

List of publications

- *1. Method for construction of characteristic polynomials via graph linearisation, K. Datta and A. K. Mukherjee, *Int. J. Quant. Chem.*, **65**, 199 (1997).
- *2. Studies on labile charge-transfer complexes between *o*-chloranil and a series of phenols, K. Datta, Asok K. Mukherjee, M. Banerjee and B. K. Seal, *Spectrochimica Acta : Part A*, **53**, 2587 (1997).
- *3. Strongly subspectral pairs in C_{50+10n} and C_{60+12n} fullerenes via a common generic graph, K. Datta, M. Banerjee and A. K. Mukherjee, *Phys. Chem. Chem. Phys.* **1**, 2919 (1999).
- *4. Ground state EDA complex formation between [60]-fullerene and a series of polynuclear aromatic hydrocarbons, K. Datta, M. Banerjee, A. K. Mukherjee, and B. K. Seal, *Perkin Trans. 2*, 531 (2000).
- *5. Study of quenching of anthracene fluorescence by [60]-fullerene, K. Datta and A. K. Mukherjee, (communicated).
- *6. Study of a novel reaction between 2,3-dichloro 1,4-naphthoquinone and N,N' -diphenyl thiourea, K. Datta, M. Banerjee and A. K. Mukherjee, (communicated).
- *7. A graph theoretical analysis of the electron acceptor properties of benzoquinones, K. Datta, D. C. Mukherjee and A. K. Mukherjee, (communicated).
8. Spectroscopic and kinetic studies on the electron donor-acceptor interaction between a series of methylated anilines and naphthalene 1,4,5,8-tetracarboxylic dianhydride, T. Roy, K. Datta, A. K. Mukherjee, M. Banerjee and B. K. Seal, *Ind. J. Chem.*, **36A**, 585 (1997).
9. Kinetic study of the decay of EDA complexes of aniline and 2,4-dimethylaniline with naphthalene 1,4,5,8-tetracarboxylic dianhydride T. Roy, K. Datta, A. K. Mukherjee, M. Banerjee and B. K. Seal, *Ind. J. Chem.*, **37A**, 1007 (1998).
10. Studies on the charge-transfer complexes of *o*-chloranil with a series of methylbenzenes, B. Chakravarty, K. Datta, A. K. Mukherjee, M. Banerjee and B. K. Seal, *Ind. J. Chem.*, **37A**, 865 (1998).
11. Study of a novel reaction between N,N' -diphenyl thiourea and *p*-chloranil through a charge-transfer intermediate, T. Roy, K. Datta, M. K. Nayak, A. K. Mukherjee, M. Banerjee and B. K. Seal, *Perkin Trans. 2*, 2219 (1999).
12. A Pascal's triangle like approach for the determination of characteristic polynomial coefficients of reciprocal graphs, B. Mandal, K. Datta, A. K. Mukherjee and M. Banerjee, *Mol. Phys.*, **96**, 1609 (1999).
13. Characteristic polynomials of linear polyacenes and their subspectrality, G. Mukherjee, K. Datta and A. K. Mukherjee, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **112**, 27 (2000)

* The contents of these papers are included in this thesis.

Ground state EDA complex formation between [60]fullerene and a series of polynuclear aromatic hydrocarbons

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Formation constants of 1:1 adducts of [60]fullerene with naphthalene, phenanthrene, anthracene, pyrene and chrysene have been determined in CCl_4 medium. Ionisation potentials of donor molecules and charge transfer (CT) transition energies of the [60]fullerene adducts have been found to correlate in accordance with the Mulliken equation. From such correlation the electron affinity of [60]fullerene has been calculated to be 2.32 eV in solution. A good estimate for the $\text{sp}^2\text{C}-\text{sp}^2\text{C}$ resonance integral β in benzenoid hydrocarbons has also been obtained from the observed CT transition energies.

Introduction

A great deal of experimental work has been done with [60]fullerene¹ in the fields of material science,²⁻¹¹ photophysical study¹²⁻¹⁶ and organic chemistry.¹⁷⁻²³ Recently it has been reported²³ that C_{60} forms Diels-Alder adducts with anthracene and pentacene. Reports on the formation of ground state electron donor-acceptor (EDA) complexes involving C_{60} are relatively few.^{14,24} Theoretically it has been predicted²⁵⁻²⁷ that the LUMO of C_{60} can accept at least six electrons. Electrochemical studies in solution have yielded 3 to 5-electron reduction potentials.^{24,28-30} With special solvent compositions Echegoyen *et al.*³¹ and subsequently Diao *et al.*³² have been able to observe six-electron reduction potential corresponding to C_{60}^{6-} . Thus C_{60} is expected to behave as an acceptor in forming EDA complexes in solution. The object of the present paper is to study the formation of EDA complexes between C_{60} and a series of polynuclear aromatic hydrocarbons (PAH) and to obtain an estimate of the electron affinity of C_{60} .

Materials and methods

[60]Fullerene, was collected from Sigma. Naphthalene and phenanthrene were purified by sublimation. Anthracene from Sigma was used without further purification. Pyrene and chrysene were purified by recrystallisation from purified ethanol and benzene respectively in dark. The solvent, CCl_4 , was purified by drying over fused CaCl_2 followed by distillation. Spectral measurements were done in a Shimadzu UV-2101PC model spectrophotometer fitted with TB-85 thermo-bath.

Results and discussion

Fig. 1 shows the electronic absorption spectrum of C_{60} in CCl_4 against the solvent as reference. The absorption spectra of two mixtures, one containing pyrene and C_{60} and the other containing naphthalene and C_{60} in CCl_4 , are shown in the same figure. In the latter two cases, solution of C_{60} at the same concentration as that in the mixture was taken as reference and it was found that the broad, longest wavelength (540 nm) absorption band of C_{60} , attributable to its $\pi-\pi^*$ HOMO-LUMO transition,²⁴ was almost completely masked (because of the pristine [60]fullerene reference) while a new band due to the charge-transfer (CT) absorption of EDA complex appeared. A similar phenomenon was observed with each of the donors studied in the present work. In the case of naphthalene and phenanthrene, closely

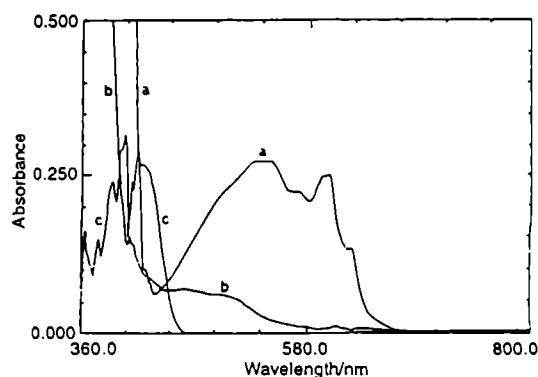


Fig. 1 Absorption spectra of C_{60} and two of its EDA complexes in CCl_4 : (a) C_{60} ($3.585 \times 10^{-4} \text{ mol dm}^{-3}$) in CCl_4 against solvent as reference; (b) C_{60} ($1.883 \times 10^{-4} \text{ mol dm}^{-3}$) + pyrene ($8.751 \times 10^{-3} \text{ mol dm}^{-3}$); (c) C_{60} ($3.585 \times 10^{-4} \text{ mol dm}^{-3}$) + naphthalene ($6.893 \times 10^{-3} \text{ mol dm}^{-3}$) against the respective C_{60} solutions as reference.

Table 1 CT absorption maxima and transition energies of C_{60} -polynuclear aromatic hydrocarbon complexes and HOMO energies (in Hückel β unit) and AM1 ionisation potentials of the donors

Donor	$\lambda_{\text{CT}}/\text{nm}^*$	$h\nu_{\text{CT}}/\text{eV}$	E_{HOMO}	I_D/eV
Naphthalene	413	3.008	0.618	8.711
Phenanthrene	413	3.008	0.605	8.617
Anthracene	511	2.431	0.414	8.123
Chrysene	472	2.632	0.520	8.371
Pyrene	454	2.737	0.445	8.131

* The longer wavelength in case of double peaks.

spaced double CT peaks were observed. Anthracene, pyrene and chrysene complexes showed broad absorption bands and λ_{max} in these cases were determined by subjecting the spectral data to a Gaussian curve fitting. The CT transition energies of the C_{60} complexes are given in Table 1 together with the Hückel energies of the highest occupied molecular orbitals (HOMO) of the PAH donors (taken from ref. 33); the AM1 ionisation potentials³⁴ (I_D) of the donors are also given in the same table. According to Mulliken's theory³⁵ the CT transition energies are related to the vertical ionisation potentials (I_D^0) of the donors by relation (1), where C_1 is given by eqn. (2). Here E_A^* is the

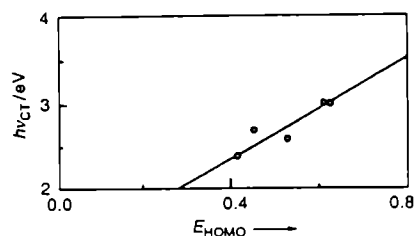


Fig. 2 Plot of $h\nu_{CT}$ against E_{HOMO} in β unit.

$$h\nu_{CT} = I_D^* - C_1 + C_2/(I_D^* - C_1) \quad (1)$$

$$C_1 = E_A^* + G_1 + G_0 \quad (2)$$

vertical electron affinity of the acceptor. G_0 is the sum of several energy terms (like dipole-dipole, van der Waals interaction, etc.) in the 'no-bond' state and G_1 is the sum of a number of energy terms in the 'dative' state. In most cases, G_0 is small and can be neglected while G_1 is largely the electrostatic energy of attraction between D^* and A^- . The term C_2 in eqn. (1) is related to the resonance energy of interaction between the 'no-bond' and 'dative' forms in the ground and excited states and for a given acceptor it may be supposed constant.³⁵ A rearrangement of eqn. (1) yields eqn. (3).

$$2I_D^* - h\nu_{CT} = (1/C_1) I_D^*(I_D^* - h\nu_{CT}) + C_1 + (C_2/C_1) \quad (3)$$

The ground state I_D values calculated for the PAHs under study by the AM1 method may be taken as their I_D^* and with the observed transition energies we have obtained the correlation (4), with a correlation coefficient of 0.99. This confirms

$$2I_D^* - h\nu_{CT} = (0.1551 \pm 0.00991) I_D^*(I_D^* - h\nu_{CT}) + (6.6907 \pm 0.4717) \quad (4)$$

the CT nature of the transitions observed and yields $C_1 = 6.45$ eV. Neglecting G_0 and taking the typical D-A distance in π -type EDA complexes to be 3.5 Å, the major part of G_1 is estimated as $e^2/4\pi\epsilon_0 r = 4.13$ eV. Now using eqn. (2) the electron affinity of C_{60} in solution is found to be 2.32 eV. This is in fair agreement with the value 2.65 eV obtained in gas phase by Smalley *et al.*³⁶ which was later confirmed by Boltalina *et al.*³⁷ and Chen *et al.*³⁸ by mass spectrometric method and also by theoretical calculation (Apostol³⁹).

A plot of $h\nu_{CT}$ against E_{HOMO} of the PAH donors (the Hückel energy of HOMO with α as the zero and β as the unit of energy) is also found to be linear (Fig. 2); the slope of this line must be equal to β , the resonance integral between two sp^2 -C atoms, in accordance with the empirical McConnell-Ham-Platt equation,⁴⁰ where E_A is the electron affinity of the acceptor

$$\begin{aligned} h\nu_{CT} &= I_D - E_A + d \\ &= -E_{HOMO}\beta + \text{constant} \end{aligned} \quad (5)$$

(C_{60}) and d is an energy term coming from solvation etc. which may be regarded as approximately constant for a given solvent and a series of structurally similar donors. In fact eqn. (5) is an approximate form of Mulliken's eqn. (1). The value of β obtained from the linear plot shown in Fig. 2 is -2.98 eV, which is in very good agreement with the value of -3.1 eV, obtained from the first four singlet-singlet transitions in benzene. All these observations definitely establish that C_{60} acts as an electron acceptor in forming EDA complexes with the polynuclear aromatic hydrocarbons studied. Stoichiometry and formation constants of the complexes were determined by

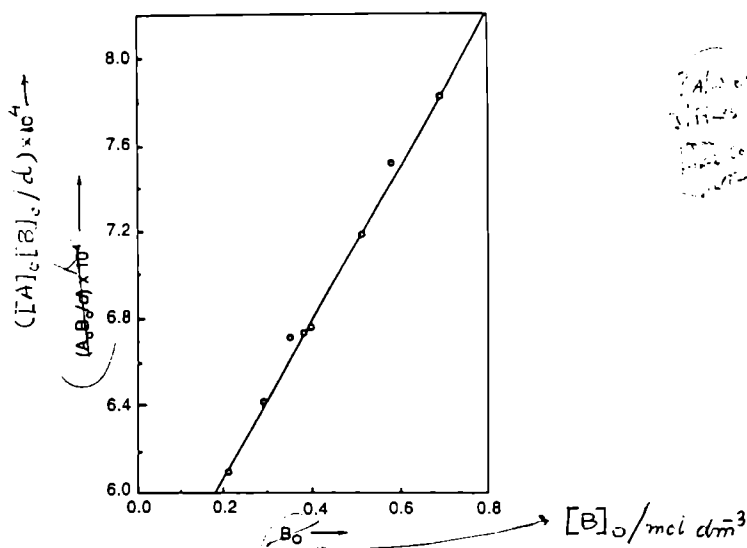


Fig. 3 Benesi-Hildebrand plot for C_{60} -naphthalene complex.

using Benesi-Hildebrand⁴¹ (B-H) and Rose-Drago⁴² equations [eqns. (6) and (7)] respectively for cells with 1 cm optical length.

$$[A]_0[B]_0/d = [B]_0/\epsilon' + 1/K\epsilon' \quad (6)$$

$$[A]_0[B]_0/d = ([A]_0 + [B]_0)/\epsilon' - d/\epsilon'^2 + 1/K\epsilon' \quad (7)$$

where $[A]_0$ and $[B]_0$ are the initial concentrations of the acceptor and donor respectively, d is the absorbance at the λ_{max} of the CT absorption band measured against the acceptor solutions, at the same molar concentration as that in the donor-acceptor mixture taken as reference. $\epsilon' = \epsilon_c - \epsilon_A$, where ϵ_c is the molar absorptivity of the complex and ϵ_A is that of the acceptor, at the wavelength of measurement. K is the formation constant of the complex. Eqn. (6) is valid under the condition⁴¹ $[B]_0 \gg [A]_0$ while eqn. (7) does not require such a condition; however, both are valid 1:1 (donor-acceptor) complexes. Absorbances at the maxima of the CT absorption bands at various concentrations of the components are shown in Table 2. Fig. 3 shows a typical B-H plot. K and ϵ' values for each system except the chrysene-fullerene complex were obtained by using the eqn. (6). In the latter case eqn. (7) was solved iteratively to get the values of K and ϵ' . Owing to low solubility of chrysene in CCl_4 , B-H condition could not be maintained in this case. Results are given in Table 2. C_{60} is thus shown to form ground state EDA complexes of 1:1 stoichiometry with each of the PAHs studied. Except for chrysene, the K values are of the order of the formation constants of typical π -type EDA complexes; for example,⁴³ K of the naphthalene-tetrachlorophthalic anhydride complex in CCl_4 medium at 301 K is $2.8 \text{ dm}^3 \text{ mol}^{-1}$. The relatively high K value for the chrysene-[60]fullerene complex may be attributed to the fact that the arrangement of hexagonal rings in chrysene molecules is similar to that in the belt region of the C_{60} surface, thereby leading to a good π -overlap. We also got a reasonable value of Hückel parameter β and also the electron affinity of [60]fullerene from the present study.

Acknowledgements

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Table 2 Data for determination of stoichiometry, formation constants and molar absorptivities of the C₆₀-polynuclear aromatic hydrocarbon complexes

Donor	10 ⁴ [A] ₀ /mol dm ⁻³	[B] ₀ /mol dm ⁻³	Absorbance at λ _{CT}	K/dm ³ mol ⁻¹	ε/dm ³ mol ⁻¹ cm ⁻¹
Naphthalene	3.5853	0.20781	0.111	0.67 ± 0.01	2778
		0.29219	0.150		
		0.35104	0.172		
		0.38359	0.187		
		0.40373	0.198		
		0.51354	0.235		
		0.58307	0.258		
		0.68932	0.294		
Phenanthrene	1.6129	0.06134	0.052	1.67 ± 0.19	3333
		0.07593	0.059		
		0.13578	0.095		
		0.17468	0.124		
		0.19002	0.127		
		0.22368	0.148		
Anthracene	1.6414	1.2764 × 10 ⁻³	0.012	10.24 ± 4.66	465
		1.6692 × 10 ⁻³	0.010		
		2.8334 × 10 ⁻³	0.014		
		3.8714 × 10 ⁻³	0.024		
		5.9333 × 10 ⁻³	0.030		
Chrysene	1.7450	2.4822 × 10 ⁻³	0.003	65.5 ± 15.19	139
		5.5485 × 10 ⁻³	0.006		
		9.7829 × 10 ⁻³	0.007		
		10.6005 × 10 ⁻³	0.012		
		11.9730 × 10 ⁻³	0.013		
		13.3289 × 10 ⁻³	0.010		
Pyrene	1.8827	3.7575 × 10 ⁻²	0.039	6.8 ± 1.03	980
		4.7299 × 10 ⁻²	0.056		
		4.7368 × 10 ⁻²	0.041		
		5.3397 × 10 ⁻²	0.049		
		6.9053 × 10 ⁻²	0.059		
		8.0919 × 10 ⁻²	0.076		
		8.7511 × 10 ⁻²	0.068		

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Method for Construction of Characteristic Polynomials via Graph Linearization

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ABSTRACT: A new method for construction of characteristic polynomials (CP) of complicated graphs having arbitrary edge and vertex weights has been developed. The method first converts the graph into isospectral linear chains with weighted vertices and edges and then builds up the CP coefficients recursively. Two types of graphs have been used for illustration, viz., (i) graphs that can be linearized by symmetry factorization and (ii) graphs without symmetry which are to be linearized by an algorithm involving walks of unit length. Both types have been illustrated, of which type (i) includes the Schlegel of fullerene fragment C_{20} and another large graph with many fused rings. © 1997 John Wiley & Sons, Inc. *Int J Quant Chem* 65: 199–204, 1997

Introduction

There exist quite a large number of methods for construction of characteristic polynomials (CP) of graphs. They may be classified into two major types, viz. (i) methods [1–7] that depend on counting of elementary subgraphs such as K_2 's and rings and (ii) methods [8–10] based on Caley-Hamilton theorem and Newton's identities [11] which require calculation of traces of the various powers of the adjacency matrix (\mathbb{A}) of the graph. While methods of type (i) bring out the combinatorial dependence of the CP coefficients on the graph

structure, they are computationally difficult, particularly for large graphs with many fused rings. On the other hand, methods of type (ii) take into account such dependence only indirectly (traces of \mathbb{A}^n may be correlated to self-returning walks of length n [12]), but are computationally facile. Randić [10] has shown how a method of the second type developed by Barakat [9] can be executed combinatorially through the use of selected Young diagrams after computing the traces of various powers of \mathbb{A} . The object of the present study is to develop a computationally facile recursive method for evaluation of CP coefficients of undirected graphs having arbitrary vertex and edge weights after linearizing the graph through symmetry factorization where possible or through a graph linearization algorithm recently developed [13] which uses walks of unit length.

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Method

The algorithm for linearizing a graph using walks of unit length was described in Ref. [13]. Sometimes this is not required and the graph may be converted into an isospectral linear chain with proper edge and vertex weights by symmetry factorization. The present algorithm for building up the CP coefficients of a weighted linear chain is based on the recurrence relation

$$C_r^{(i)} = C_r^{(i-1)} + h_i C_{r-1}^{(i-1)} - k_{i-1,i}^2 C_{r-2}^{(i-2)} \quad (1)$$

$$C_0^{(i)} = 1,$$

where $C_r^{(i)}$ means the r th coefficient of the CP, $P(L_i; x)$, of a linear chain with i vertices:

$$P(L_i; x) = \sum_{r=0}^i (-1)^r C_r^{(i)} x^{i-r}, \quad (2)$$

where h_i is the weight of the i th vertex and $k_{i-1,i}$ is the weight of the edge connecting the vertices labeled $i-1$ and i . Equation (1) can be derived from the Heilbronner recurrence relation [14] applied to a weighted linear chain from one end:

$$P(L_i; x) = (x - h_i)P(L_{i-1}; x) - k_{i-1,i}^2 P(L_{i-2}; x). \quad (3)$$

An easy procedure for executing the recursive work required by Eq. (1) follows:

1. Write down the coefficients (without sign) of the $(i-1)$ th chain in a row.

2. Multiply each coefficient by h_i and write them below the above row displacing one place to the right.
3. Multiply the coefficients of the $(i-2)$ th row by $-k_{i-1,i}^2$ and write them displaced two places to the right.
4. Add columnwise to get the coefficients $C_r^{(i)}$. Insert the sign of $(-1)^{r-1}$ before each $C_r^{(i)}$.

Illustrations

CASE I: GRAPHS LINEARIZED BY SYMMETRY FACTORIZATION

(a) The graph G_1 (Fig. 1) can be converted into mirror-plane fragments G_1^+ and G_1^- by McClelland's method [15-17] as shown in Figure 1. We have chosen this graph because it contains as a subgraph the carbon atom skeleton of biphenylene, which was used by Hosoya [4] to illustrate his method of construction of CP coefficients. The building up of the CP coefficients of G_1^+ by the present method is shown in Table I. These yield, according to Eq. (2),

$$P(G_1^+; x) = x^8 - 5x^7 + 3x^6 + 17x^5 - 19x^4 - 17x^3 + 21x^2 + 5x - 5. \quad (4)$$

The CP of G_1^- can be similarly constructed. It is noteworthy here that the portions of G_1^+ and G_1^- up to the sixth vertex are the mirror plane frag-

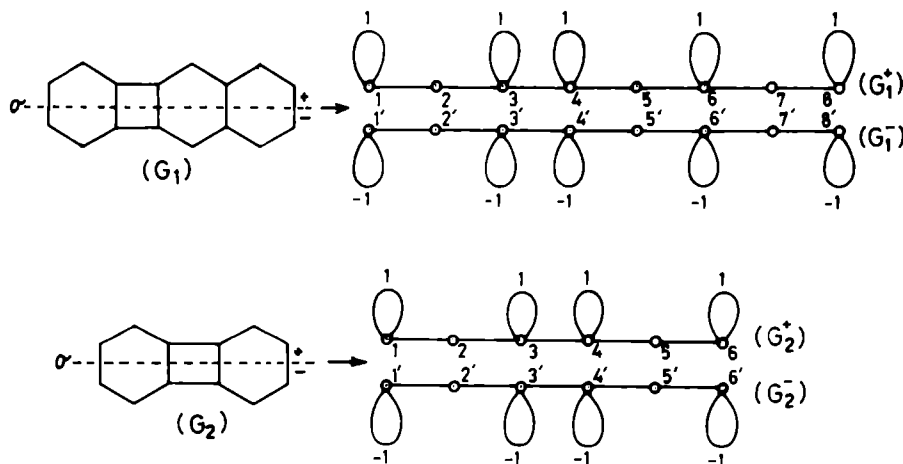


FIGURE 1. Linearization of a graph with many fused rings by using plane of symmetry.

TABLE I
Building up of the coefficients of G_1^+ .

$L_0:$	1										
$h_1L_0:$		1									
$L_1:$	1	1									
$h_2L_1:$			0								
$-k_{1,2}^2L_0:$				-1							
$L_2:$	1	1	-1								
$h_3L_2:$				1							
$-k_{2,3}^2L_1:$					-1						
$L_3:$	1	2	-1	-2							
$h_4L_3:$					2						
$-k_{3,4}^2L_2:$						-1					
$L_4:$	1	3	0	-4	-1						
$h_5L_4:$						0					
$-k_{4,5}^2L_3:$							-1				
$L_5:$	1	3	-1	-6	0	2					
$h_6L_5:$							3				
$-k_{5,6}^2L_4:$								-1			
$L_6:$	1	4	1	-10	-6	6	3				
$h_7L_6:$								0			
$-k_{6,7}^2L_5:$									-2		
$L_7:$	1	4	0	-13	-5	12	3	-2			
$h_8L_7:$										3	
$-k_{7,8}^2L_6:$											-3
$L_8:$	1	5	3	-17	-19	17	21	-5	-5		
$(-1)^r:$		(-)		(-)		(-)		(-)			

ments of G_2 and so

$$\begin{aligned}
 P(G_2; x) &= P(L_6^+; x)P(L_6^-; x) \\
 &= (x^6 - 4x^5 + x^4 + 10x^3 \\
 &\quad - 6x^2 - 6x + 3) \\
 &\quad \times (x^6 + 4x^5 - x^4 - 10x^3 \\
 &\quad - 6x^2 + 6x + 3) \\
 &= x^{12} - 14x^{10} + 69x^8 - 154x^6 \\
 &\quad + 162x^4 - 72x^2 + 9, \quad (5)
 \end{aligned}$$

which is the same as that obtained by Hosoya [4] but now obtained far more easily.

(b) The graph G_3 (Fig. 2) is the Schlegel of fullerene fragment, C_{20} , drawn by the circumscribing principle given by Dias [18]. Following the method of Davidson [19] and Shen [20] and utilizing a fivefold symmetry axis it can be shown [21] that the adjacency matrix of this Schlegel can be factorized into five blocks each of which can be represented by the graph G_4 (Fig. 2), with $h = w^0 + w^5 = 2$ for the first block, $w + w^4 = 2 \cos(2\pi/5)$ for the second and fifth blocks, and $w^2 + w^3 = 2 \cos(4\pi/5)$ for the third and fourth blocks [$w = \exp(2\pi i/5)$]. Mirror plane fragmentation of G_4 gives the three-chain G_4^+ and an isolated vertex (G_4^-) with weight -1 . Since such fragmentation is possible for all the five blocks, it immediately follows that -1 is a fivefold degenerate eigenvalue of G_3 . The present procedure gives (as shown in Table II).

$$\begin{aligned}
 P(G_4^+; x) &= x^3 - (h+1)x^2 + (h-3)x + (2h+1), \\
 P(G_4^-; x) &= (x+1). \quad (6)
 \end{aligned}$$

Using appropriate values of h as indicated earlier,

we obtain the CP of C_{20} in the factorized form,

$$\begin{aligned}
 P(G_3; x) &= [P(G_4^+; x)]_{h=2} [P(G_4^+; x)]_{h=0.618}^2 \\
 &\quad \times [P(G_4^+; x)]_{h=-1.618}^2 (x+1)^5 \\
 &= (x^3 - 3x^2 - x + 5) \\
 &\quad \times (x^3 - 1.618x^2 - 2.382x + 2.236)^2 \\
 &\quad \times (x^3 + 0.618x^2 - 4.618x - 2.236)^2 \\
 &\quad \times (x+1)^5 \\
 &= (x^3 - 3x^2 - x + 5) \\
 &\quad \times (x^6 - x^5 - 8x^4 + 6x^3 \\
 &\quad + 16x^2 - 5x - 5)^2 (x+1)^5. \quad (7)
 \end{aligned}$$

TABLE II Building up of the coefficients G_4^+ .

$L_0:$	1			
$h_1 L_0:$		1		
$L_1:$	1	1		
$h_2 L_1:$			0	0
$-k_{1,2}^2 L_0:$				-2
$L_2:$	1	1		-2
$h_3 L_2:$			h	h
$-k_{2,3}^2 L_1:$				-1
	1	$(h+1)$	$(h-3)$	$-(1+2h)$
$(-1)^r:$	$(-)$			$(-)$

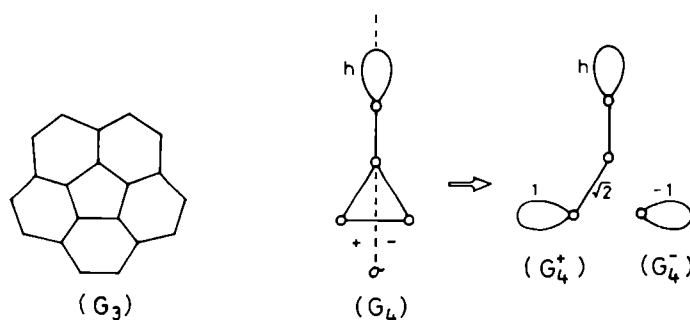


FIGURE 2. Linearization of the C_{20} Schlegel using fivefold symmetry and plane of symmetry.

CASE II: GRAPHS THAT CANNOT BE SYMMETRY FACTORIZED

Such a graph is G_5 (Fig. 3), which was used in Ref. [13] for illustration of the graph linearization algorithm using walks of unit length. The isospectral linear chain that can be obtained from G_5

through this algorithm is $G_5(L)$ (Fig. 3). Using the present procedure the CP coefficients are built up in Table III. It is found that

$$P(G_5; x) = P(G_5(L); x) = x^5 - 2x^4 - 5x^3 + 5x^2 + 5x - 2. \quad (8)$$

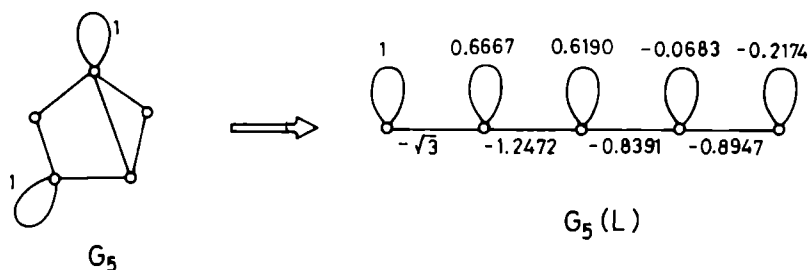


FIGURE 3. Linearization of a graph without symmetry using walks of unit length.

TABLE III Building up the CP coefficients of the nonsymmetric graph G .

$L_0:$	1					
$h_1 L_0:$		1				
$L_1:$	1	1				
$h_2 L_1:$		0.6667	0.6667			
$-k_{1,2}^2 L_0:$			-3			
$L_2:$	1	1.6667	-2.3333			
$h_3 L_2:$		0.6190	1.0317	-1.4443		
$-k_{2,3}^2 L_1:$			-1.5555	-1.5555		
$L_3:$	1	2.2857	-2.8571	-2.9998		
$h_4 L_3:$		-0.0683	-0.1561	+0.1951	+0.2049	
$-k_{3,4}^2 L_2:$			-0.7041	-1.1735	+1.6428	
$L_4:$	1	2.2174	-3.7173	-3.9782	1.8477	
$h_5 L_4:$		-0.2174	-0.4821	+0.8081	+0.8649	-0.4017
$-k_{4,5}^2 L_3:$			-0.8005	-1.8297	+2.2871	+2.4013
$L_5:$	1	2	-5	-5	5	2
$(-1)^r:$		(-)		(-)		(-)

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Studies on labile charge-transfer complexes between *o*-chloranil
and a series of phenols

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Studies on labile charge-transfer complexes between *o*-chloranil and a series of phenols

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Abstract

The electron donor–acceptor (EDA) interactions between *o*-chloranil and a series of phenols have been studied in dioxan medium. Except for resorcinol, the EDA complexes are formed instantaneously on mixing the donor and the acceptor solutions and then they decay slowly into secondary products. In case of resorcinol, formation and decay of the EDA complex are slow and simultaneous. The kinetics of all these reactions have been studied spectrophotometrically and the formation constants of EDA complexes have been determined from kinetic data. The $h\nu_{CT}$ values change systematically as the number and position of the –OH groups change in the aromatic ring of the phenol moiety. From the trends in the $h\nu_{CT}$ values, the Hückel parameters ($h_{\bar{O}}$ and $k_{C-\bar{O}}$) for the –OH group, required for a PMO calculation on phenols, have been obtained in a straightforward way and the values so obtained, viz., 1.8 and 1.0 respectively, are close to the ones (1.8 and 0.8) recommended by Streitwieser on the basis of other evidences. © 1997 Elsevier Science B.V.

Keywords: Electron donor–acceptor interaction; *o*-Chloranil; Hückel parameters

1. Introduction

Electron donor–acceptor (EDA) complexes are of importance not only for their occurrence in biological systems [1,2] and as intermediates in many reactions in non-aqueous [3–5] and aqueous [6] media, but also as potential materials for second order nonlinear optical activity [7]. Although there exists a vast literature on theoretical [8–10] and experimental studies [11–13] on stable EDA complexes, reports on the decay kinetics of such complexes are comparatively scanty

[14]. In spite of some recent reports [15–19], many such unstable complexes have yet to be investigated.

In the present paper, we report on the EDA interactions of *o*-chloranil with a series of phenols. In some previous works [20,21], we investigated the interaction of *p*-chloranil with the same series of phenols. It was found that all these EDA complexes (except that with *p*-quinol) were stable. In contrast, *o*-chloranil forms unstable EDA complexes with all the phenols under investigation as will be evident from subsequent discussion. Though isomeric, the two chloranils differ markedly in their electron accepting properties:

* Corresponding author.

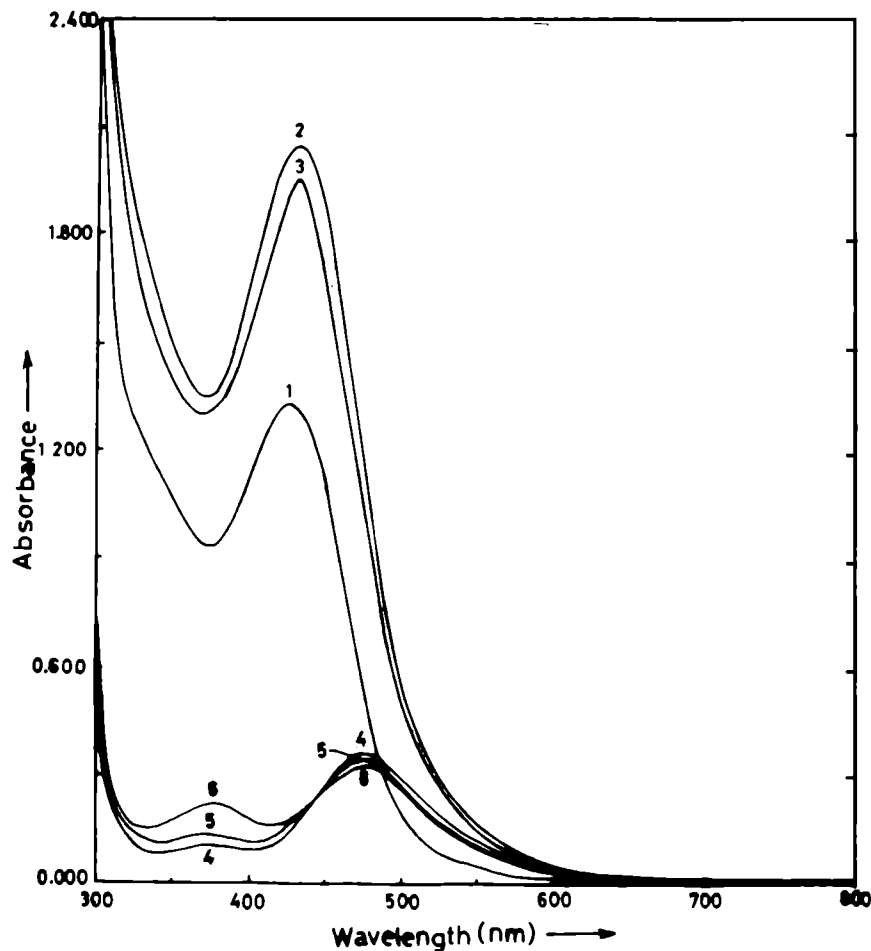


Fig. 1. Spectra of (1): $9.6748 \times 10^{-4} \text{ mol dm}^{-3}$ of *o*-chloranil vs. dioxan; (2) and (3): mixture of $9.6748 \times 10^{-4} \text{ mol dm}^{-3}$ of *o*-chloranil and $3.4910 \text{ mol dm}^{-3}$ of phenol vs. dioxan at $t = 2$ and 45 min respectively; (4), (5) and (6): the same reaction mixture vs. *o*-chloranil at $t = 2, 45 \text{ min}$ and 20 h respectively.

o-chloranil has a long π -conjugation while *p*-chloranil is a crossed conjugated system [22]; this makes the energy of the lowest unoccupied MO much lower in case of the *o*-isomer. Our objective is 2-fold: (1) to establish that *o*-chloranil forms unstable (labile) EDA complexes with phenols and to explain the variation of λ_{CT} in the series with changes in the number and position of OH groups in the phenol moiety using Mulliken's theory and (2) to obtain the stoichiometry and formation constants of the complexes from a kinetic study of their formation and decay in dioxan medium.

2. Experimental

Phenol was distilled twice just before use. The other phenols, viz. catechol, hydroquinone, resorcinol, α -naphthol and β -naphthol were purified by sublimation. Dioxan was purified as follows: 40 ml of conc. HCl was added to 1 dm³ of dioxan and air was passed through the mixture for 7 h. Then an excess of solid KOH was added and kept overnight, the supernatant dioxan was filtered out and refluxed with metallic sodium for 5 h and then distilled just before use. *o*-Chloranil (Aldrich) was purified by sublimation. Spectral

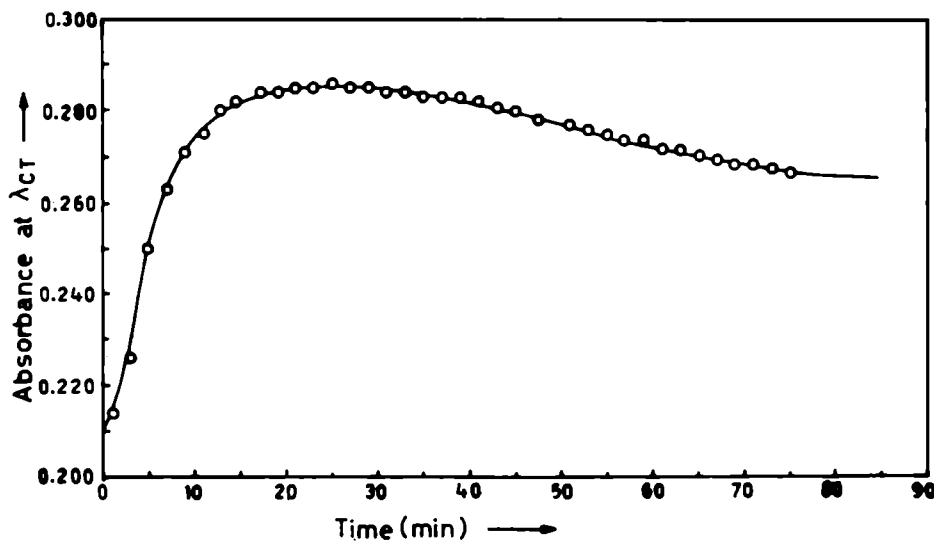


Fig. 2. Variation of absorbance at λ_{CT} with time for resorcinol-*o*-chloranil complex: $[A]_0 = 6.2 \times 10^{-4} \text{ mol dm}^{-3}$ and $[B]_0 = 0.69 \text{ mol dm}^{-3}$.

measurements were done on a Shimadzu UV160A model spectrophotometer.

3. Discussion

3.1. Analysis of CT absorption bands

Against dioxan as the reference, the absorption spectrum of $9.6748 \times 10^{-4} \text{ mol dm}^{-3}$ of *o*-chloranil solution is shown in Fig. 1, together with that of a mixture of $3.4910 \text{ mol dm}^{-3}$ of phenol and $9.6748 \times 10^{-4} \text{ mol dm}^{-3}$ of *o*-chloranil at $t = 2, 45 \text{ min}$ and after about 20 h (curves 1, 2 and 3 of Fig. 1 respectively). During the entire experi-

ment, the solutions were kept in dark. In dioxan, *o*-chloranil absorbs at 425 nm ($n-\pi^*$ transition). Fig. 1 shows that measurement against dioxan reveals no new peak on mixing phenol with *o*-chloranil, but the absorption is intensified and the intensity changes with time. To eliminate the absorption due to *o*-chloranil, the spectra of the

Table 1
Experimental CT transition energies and calculated perturbational coefficients of the phenol-*o*-chloranil complexes

Donor	λ_{CT} (nm)	$h\nu_{CT}$ (eV)	$\Sigma_r C_{rj}^2$	$h\nu_{CT} + \epsilon_j^0$ (eV)
Phenol	480.5	2.506	0.5714	2.5059
Catechol	570.0	2.113	0.5509	3.0269
<i>p</i> -Quinol	530.0	2.272	0.6646	3.2363
Resorcinol	490.0	2.457	0.5833	2.4573
α -Naphthol	520.0	2.316	0.4500	2.3156
β -Naphthol	484.0	2.488	0.5294	2.4878

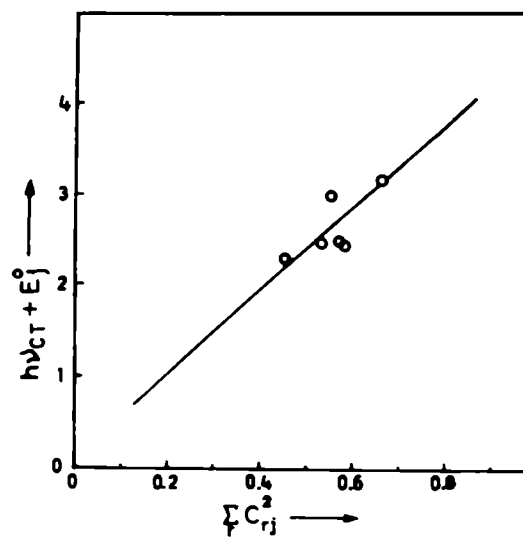


Fig. 3. Plot of $h\nu_{CT} + \epsilon_j^0$ vs. $\Sigma_r C_{rj}^2$.

Table 2
Variation of absorbance at λ_{CT} with time for *o*-chloranil–phenol mixtures

Absorbance	Time (min)
0.111	2
0.109	7
0.107	10
0.106	15
0.106	18
0.104	22
0.104	27
0.102	33
0.100	38
0.099	43
0.098	48

$[A]_0 = 1.8112 \times 10^{-4} \text{ mol dm}^{-3}$, $[B]_0 = 2.6398 \text{ mol dm}^{-3}$, $T = 298 \text{ K}$

mixtures were recorded against an *o*-chloranil solution of the same concentration as that in the mixture, as reference. A new broad peak at 480 nm, ascribable to the CT absorption of *o*-chloranil–phenol EDA complex, now appeared. The intensity of absorption at this new peak (λ_{CT}) gradually decreases with time and simultaneously a second peak at $\lambda = 376 \text{ nm}$ appeared with a gradual increase in intensity. The latter is ascribable to the product of decay of the EDA complex (curves 4, 5 and 6 of Fig. 1). The absorbance at λ_{CT} decreases with time in case of all the phenols studied, except for resorcinol where the absorbance at first increases and then decreases after reaching a maximum (Figs. 1 and 2). The λ_{CT} values and the corresponding transition energies ($h\nu_{CT}$) are given in Table 1. They are found to change as the number and position of the phenolic OH groups change in the phenol moiety. To explain this with the help of Mulliken's theory [23], a simple perturbational calculation by the Coulson-Longuet-Higgins method [24] was carried out. According to this method, the energy (ε_j) of the highest occupied molecular orbital (HOMO) of a phenol is given by,

$$\varepsilon_j = \varepsilon_j^0 + h_{\bar{O}}\beta \sum_r C_{rj}^2 + 2(k_{C-\bar{O}} - 1)\beta \sum_{r < s} C_{rj}C_{sj} \quad (1)$$

Here the unperturbed system is taken to be the radical obtained by replacing the –OH group of phenol by –CH₂; ε_j^0 is the corresponding unperturbed HOMO energy. The perturbational Hückel parameters [24] $h_{\bar{O}}$ and $k_{C-\bar{O}}$ are defined as

$$\alpha_{\bar{O}} = \alpha + h_{\bar{O}}\beta \quad \text{and} \quad \beta_{C-\bar{O}} = k_{C-\bar{O}}\beta \quad (2)$$

where α and β are, respectively, the coulomb integral of a sp² hybridised carbon atom and the resonance integral between two adjacent sp²-carbon atoms in benzene. The perturbational quantities were calculated graph-theoretically in our previous works [20,21] and have been used here (Table 1). According to Mulliken's theory, $h\nu_{CT}$ is related to the ionisation potential (I_D) of donor (D) and electron affinity (E_A) of acceptor (A) by the equation

$$h\nu_{CT} = I_D - E_A + \Delta \quad (3)$$

where the energy term, Δ , is composed of solvation, van der Waals interactions in ground state and Coulombic attraction between D⁺ and A[–] in the excited state. For a fixed acceptor, and a series of structurally similar donors in a given solvent, Eq. (3) takes the form

$$h\nu_{CT} = I_D + \text{constant} \quad (4)$$

Since I_D , in turn, is the negative of the HOMO energy of the phenol, we have from Eq. (1) and Eq. (4)

$$h\nu_{CT} + \varepsilon_j^0 = -h_{\bar{O}}\beta \sum_r C_{rj}^2 + 2(k_{C-\bar{O}} - 1)\beta \sum_{r < s} C_{rj}C_{sj} + \text{constant} \quad (5)$$

Fig. 3 shows a plot of $h\nu_{CT} + \varepsilon_j^0$ against $\sum_r C_{rj}^2$ which is linear with a correlation coefficient of 0.72.

The linearity suggests that the second term in Eq. (5) has no effect which implies that $k_{C-\bar{O}} = 1$. From the slope of the line we find $h_{\bar{O}} = 1.8$ (taking $\beta = -3.1 \text{ eV}$ as obtained from the first four singlet–singlet transitions in benzene). These values of $h_{\bar{O}}$ and $k_{C-\bar{O}}$ are in excellent agreement with Streitwieser's [25] recommended values (1.8 and 0.8 respectively) and also with the ones ob-

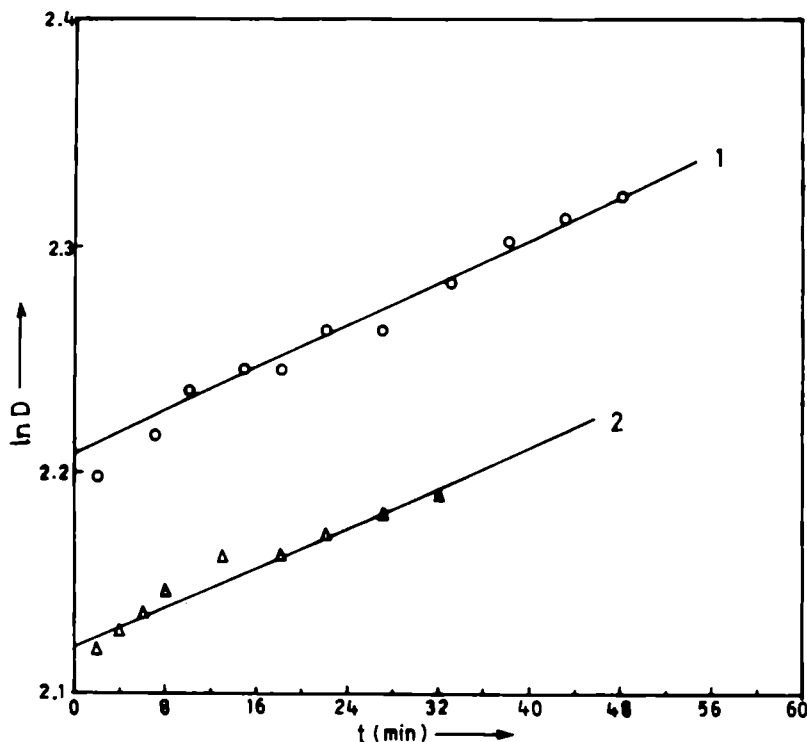


Fig. 4. Plots of $\ln D$ vs. time for *o*-chloranil-phenol mixture: (1) $[A]_0 = 1.81 \times 10^{-4} \text{ mol dm}^{-3}$ and $[B]_0 = 2.64 \text{ mol dm}^{-3}$, (2) $[A]_0 = 2.17 \times 10^{-4} \text{ mol dm}^{-3}$ and $[B]_0 = 2.53 \text{ mol dm}^{-3}$.

tained from a similar study of the EDA complexes of the same series of phenols with *p*-chloranil as acceptor [20,21].

3.2. Results of kinetic studies

Except for resorcinol, complexes of all the phenols (B) with *o*-chloranil (A) were formed instantaneously on mixing the solutions in dioxan and their decay started from the very beginning. Variation of absorbance of the B-A mixtures with time seemed to fit into the reaction scheme,



This scheme requires:

$$\ln D = -k_1 t + \ln D_0 \quad (6)$$

where D_0 is the zero time absorbance of the complex AB and D is the absorbance at time t . Experimental data are given in Table 2 for a typical system (phenol + *o*-chloranil). A typical

plot supporting Eq. (6) is shown in Fig. 4, where parallel straight lines have been obtained with different sets of initial concentrations of A and B. The D_0 values of all the complexes (except that for resorcinol) are collected in Table 3 together with the initial concentrations $[A]_0$ and $[B]_0$. From these data, the formation constants (K) and effective molar absorptivities $\epsilon_C - \epsilon_A$ at λ_{CT} (where ϵ_C and ϵ_A are molar absorptivities of the complex and the acceptor respectively) were determined using the Rose-Drago (RD) equation [26].

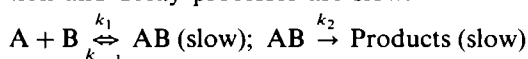
$$\begin{aligned} [A]_0[B]_0 / D_0 \\ = 1/K(\epsilon_C - \epsilon_A) + ([A]_0 + [B]_0) / (\epsilon_C - \epsilon_A) \\ - D_0 / (\epsilon_C - \epsilon_A)^2 \end{aligned} \quad (7)$$

A computer programmed least-square method [27] was used for this purpose. Formation constants (K) of the complexes and values of $(\epsilon_C - \epsilon_A)$ obtained from such calculations are summarised in Table 3.

Table 3
Absorbance (D_0) at λ_{CT} of the mixtures of *o*-chloranil and different phenols at $t = 0$ with various initial concentrations

Donor (B)	$10^4[A]_0$ (mol dm ⁻³)	$[B]_0$ (mol dm ⁻³)	D_0 (mol dm ⁻³)	Formation constant K	ϵ_C	Decay constant k_1 , (min ⁻¹)
Phenol	1.8112	2.6398	0.110	0.10 ± 0.01	3540 ± 60	$(2.04 \pm 0.28) \times 10^{-3}$
	2.1734	2.5342	0.120			
	2.1734	1.9007	0.110			
	2.7168	2.3758	0.121			
	2.7168	1.5839	0.094			
<i>p</i> -Quinol	1.5658	0.6204	0.080	0.13 ± 0.04	$10\,121 \pm 53$	$(11.86 \pm 0.26) \times 10^{-3}$
	2.3487	0.4907	0.092			
	2.3487	0.4417	0.099			
	1.2195	0.4809	0.086			
	1.0163	0.5009	0.090			
α -Naphthol	1.8970	1.0573	0.098	0.86 ± 0.17	1210 ± 56	$(3.42 \pm 0.34) \times 10^{-2}$
	2.4390	1.0196	0.123			
	2.1341	1.0408	0.082			
	2.1341	0.8921	0.090			
β -Naphthol	0.7805	0.5490	0.198	2.03 ± 0.47	5164 ± 60	$(7.70 \pm 3.0) \times 10^{-3}$
		0.4270	0.147			
		0.3660	0.147			
		0.3050	0.165			
		0.2440	0.120			
		0.3420	0.113			

The decay of catechol-*o*-chloranil complex was found to be very fast and so its kinetics could not be followed at 298 K. However, its λ_{CT} was determined by lowering the temperature. For resorcinol-*o*-chloranil EDA complex, both formation and decay processes are slow:



With such a scheme it can be seen that the absorbance at λ_{CT} increases initially with time and then decreases after reaching a maximum value, D_{max} , and the D_{max} is given by

Table 4
Absorbance at λ_{CT} at the time of maximum formation of *o*-chloranil-resorcinol complex

$[B]_0$, mol dm ⁻³	D_{max}
0.7815	0.279
0.6947	0.286
0.6078	0.283
0.5210	0.263

$[A]_0 = 6.1984 \times 10^{-4}$ mol dm⁻³, $T = 298$ K

$$[A]_0[B]_0 = (k_{-1} + k_2) / k_1 + ([A]_0 + [B]_0)D_{max} / (\epsilon_C - \epsilon_A) \quad (8)$$

Variation of absorbance at λ_{CT} for the *o*-chloranil-resorcinol complex with time is shown in Fig. 2 for a particular set of initial concentrations, $[A]_0$ and $[B]_0$. The D_{max} values for a number of such sets are shown in Table 4. Fig. 5 shows a plot of $[A]_0[B]_0$ vs. $([A]_0 + [B]_0)D_{max}$ which is an excellent straight line (correlation coefficient 0.99). From the slope and intercept values, a Michaelis-Menten [28] type constant $(k_{-1} + k_2) / k_1$ and the effective molar absorptivity $(\epsilon_C - \epsilon_A)$ could be found to be 0.47×10^{-4} and 500 respectively.

The initial points in Fig. 4 deviate markedly from the least squares straight line. This indicates that a process even faster than the one mentioned in the proposed scheme occurs. However, this cannot be studied without the help of a fast-kinetics technique.

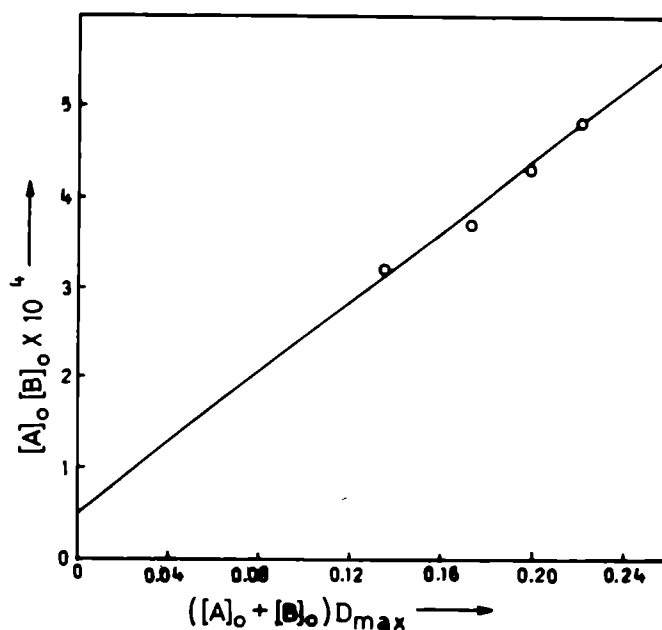


Fig. 5. Plot of $[A]_0[B]_0$ vs. $([A]_0 + [B]_0) D_{max}$ for *o*-chloranil–resorcinol complex.

The molar absorptivities (ϵ_A) of *o*-chloranil were measured at the wavelengths of CT absorption of each complex and the same were added to $(\epsilon_C - \epsilon_A)$ values in order to get the ϵ_C for each complex.

Though the products have not been isolated, preliminary cyclic voltammetric studies with the reaction mixtures indicate that the reactions are of a redox nature—*o*-chloranil is reduced and phenol is oxidised to the corresponding quinone. Since resorcinol is not easily oxidised, owing to the impossibility of *m*-quinone, the reaction in this case follows a path different from that of the others. Detailed investigation along this line will be published subsequently.

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Strongly subspectral pairs in C_{50+10n} and C_{60+12n} fullerenes via a common generic graph

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A convenient scheme has been developed for drawing the Schlegel digrams (graphs) of C_{50+10n} and C_{60+12n} ($n = \text{integer}$) fullerenes maintaining five-fold and six-fold rotational symmetry, respectively. It has been found that after symmetry-factorisation, $10 + 2n$ eigenvalues common to C_{50+10n} and C_{60+12n} fullerenes can be obtained from a generic graph and for this reason $(C_{60}, C_{72}), (C_{70}, C_{84}), (C_{80}, C_{96}) \dots$, corresponding to $n = 1, 2, 3, \dots$ respectively, are strongly subspectral pairs having 12, 14, 16, ... common eigenvalues respectively. Of the $10 + 2n$ common eigenvalues, $n + 3$ can be expressed in the analytic form: $\lambda_j = -1 + 2 \cos[j\pi/(n + 4)], j = 1, 2, \dots, n + 3$. The other $n + 7$ common eigenvalues can be obtained from a weighted linear chain whose characteristic polynomial can be easily derived by means of a recently developed scheme; a sample calculation for $n = 1$ has been shown. Results for a number of subspectral pairs have been tabulated.

Introduction

Fullerenes, the carbon clusters discovered in the laser vapours of graphite,¹ have been proved to be objects of great theoretical and experimental interest.²⁻⁸ Owing to the absence of all electron *ab-initio* calculations for general fullerenes, graph theory in Huckel formalism is used⁹⁻²³ for analysis of electronic factors such as closed shell configuration, HOMO-LUMO gap *etc.* For example, Aihara²⁴ has recently examined the stabilities of molecular ions of C_{60} in terms of topological resonance energy. Complete analytic solutions for the eigenvalues of buckytubes and buckytori have been given by Klein *et al.*²⁵ in terms of three different nearest neighbour resonance integrals considering the curvatures of the clusters along three different directions. Kirby *et al.*²⁶ have given analytic forms of the eigenvalues of toroidal polyhexes. Fowler¹³ has shown that every third member of C_{70+30n} and C_{84+36n} ($n = \text{non-negative integer}$) fullerenes has a closed π -electronic structure below a non-bonding level. Fowler *et al.*^{27,28} have also considered fullerenes with seven-fold and higher symmetry. Our object in the present paper is to show that strong subspectrality exists among pairs of C_{50+10n} and C_{60+12n} fullerene graphs as a result of the fact that a substantial part of their eigenspectra can be obtained from a common generic graph. For this purpose we need a planar graph (Schlegel diagram) of the fullerenes under consideration. Dias²⁹ has given a circumscribing algorithm for the construction of such diagrams in the case of general fullerenes. In this scheme one is not sure whether the symmetry of the excised internal structure is preserved in its successor or whether the twelve pentagons (as required by Euler's formula) are always separated. A more general procedure is Tutte's baricentric method,³⁰ which with suitable manipulation may reveal the full point group symmetries of the fullerene. However, we want to utilise only the five- and six-fold rotational axes of C_{50+10n} and C_{60+12n} to find out strongly subspectral pairs and for this purpose a relatively simpler algorithm, that maintains C_5 and C_6 symmetry axes and separation of pentagons, has been developed first; then the graphs have been factorised to obtain a generic graph which contains many eigenvalues common to specific pairs of fullerenes.

Scheme for drawing the Schlegel diagrams of C_{50+10n} and C_{60+12n} fullerenes

For this purpose we first define *horizontal* and *transverse* placing of an edge in a bay or vee region: if the two vertices of an edge are joined to the terminals of a bay or vee, it is horizontally placed; if only one vertex is joined to the terminals of a bay or vee, its placing will be called transverse (Fig. 1). The following steps are to be followed successively:

I. For C_{50+10n} (type I) fullerenes start with the planar graph of C_{20} obtained by surrounding a pentagon with five hexagons. For fullerenes of the formula C_{60+12n} (type II), start with the planar graph of C_{24} obtained by surrounding a hexagon with six hexagons.

II. Cap each vee region with one edge placed horizontally. This gives the graph of C_{30} for type I and that of C_{36} for type II.

III. Cap each bay region with one horizontal edge.

IV. Cap each newly produced bay region with an edge horizontally to get C_{50} for type I and C_{60} for type II, avoiding fusion of pentagons and maintaining five-fold and six-fold rotational symmetry respectively. Capping each new bay region with one horizontal edge may now be continued n times, where $n = 1, 2, 3, \dots$. This will only increase the number of hexagons that separate the twelve pentagons required by Euler's formula.

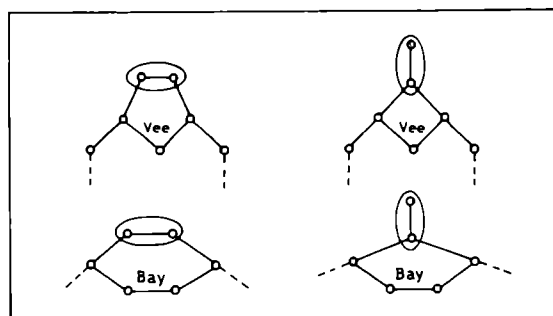


Fig. 1 Transverse and horizontal placing of edges.

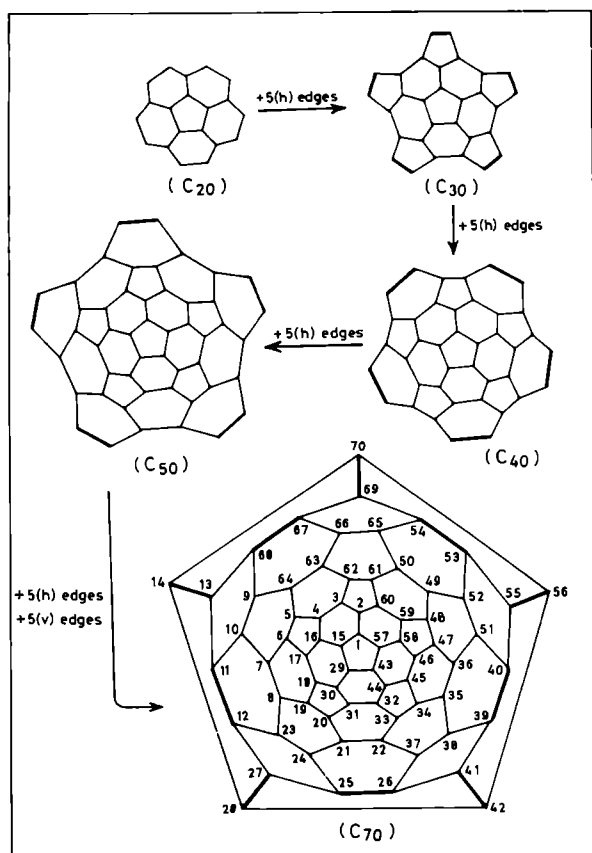


Fig. 2 Construction of C_{50+10n} fullerene graph with five-fold symmetry and isolated pentagons: an illustration with $n = 2$ i.e., C_{70} .

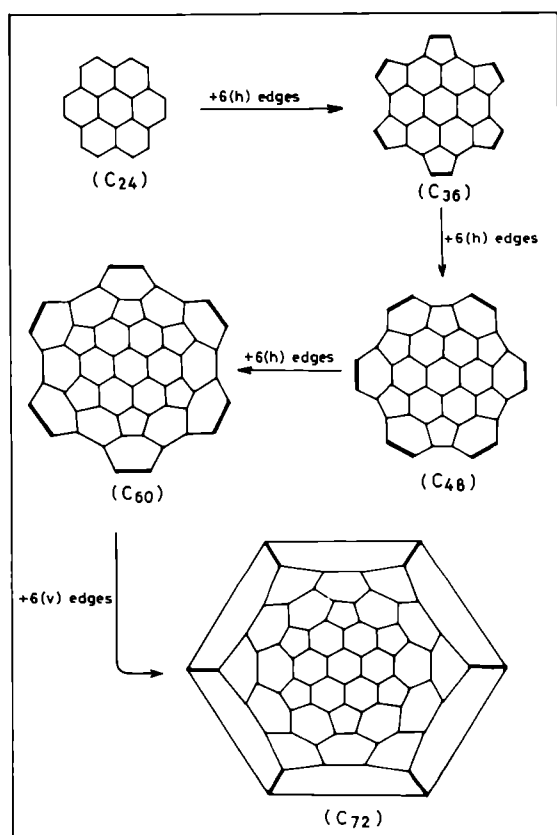


Fig. 3 Construction of C_{60+12n} fullerene (C_{72}) graph with six-fold symmetry and isolated pentagons: an illustration with $n = 1$ i.e., C_{72} .

V. Cap each new bay region with a transverse edge and join the pendant vertices. This will give the Schlegel diagram of a C_{50+10n} or a C_{60+12n} fullerene with five-fold and six-fold symmetry respectively. This scheme is illustrated in Figs. 2 and 3 for C_{70} and C_{72} .

Factorization of the planar graph of C_{50+10n} using five-fold symmetry

Labeling the vertices according to the Davidson-Shen^{31,32} algorithm for factorization of graphs with five-fold symmetry, we get $10 + 2n$ circuits as indicated in Table 1. In Fig. 2, the vertices of C_{70} have been labeled according to this scheme. With such labels the adjacency matrix A of the graph is found to be circulanty partitioned as:

$$A = \begin{bmatrix} B_1 & B_2 & B_3 & B_4 & B_5 \\ B_5 & B_1 & B_2 & B_3 & B_4 \\ B_4 & B_5 & B_1 & B_2 & B_3 \\ B_3 & B_4 & B_5 & B_1 & B_2 \\ B_2 & B_3 & B_4 & B_5 & B_1 \end{bmatrix} \quad (1)$$

where B_1 is the $(10 + 2n) \times (10 + 2n)$ block,

$$B_1 = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & - & - & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & - & - & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 1 & - & - & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & - & - & 0 & 0 \\ - & - & - & - & - & - & - & - & - & - \\ - & - & - & - & - & - & - & - & - & - \\ - & - & - & - & - & - & - & - & - & - \\ 0 & 0 & 0 & 0 & 0 & 0 & - & - & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & - & - & 1 & 0 \end{bmatrix} \quad (2)$$

The other blocks B_2 to B_5 can be similarly written down by looking at the vertex labels in the Schlegel diagram. After such partitioning, the Davidson-Shen^{31,32} algorithm shows that A becomes isospectral with the block diagonal matrix A' :

$$A' = \begin{bmatrix} A_1 & & & & \\ & A_2 & & & \\ & & A_3 & & \\ & & & A_4 & \\ & & & & A_5 \end{bmatrix} \quad (3)$$

where,

$$A_{j+1} = \sum_{k=0}^4 B_{k+1} \omega^{jk}, \quad \omega = \exp(2\pi i/5), \quad i = \sqrt{-1},$$

$$j = 0, 1, 2, 3, 4 \quad (4)$$

It can now be readily verified that the block A_1 is the adjacency matrix of the vertex-weighted graph G_A (Fig. 4), where, $h = 1 + \omega^5 = 2$.

A mirror-plane factorisation of G_A gives the fragments G_A^+ and G_A^- which are linear chains with $(n + 7)$ and $(n + 3)$ ver-

Table 1 Pentagonal circuits of C-atom resulting from C_5 symmetry of fullerene

Circuit no.	Vertex labels
1	1, 11 + 2n, 21 + 4n, 31 + 6n, 41 + 8n
2	2, 12 + 2n, 22 + 4n, 32 + 6n, 42 + 8n
—	—
10 + 2n	10 + 2n, 20 + 4n, 30 + 6n, 40 + 8n, 50 + 10n

Table 2 Eigenspectra of G_A i.e., common eigenvalues of some strongly subspectral fullerene pairs

n	G_A^+	G_A^-
1	3.000, 2.303, 1.820, 1.000, 2.757, -0.139, -1.303, -1.438	-0.382, -2.618, -2.618, -0.382
2	-1.414, -1.343, -0.414, 0.529, 1.414, 2.000, 2.424, 2.814, 3.000	-2.732, -2.000, -1.000, 0.000, 0.732
3	-1.401, -1.362, -0.586, 0.174, 1.000, 1.680, 2.133, 2.508, 2.854, 3.000	-2.802, -2.247, -1.445, -0.555, 0.247, 0.802
4	-1.393, -1.372, -0.698, -0.085, 0.641, 1.333, 1.863, 2.241, 2.587, 2.883, 3.000	-2.848, -2.414, -1.765, -1.000, -0.235, 0.414, 0.848
5	-1.388, -1.377, -0.772, -0.274, 0.350, 1.000, 1.572, 2.000, 2.334, 2.651, 2.904, 3.000	-2.879, -2.532, -2.000, -1.347, -0.653, 0.000, 0.532, 0.879

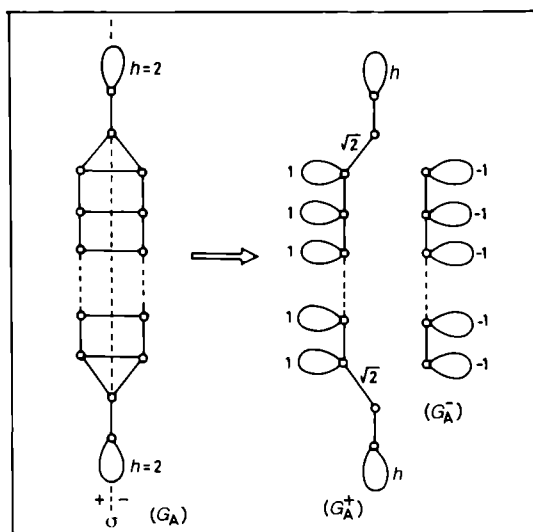


Fig. 4 The generic graph (G_A) giving the common eigenvalues of C_{50+10n} and C_{60+12n} and its factorisation.

L_0 :	1								
$h_1 L_0$:	2								
L_1 :	1	2							
$h_2 L_1$:	0	0							
$-(1)^2 L_0$:			-1						
L_2 :	1	2	-1						
$h_3 L_2$:	1	2	-1						
$-(\sqrt{2})^2 L_1$:			-2	-4					
L_3 :	1	3	-1	-5					
$h_4 L_3$:	1	3	-1	-5					
$-(1)^2 L_2$:			-1	-2	1				
L_4 :	1	4	1	-8	-4				
$h_5 L_4$:	1	4	1	-8	-4				
$-(1)^2 L_3$:			-1	-3	1				
L_5 :	1	5	4	-10	-11	1			
$h_6 L_5$:	1	5	4	-10	-11	1			
$-(1)^2 L_4$:			-1	-4	-1	8			
L_6 :	1	6	8	-10	-22	-2	5		
$h_7 L_6$:	0	0	0	0	0	0	0		
$-(\sqrt{2})^2 L_5$:			-2	-10	-8	20	22		
L_7 :	1	6	6	-20	-30	18	27	-2	
$h_8 L_7$:	2	12	12	-40	-60	36	54	-4	
$-(1)^2 L_6$:			-1	-6	-8	10	22	-5	
L_8 :	1	8	17	-14	-78	-32	85	54	-9
			↓			↓			↓

$$P(G_A^+; x) = x^8 - 8x^7 + 17x^6 + 14x^5 - 78x^4 + 32x^3 + 85x^2 - 54x - 9$$

Scheme 1 Construction of CP of G_A^+ with $n = 1$.

tices respectively (Fig. 4). The eigenvalues of G_A^- are:

$$\lambda_j = -1 + 2 \cos[j\pi/(n+4)], j = 1, 2, 3, 4, \dots, n+3 \quad (5)$$

It can further be verified that $A_2 = A_3$ and $A_3 = A_4$. Graphs corresponding to these matrices have directed edges with complex weights. Hence in this work we are considering only A_1 . The characteristic polynomials (CP) for G_A^+ (with any value of n) can be easily constructed by a recently developed³³ method. A simple calculation is shown in Scheme 1.

Factorisation of the planar graph of C_{60+12n} fullerenes using six-fold rotational symmetry

Using the same type of vertex labeling scheme with the help of C_6 -symmetry as used in the previous section and following the Davidson-Shen algorithm it is found that the block A_1 for the graphs of type II again corresponds to the graph G_A of Fig. 4 with $h = 1 + \omega^6 = 2$, where $\omega = \exp(2\pi i/6)$. The reason for this is that $(50 + 10n)/5 = (60 + 12n)/6 = 2n + 10 =$ number of vertices in G_A . Thus G_A (Fig. 4) is a generic graph giving the eigenvalues common to the two types of fullerenes considered in this work. The eigenvalues of G_A with $n = 1, 2, 3, 4$ and 5 i.e., the common eigenvalues of the pairs (C_{60}, C_{72}) , (C_{70}, C_{84}) , (C_{80}, C_{96}) , (C_{90}, C_{108}) and (C_{100}, C_{120}) are shown in Table 2.

Conclusions

It is proved that $10 + 2n$ eigenvalues of C_{50+10n} and C_{60+12n} fullerenes are identical and can be obtained from the same generic graph G_A (Fig. 4) having $10 + 2n$ vertices. Thus (C_{60}, C_{72}) , (C_{70}, C_{84}) , (C_{80}, C_{96}) ... are strongly subspectral pairs having at least 12, 14, 16 ... eigenvalues, respectively, in common. $(n+3)$ out of the $2n+10$ common eigenvalues of the two series are given by formula (5). We also observed two important spectral features, viz. (i) the highest common eigenvalue 3.0 (which is a consequence of degree-3 regularity) of all fullerene graphs is contained in G_A^+ and (ii) every third member from C_{70}/C_{84} has a non-bonding level, the zero eigenvalue being contained in the corresponding G_A^+ . This is consistent with Fowler's observation¹³ that a non-bonding level exists above a closed shell electronic structure in every third member from C_{70}/C_{84} .

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