

## Study of trends in charge-transfer absorption maxima of some $\pi$ -type molecular complexes using graph-theoretical techniques

DEBES K DAS<sup>1</sup>, ASOK K MUKHERJEE\*<sup>2</sup> and IVAN GUTMAN<sup>3</sup>

<sup>1</sup>Chemistry Department, Bankura Sammilani College, Bankura 722 101, India

<sup>2</sup>Department of Chemistry, Burdwan Raj College, Burdwan 713 104, India

<sup>3</sup>Faculty of Science, University of Kragujevac, YU-34000 Kragujevac, Yugoslavia

MS received 10 February 1990; revised 25 June 1990

**Abstract.** The change in charge-transfer absorption maxima of the  $\pi$ -type molecular complexes formed between chloranil and a series of phenols with varying number and position of the phenolic OH group(s) is shown to follow a certain trend. For this purpose the Coulson–Longuet-Higgins method in HMO formalism is used. The necessary eigenvector components are computed by employing a recently developed graph-theoretical technique, which avoids the calculation of the unnecessary eigenvectors. From the trends in the charge-transfer bands, the perturbational HMO parameters  $h$  and  $k$  for the phenolic oxygen and the C(sp<sup>2</sup>)–O bond, respectively, were obtained in a straightforward way and found to be in good agreement with previously recommended values, determined by other methods.

**Keywords.** Charge-transfer complex; Ulam subgraph; characteristic polynomial; eigenvector; HMO parameter.

### 1. Introduction

The electronic charge-transfer (CT) transition energies of molecular (or, electron donor–acceptor, EDA) complexes are given by the empirical McConnell–Hain–Platt (McConnell *et al* 1953) equation,

$$h\nu_{CT} = I_D - E_A - C, \quad (1)$$

which was later theoritised by Mulliken and Person (1961). Here  $I_D$  is the vertical ionization potential of the donor,  $E_A$  is the vertical electron affinity of the acceptor and  $C$  is a term obtained from various factors like solvation of the donor and acceptor in their ground states before complex formation and of the complex in the excited state, coulombic attraction between the positively charged donor and the negatively charged acceptor in the excited state (Mulliken and Person 1969) etc. Working with a common acceptor and a series of structurally similar donors in a given solvent, one expects from (1) a linear relationship between  $\nu_{CT}$  and  $I_D$ . The latter, in turn, may be regarded as the negative of the energy ( $E_D$ ) of the highest occupied molecular orbital (HOMO) of the donor. Thus one obtains

$$h\nu_{CT} = -E_D + \text{const.} \quad (2)$$

---

\*For correspondence

## 2. Principles and method

According to the Coulson–Longuet-Higgins (Coulson and Longuet-Higgins 1947) perturbational method in HMO formalism,  $E_D$  of a phenol is obtained from the HOMO energy ( $E_j^0$ ) of the corresponding parent hydrocarbon produced by replacing  $-\text{OH}$  by  $-\text{CH}_2$ , by applying the equation

$$E_D = E_j^0 + h_o \beta \sum_r C_{rj}^2 + (k_{C-O} - 1) \beta \sum_{r \neq s} C_{rj} C_{sj}, \quad (3)$$

where the  $j$ th MO is the HOMO,  $r$  is the location of the oxygen atom in the phenol and  $s$  is the position adjacent to  $r$  in the aromatic ring. Here  $h_o$  and  $k_{C-O}$  are the heteroatom perturbational parameters for the coulomb and resonance integrals, respectively, viz.

$$\alpha_o = \alpha + h_o \beta \text{ and } \beta_{C-O} = k_{C-O} \beta, \quad (4)$$

where  $\alpha$  and  $\beta$  are respectively the coulomb integral of an  $sp^2$  carbon atom and the resonance integral of two adjacent  $sp^2$  carbon atoms. Combining (2) and (3) one obtains

$$(h\nu_{CT} + E_j^0) = -h_o \beta \sum_r C_{rj}^2 - (k_{C-O} - 1) \beta \sum_{r \neq s} C_{rj} C_{sj} + \text{const.} \quad (5)$$

After computing the  $E_j^0$  values and the atomic orbital coefficients (eigenvector components) of the HOMO of the parent hydrocarbon corresponding to the phenols under study, the validity of (5) can be tested by a linear regression analysis. Good correlation coefficients would lead to the conclusion that the changes in  $\nu_{CT}$  are stipulated by the number and location of phenolic OH groups. The parameters  $h_o$  and  $k_{C-O}$  can also be estimated from such an analysis and their closeness to the values determined previously by other methods would be further support for the present approach.

## 3. Graph-theoretical techniques for the determination of the HOMO eigenvalues and eigenvector components

The unperturbed systems corresponding to the phenols (donors) under study are hydrocarbon radicals. Their  $\sigma$ -bond skeletons are represented in the usual manner by undirected, unweighted graphs (Gutman and Polansky 1986). A molecular graph of this kind is denoted by  $G$ .

We are interested in the MO of the parent hydrocarbon, which corresponds to the HOMO of the respective phenol. Although Hall (1977) claimed that "the variation in HOMO eigenvalue from molecule to molecule follows too complicated a pattern to be summarized in general rules", efforts have been made to establish the dependence of this quantity on molecular structure (Gutman and Rouvray 1979; Graovac and Gutman 1980; Gutman 1981; Kiang and Chen 1983). The HOMO coefficients, however, have not yet been analysed by graph-theoretical methods. In the present paper we compute the HOMO coefficients using a recently obtained result (Mukherjee and Datta 1989), according to which the eigenvector component (i.e. the coefficient

of the respective atomic orbital) corresponding to the  $r$ th atom in the  $j$ th LCAO–MO of a conjugated molecule is given by

$$C_{rj}^2 = [P(G - v_r; x)/P'(G; x)]_{x=x_j} \quad (6)$$

Here  $P(G; x)$  stands for the characteristic polynomial (CP) of the graph  $G$  and  $P'(G; x)$  is its first derivative. For details on the calculation of characteristic polynomials and an exhaustive list of both mathematical and chemical publications on this issue see Cvetkovic *et al* (1980, 1988). In (6)  $G - v_r$  is the Ulam subgraph (Ulam 1960) obtained by deleting from  $G$  the  $r$ th vertex and the edges incident to it. By  $x_j$  we denote the eigenvalue corresponding to the  $j$ th MO. In (6)  $x_j$  may be any MO, but we intentionally choose  $x_j = E_j^0$  (in  $\beta$  units, as usual).

All the eigenvalues of the graph  $G$  can be obtained by solving the equation  $P(G; x) = 0$ . This can be achieved by using standard iterative procedures, say the Newton–Raphson method (see, for example, Demidovich and Maron 1976). We, however, require only one of these eigenvalues, namely the one corresponding to HOMO. In order to avoid the calculation of the unnecessary roots we first locate the position of  $x_j$  by means of the Budan–Fourier theorem (see, for example, Kurosh 1969). Once this is done, the Newton–Raphson method gives a rapid convergence to  $x_j$ .

The phenolic compounds under study are phenol, hydroquinone, resorcinol,  $\alpha$ -naphthol and  $\beta$ -naphthol. The graphs representing the respective parent hydrocarbons are  $G_1$ – $G_5$ , and are depicted in figure 1. Their CPs are given in table 1. Since the phenolic OH groups correspond to pendant vertices of the graphs  $G_1$ – $G_5$ , the usage of (6) is greatly facilitated because of the relations

$$\begin{aligned} G_1 - v_1 &= G_{\text{benz}}, & G_2 - v_1 &= G_2 - v_2 = G_1, \\ G_3 - v_1 &= G_3 - v_2 = G_1, & G_4 - v_1 &= G_5 - v_1 = G_{\text{naph}}, \end{aligned} \quad (7)$$

where  $G_{\text{benz}}$  and  $G_{\text{naph}}$  stand for the molecular graphs of benzene and naphthalene, respectively. Thus only three Ulam subgraphs have to be examined, namely  $G_{\text{benz}}$ ,  $G_{\text{naph}}$  and  $G_1$ .

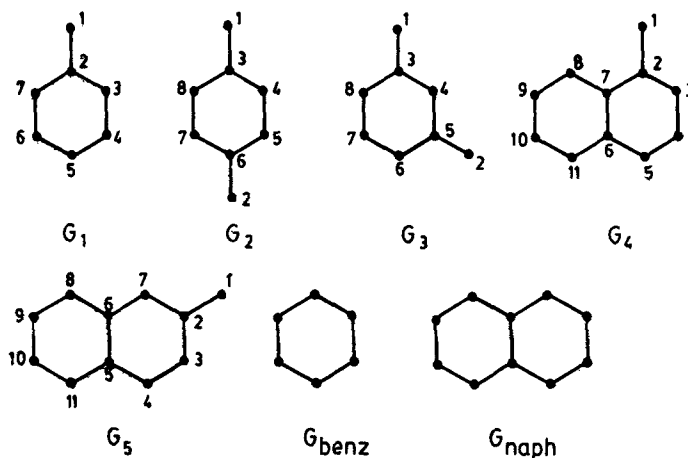


Figure 1. Graphs and Ulam subgraphs required in this communication.

**Table 1.** Characteristic polynomials of the graphs and Ulam subgraphs depicted in figure 1.

Graph	Characteristic polynomial
$G_1$	$x^7 - 7x^5 + 13x^3 - 7x$
$G_2$	$x^8 - 8x^6 + 18x^4 - 12x^2 + 1$
$G_3$	$x^8 - 8x^6 + 18x^4 - 12x^2$
$G_4$	$x^{11} - 12x^9 + 50x^7 - 91x^5 + 72x^3 - 20x$
$G_5$	$x^{11} - 12x^9 + 50x^7 - 90x^5 + 69x^3 - 17x$
$G_{\text{benz}}$	$x^6 - 6x^4 + 9x^2 - 4$
$G_{\text{naph}}$	$x^{10} - 11x^8 + 41x^6 - 65x^4 + 43x^2 - 9$

From table 1 we find that the coefficients of  $P(G_1; x)$  have three changes of sign and  $x$  as a factor. Thus according to the Descartes rule,  $G_1$  has three positive and one zero eigenvalue. Hence for phenol, possessing eight  $\pi$ -electrons,

$$x_j = E_j^0 = 0.0,$$

and using (6)

$$C_{r_j}^2 = [P(G_{\text{benz}}; x)/P'(G_1; x)]_{x=0} = 0.5714.$$

Similarly  $P(G_2; x)$  has four positive but non-zero eigenvalues. With 10  $\pi$ -electrons for hydroquinone,  $x_j$  should therefore be the lowest lying negative eigenvalue. Applying the Budan–Fourier theorem we establish the number of negative zeros of  $P(G_2; x)$  in the interval  $(-1, 0)$ . This theorem states that for a polynomial  $P(x)$  of degree  $n$ , all the zeros of which are real, the number of zeros lying in the interval  $(a, b)$ ,  $a < b$ , is equal to  $N(a) - N(b)$ , where  $N(t)$ ,  $t = a, b$ , is the number of sign changes in the sequence  $P(t), P^{(1)}(t), P^{(2)}(t), \dots, P^{(n)}(t)$ , and where  $P^{(k)}(t)$  denotes the  $k$ th derivative of  $P(x)$  at  $x = t$  (Kurosh 1969).

With  $x = -1$ ,  $P(G_2; x)$  and its eight derivatives yield the sequence  $[- - + + - - + - +]$  implying  $N(-1) = 5$ . Similarly, for  $x = 0$  we obtain the sequence  $[+ 0 - 0 + 0 - 0 +]$  resulting in  $N(0) = 4$ . Consequently, exactly one zero of  $P(G_2; x)$  is lying in the interval  $(-1, 0)$ .

In order to compute this zero we start with the guess  $x_j = -0.5$  and apply the Newton–Raphson method. After only three iterations  $x_j$  converges to  $-0.31110$ . With this value (6) and (7) give

$$\sum_{r=1}^2 C_{r_j}^2 = 2[P(G_1; x)/P'(G_2; x)]_{x=-0.31110} = 0.6646.$$

The coefficients of  $P(G_3; x)$  have three sign changes and  $x^2$  as a factor. Hence the unperturbed system corresponding to resorcinol has three positive and two zero eigenvalues and consequently the eigenvector of  $G_3$  corresponding to the HOMO of resorcinol is doubly degenerate. Direct application of (6) cannot give the two degenerate eigenvectors and we have to apply a graph-theoretical symmetry-factorization technique (McClelland 1974, 1982; Hall 1977; King 1977; D' Amato 1979; Datta and Mukherjee 1989) as shown in figure 2.

Let  $\phi_1, \phi_2, \dots, \phi_8$  represent the  $\pi$ -type orbitals acting as bases to describe the

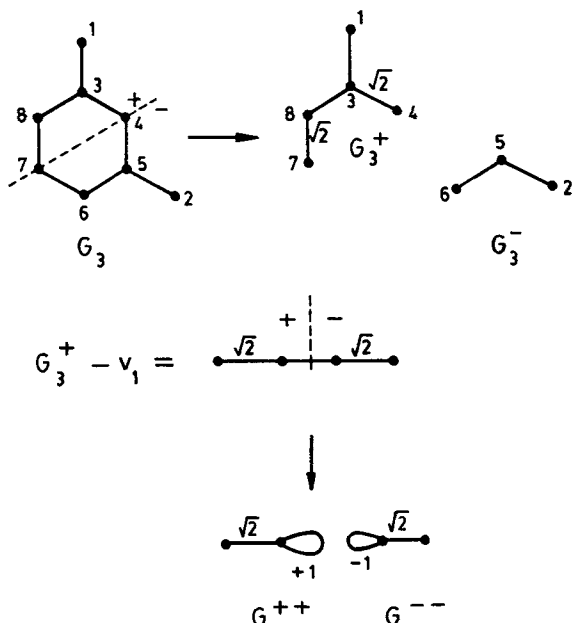


Figure 2. Factorization of  $G_3$ .

vertices of  $G_3$ . Linear combinations of these basis functions produce the Hückel MOs if the  $m$ -quinodimethane radical,  $G_3$ . Taking the vertical plane through the vertices 4 and 7 as a symmetry plane, and employing the aforementioned factorization procedure we get the factor graphs  $G_3^+$  and  $G_3^-$  whose CPs are

$$P(G_3^+; x) = x^5 - 6x^3 + 6x \text{ and } P(G_3^-; x) = x^3 - 2x. \tag{8}$$

The basis functions describing the vertices of  $G^+$  and  $G^-$  are

$$\begin{aligned} \psi_1 &= (1/\sqrt{2})(\phi_1 + \phi_2), & \psi_2 &= (1/\sqrt{2})(\phi_1 - \phi_2), \\ \psi_3 &= (1/\sqrt{2})(\phi_3 + \phi_5), & \psi_4 &= \phi_4, \\ \psi_5 &= (1/\sqrt{2})(\phi_3 - \phi_5), & \psi_6 &= (1/\sqrt{2})(\phi_8 - \phi_6), \\ \psi_7 &= \phi_7, & \psi_8 &= (1/\sqrt{2})(\phi_8 + \phi_6). \end{aligned} \tag{9}$$

Of these,  $\psi_2, \psi_5$  and  $\psi_6$  are bases for  $G_3^-$  and the others for  $G_3^+$ . The Ulam subgraph  $G_3^+ - v_1$  can be further factorized into  $G^{++}$  and  $G^{--}$ , as shown in figure 2.

Equations (8) show that the two zero eigenvalues of  $G_3$  are associated with two different factor graphs and thus this degeneracy is “accidental”. It should be so because the  $C_{2v}$  point group to which  $m$ -quinodimethane belongs has no  $E$ -type irreducible representation (Gutman and Polansky 1986).

To find the square of the eigencoefficients by the Ulam subgraph method (Mukherjee and Datta 1989) we apply (6) separately to  $G_3^+$  and  $G_3^-$ . In the  $\psi$ -basis, for  $G_3^+$  we have

$$(C_{1j}^2)' = [P(G^{++}; x)P(G^{--}; x)/P'(G_3^+; x)]_{x=0} = 2/3.$$

The prime is used to indicate that the basis vectors have been changed from  $\phi$  to  $\psi$ . Since  $|C_{1j}| \psi_1 = |C_{1j}|(1/\sqrt{2})(\phi_1 + \phi_2)$ , the square of the eigencoefficient of  $\phi_1$  in one of the MOs of  $G_3$  with  $x_j = 0$  is

$$C_{1j}^2 = (2/3) \cdot (1/\sqrt{2})^2 = 0.3333.$$

Using an analogous procedure,  $C_{2j}^2$  for the second eigenvector with  $x_j = 0$  is obtained from  $G_3$  as follows:

$$C_{2j}^2 = [(x^2 - 1)/(3x^2 - 2)]_{x=0} \cdot (1/\sqrt{2})^2 = 0.25.$$

Resorcinol has ten  $\pi$ -electron and so perturbations on both the NBMOs are to be considered. In the Coulson–Longuet-Higgins perturbational method there is no way to decide which of the two (accidentally) degenerate MOs of the parent hydrocarbon are to be associated with the HOMO.

The HOMO energy of resorcinol can be computed as follows. We first calculate the result of perturbation on the eigencoefficient of vertex 2 caused by the introduction of OH at vertex 1 and then using this new eigencoefficient compute the effect of introduction of OH at vertex 2. This requires an *a priori* knowledge of the values of  $h_o$  and  $k_{c-o}$ . On the other hand our goal is to determine these parameters from the CT bands. Therefore we have adopted a kind of “averaging” so that

average perturbational coefficient =

$$\frac{1}{2}[C_{1j}^2 \text{ for one of the degenerate MOs} + C_{2j}^2 \text{ for the other}],$$

i.e.

$$\langle C_{1j}^2 \rangle = \langle C_{2j}^2 \rangle = (0.25 + 0.3333)/2.$$

Then for resorcinol,

$$\sum_{r=1}^2 C_{rj}^2 = 0.5833.$$

The CP of  $G_4$  shows that it has five positive and one zero eigenvalue. Since  $\alpha$ -naphthol has 10  $\pi$ -electrons, we have  $x_j = 0$  and

$$C_{1j}^2 = [P(G_{naph}; x)/P'(G_4; x)]_{x=0} = (-9)/(-20) = 0.45.$$

In the same way it can be shown that for  $\beta$ -naphthol  $x_j = 0$  and

$$C_{1j}^2 = 0.5294.$$

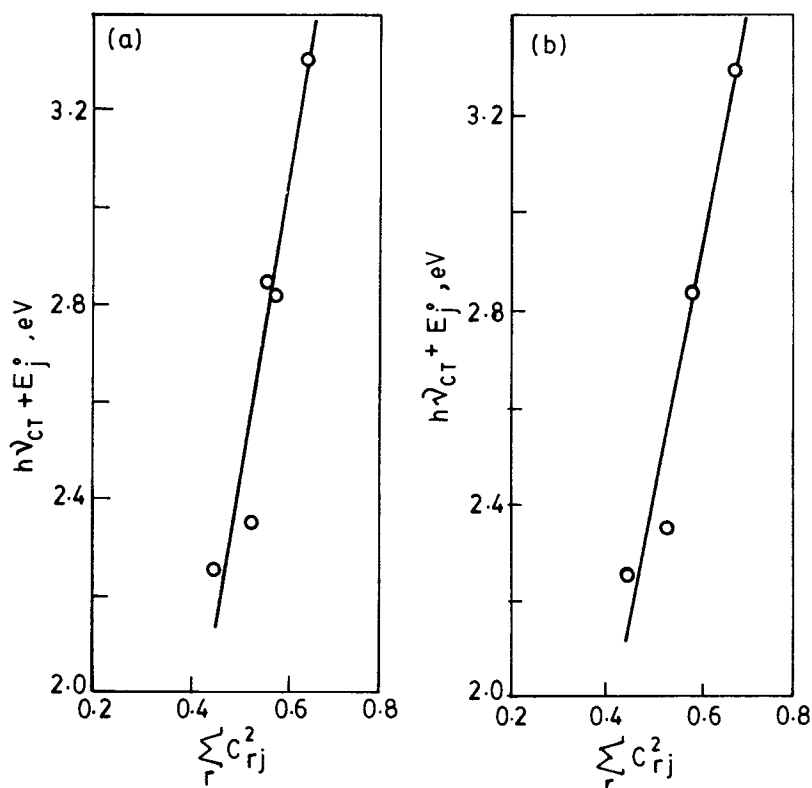
In table 2 are collected the wavelengths of the CT absorption maxima, the CT transition energies ( $h\nu_{CT}$ ), the  $E_j^0$  values and the calculated perturbational coefficients  $\Sigma C_{rj}^2$ . The CT spectral data are taken from Seal and Mukherjee (1987).

#### 4. Results and discussion

The experimental CT transition energies and theoretically computed perturbational coefficients shown in table 2, have been analysed in two ways.

**Table 2.** Wavelengths of charge-transfer absorption maxima for chloranil-phenol complexes in dioxane medium and the respective perturbational parameters;  $E_j^0 = x_j\beta = -3.1x_j$  eV.

Donor	$\lambda_{CT}$ [nm]	$h\nu_{CT}$ [eV]	$E_j^0$ [eV]	$h\nu_{CT} + E_j^0$	$\sum_r C_{rj}^2$
Phenol	437	2.8398	0	2.8398	0.5714
$\alpha$ -Naphthol	550	2.2564	0	2.2564	0.4500
$\beta$ -Naphthol	528	2.3504	0	2.3504	0.5294
Hydroquinone	530	2.3414	0.9644	3.3059	0.6646
Resorcinol	440	2.8205	0	2.8205	0.5833



**Figure 3.** Plot of  $(h\nu_{CT} + E_j^0)$  against  $\sum_r C_{rj}^2$ : (a) resorcinol included; and (b) resorcinol excluded.

#### 4.1 Including resorcinol

From the first four singlet-singlet absorption bands of benzene the value of  $\beta$  has been estimated to be  $-3.1$  eV. Then a plot of  $(h\nu_{CT} + E_j^0)$  in eV against  $\sum_r C_{rj}^2$  is found to be an excellent straight line (figure 3a). Least-squares evaluation gives

$$(h\nu_{CT} + E_j^0) = 5.1639 \sum_r C_{rj}^2 - 0.1758, \quad (10)$$

with a correlation coefficient of 0.956. With five data points this is quite reliable.

Comparing (10) and (5) we find,

$$-h_o\beta = 5.1639 \text{ and } (k_{c-o} - 1)\beta = 0.0,$$

from which, putting  $\beta = -3.1 \text{ eV}$  we obtain

$$h_o = 1.666 \text{ and } k_{c-o} = 1.$$

These values for  $h_o$  and  $k_{c-o}$  are close to the values  $h_o = 2$  and  $k_{c-o} = 0.8$  as recommended by Streitwieser (1961).

#### 4.2 Excluding resorcinol

If we exclude resorcinol in order to avoid the complications caused by the degeneracy of the HOMO, we again get an excellent linear plot of  $(hv_{CT} + E_j^0)$  versus  $\sum C_{rj}^2$  which is shown in figure 3b. Least-squares analysis gives

$$(hv_{CT} + E_j^0) = 5.2016 \sum C_{rj}^2 - 0.1806, \quad (11)$$

with a correlation coefficient of 0.969. When (11) is compared with (5) and the value  $-3.1 \text{ eV}$  used for  $\beta$ , one finds,

$$h_o = 1.6779 \text{ and } k_{c-o} = 1.$$

The above analysis not only explains the systematic variation of CT transition energies of the EDA complexes, but also gives the HMO parameters of oxygen in a straightforward way. Moreover, it demonstrates how an appropriate combination of graph-theoretical and algebraic techniques enables one to obtain only the desired eigenvalue and eigenvector of the molecular graph without computing the unnecessary eigenvectors.

It is worthwhile at this point to discuss something about solvent interactions. Such interactions are included in the  $C$  term of (1) and if  $C$  does not remain constant, the linear equation (2) fails. Although the same solvent has been used in this work,  $C$  should not strictly remain constant because the donor structure varies. However, such variations in  $C$  are usually small and it has been found in many cases that CT transition energy gives a straight line when plotted against  $I_D$  (see, for example, McConnell *et al* 1953); in Mulliken's theory it is a parabola (Mulliken and Person 1961) but with a small number of donors with some structural similarity, a part of the parabola, appearing to be a straight line with unit slope, is obtained. Solvent interaction in CT transition is prominent when the ground state is ionic and the (CT) excited state is non-ionic (for example in N-alkyl pyridinium iodides). But when the ground state is predominantly non-ionic (D---A) and the excited state is predominantly ionic ('dative',  $D^+ \text{---} A^-$ ) solvent molecules do not get time to re-orient themselves to stabilise the CT-excited state during the process of electronic transition (Franck-Condon principle); thus the contribution of solvent interaction to CT transition energy is small and  $C$  remains approximately constant in the present work.



## References

- Coulson C A and Longuet-Higgins H C 1947a *Proc. R. Soc. (London)* **A191** 39  
Coulson C A and Longuet-Higgins H C 1947b *Proc. R. Soc. (London)* **A192** 16  
Cvetković D, Doob M, Gutman I and Torgasev A 1988 *Recent results in the theory of graph spectra* (Amsterdam: North-Holland)  
Cvetković D, Doob M and Sachs H 1980 *Spectra of graphs – theory and application* (New York: Academic Press)  
D'Amato S S 1979a *Mol. Phys.* **37** 1363  
D'Amato S S 1979b *Theor. Chim. Acta* **53** 319  
Datta K K and Mukherjee A K 1989 *Proc. Indian Acad. Sci. (Chem. Sci.)* **101** 143  
Demidovich B P and Maron I A 1976 *Computational mathematics* (Moscow: Mir) p. 176  
Graovac A and Gutman I 1980 *Croat. Chem. Acta* **53** 45  
Gutman I 1981 *Match* **11** 75  
Gutman I and Polansky O E 1986 *Mathematical concepts in organic chemistry* (Berlin: Springer-Verlag)  
Gutman I and Rouvray D H 1979 *Chem. Phys. Lett.* **62** 384  
Hall G G 1977 *Mol. Phys.* **33** 551  
Kiang Y S and Chen E T 1983 *Pure Appl. Chem.* **55** 283  
King R B 1977 *Theor. Chim. Acta* **44** 223  
Kurosh A G 1969 *Higher algebra* (Moscow: Nauka)  
McConnell H, Ham J and Platt J 1953 *J. Chem. Phys.* **21** 66  
Mulliken R S and Person W B 1961 *Annu. Rev. Phys. Chem.* **13** 107  
Mulliken R S and Person W B 1969 *Molecular complexes* (New York: Wiley) p. 120  
McClelland B J 1974 *J. Chem. Soc. Faraday Trans. 2* **70** 1453  
McClelland B J 1982a *Mol. Phys.* **45** 189  
McClelland B J 1982b *J. Chem. Soc. Faraday Trans. 2* **78** 911  
Mukherjee A K and Datta K K 1989 *Proc. Indian Acad. Sci. (Chem. Sci.)* **101** 499  
Seal B K and Mukherjee A K 1987 *Indian J. Chem.* **A26** 367  
Streitwieser A 1961 *Molecular orbital theory for organic chemists* (New York: Wiley) p. 135  
Ulam S 1960 *A collection of mathematical problems* (New York: Wiley) p. 29