_4, \\ &= P[L_5^{(1)}(h, k); x]/P'(G_7; x), \text{ at } x = x_4, \\ &= 0.14676. \end{aligned} \tag{33}$$

Results of such calculations for methylated anilines and methylated N,N-dimethyl anilines are given in tables 4 and 5, respectively, together with experimental CT-transition energies. When the  $h\nu_{\text{CT}}$  values of the molecular complexes of these anilines with TCNE in  $\text{CHCl}_3$  solvent are plotted against the perturbational coefficients

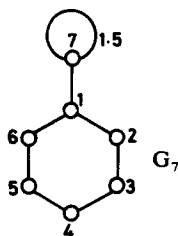


Figure 6. Molecular graph of aniline.

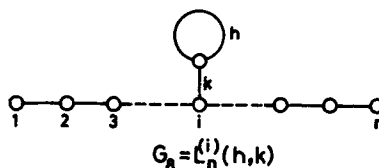


Figure 7. A linear chain having a pendant vertex of weight  $h$  attached to the  $i$ th vertex by an edge of weight  $k$ .

$\sum_r C_{rj}^2$  ( $j = \text{HOMO}$ ), we get the least-squares linear correlation:

$$h\nu_{\text{CT}} = -0.3884 \sum_r C_{rj}^2 + 1.9832, \quad (34)$$

with a correlation coefficient of 0.95. The slope gives a very low value of  $h_{\text{Me}}$ , viz.  $-0.12$ . The standard deviations in the slopes and intercepts are  $\pm 10.3$  and  $\pm 0.96\%$ , respectively. But such large standard deviations can be greatly reduced if we consider the methylated N,N-dimethylanilines separately. Owing to steric hindrance by ortho-hydrogen atoms or ortho-substituents, the  $-\text{NMe}_2$  group is twisted by some angle  $\theta$  about the C-N bond so that the  $2p_z$  orbital of N no longer remains parallel to those of the C-atoms in the ring. This twisting causes a change in the C-N resonance integral according to (20), and the HOMO wavefunction is modified as,

$$\begin{aligned} \psi'_4 &= \psi_4 + \sum_{i \neq 4}^{\text{occ}} H_{i,4} \psi_4 / (E_4 - E_i) \\ &= \psi_4 + \sum_{i \neq 4}^{\text{occ}} H_{i,4} \psi_4 / (x_4 - x_i), \end{aligned} \quad (35)$$

where  $i$  is the index for the occupied MO's and  $H_{i,4}$  is the matrix element of the perturbation operator corresponding to the twisting of the  $2p_z$  orbital of the N-atom. In the graph  $G_7$  where N occupies the 7th position, the modification of the atomic orbital coefficients resulting from (35) is given by

$$C'_{r4} = C_{r4} + 2C_{r4} \delta\beta_{17} \sum_{i \neq 4}^{\text{occ}} C_{1i} C_{7i} / (x_4 - x_i). \quad (36)$$

The energy of the HOMO is modified by the above perturbation as,

$$E_4 = E_4^0 + 2\delta\beta_{17} C_{14} C_{74},$$

or, writing  $x_j$  for  $E_j$ ,

$$x_4 = x_4^0 + 2\delta\beta_{17} C_{14} C_{74}. \quad (37)$$

A combination of (13), (25) and (37) gives, for the sterically hindered cases (i.e., methylated N,N-dimethylanilines)

$$h\nu_{\text{CT}} + x_4^0 + 2\delta\beta_{17} C_{14} C_{74} = -h_{\text{Me}} \beta \sum_r (C'_{r4})^2 + \text{constant}$$

or

$$h\nu_{\text{CT}} + 2\delta\beta_{17} C_{14} C_{74} = -h_{\text{Me}} \beta \sum_r (C'_{r4})^2 + \text{constant}, \quad (38)$$

where  $C'_{r4}$  is the coefficient of the  $r$ th atom in the perturbed HOMO of the donor and  $r$  denotes the location of the methyl group. It is found that with  $\delta\beta = -0.15\beta$ , the graphical plot for the complexes of N,N-dimethylanilines according to (38), and the plot of  $h\nu_{\text{CT}}$  against  $\sum_r C_{rj}^2$  for the methyl substituted anilines, form a single straight line. By least-squares method the slope and intercept of this straight line are found

to be  $-0.7145$  and  $2.0293$  with improved standard deviations of  $5.18\%$  and  $0.84\%$ , respectively, and the correlation coefficient,  $0.99$ , is also better than that of (34). The value,  $h_{Me} = -0.23$ , now obtained from the slope is in fair agreement with the values obtained by some other workers [for example, Lepley (1964) obtained  $h_{Me} = -0.29$ , Keyserl (1974) obtained  $h_{Me} = -0.3$ ] from CT bands but without using graph-theoretical methods. The angle of twist  $\theta$  is obtained as follows:

$$\beta_{C-N} = k_{C-N}\beta = \beta \text{ (as } k_{C-N} = 1),$$

$$\delta\beta_{C-N} = -0.15\beta = \beta_{C-N}\cos\theta - \beta = (\cos\theta - 1)\beta,$$

which yields  $\cos\theta = 0.85 = \cos 32^\circ$ .

The value ( $\theta = 32^\circ$ ) is in excellent agreement with the value ( $34^\circ$ ) obtained from dipole moment measurements (Smith 1955).

#### 4. Conclusions

The first part of the work reports a graph theoretical formula for computing products of MO coefficients corresponding to any desired eigenvalue within the Hückel model. In the second part, this formula has been used to explain the trends in CT bands of many molecular complexes. From such trends, the Hückel parameters  $h$  and  $k$  of conjugated N-atoms and also of the  $CH_3$ -groups exerting inductive effects have been determined. Some steric features of polynuclear aromatic amines and N,N-dimethyl anilines have been derived from the CT bands, which agree with dipole moment results. In passing, a general formula for the CP of a linear chain having a branch with a weighted pendant vertex has been constructed and used in the calculations.

Although the Hückel theory is a naive- $\pi$ -electron theory, and many sophisticated methods are now available, it has not yet lost its relevance or utility for more than one reason. Firstly, many experimentally observed trends can be interpreted in spite of the crude assumptions because empirical values of  $\alpha$  and  $\beta$  are used which implicitly take into account the intricate many-electron effects (Fukui 1962). Secondly, Hückel results are often better than those given by some other methods of calculation involving fewer approximations (Hess and Schaad 1971; Cvetković *et al* 1979). Thirdly, for a sophisticated all-electron (or all-valence-electron) calculation the experimental organic molecules (for example, those forming CT complexes) are large enough, necessitating large computers. To a chemist interested in explaining the trends in some experimental results, simpler methods may not seem less satisfactory than the sophisticated ones. Most importantly, graph theory in quantum chemistry has so far been found to suit most HMO formalisms. The last factor has prompted us to determine methods of application of GT in the field of CT complexes. The validity of the new graph-theoretic formula has been established not only by the agreement of the  $h$  and  $k$  values determined presently, with those obtained many years ago by other methods, but also by structural information obtained from dipole moment measurements.

#### Acknowledgements

The authors thank the referees for their valuable comments. DKD is also grateful to the University Grants Commission for financial assistance to this project.

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