

The thesis consists of two parts . Part I deals with graph theoretical methodologies (in HMO formalism) relevant to the analysis of certain experimentally observed trends and eigenspectra of some fullerene graphs . Part II consists of experiments on EDA interactions where the acceptors are [60]C₆₀ fullerene , *o*-chloranil (3,4,5,6-tetrachloro 1,2-benzoquinone) and 2,3-dichloronaphthoquinone and the donors are (i) a series of phenols, (ii) a series of polynuclear aromatic hydrocarbons and (iii) N-N' diphenyl thiourea .

The works described in Part I may be summarised as follows.

1. A convenient method for construction of characteristic polynomials of linear graphs with arbitrary vertex- and edge-weights has been developed . This method has been shown to be particularly useful for construction of CP of graphs which can be linearised by symmetry factorisation .

2. In search of an application of the method to general fullerene graphs, a method for construction of the Schlegel diagram of C_{50+10n} and C_{60+12n} (n = an integer) has been developed , maintaining 5- and 6-fold symmetry axes respectively and isolation of pentagons ; these graphs were then symmetry factorised by Davidson-Shen method and one component block was factorised into vertex- and edge-weighted linear graphs to which the method described in (1) could be applied . Results of this work are the following :

(a) The pairs (C_{50+10n} and C_{60+12n}), n = 1,2,3,... are strongly subspectral with 10+2n common eigenvalues , all being derivable from a common generic graph (G_A) with 10+2n vertices .

(b) G_A has a mirror plane symmetry and thus can be factorised into linear fragments G_A⁺ and G_A⁻ . The fragment G_A⁻ has eigenvalues given by the general formula

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

To the other fragment (G_A⁺) the method developed in (1) can be applied to obtain the CP.

(c) The highest eigenvalue , 3 , which is a consequence of degree-3 regularity of fullerene graphs) is contained in G_A⁺ .

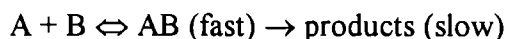
(d) Every third member from C_{70} / C_{84} (i.e., from $n=3$) has a non-bonding level, the zero eigenvalue being contained in G_A^- . This is consistent with Fowler's observation¹¹⁵ that a non-bonding level exists above a closed shell electronic structure in every third member from C_{70} / C_{84} .

3. A comparison of the electron acceptor properties of *o*- and *p*- benzoquinones and the corresponding quinols has been done graph theoretically where the method developed in (1) has been used.

4. Besides these, the method of construction of CP developed in (1) has been shown to be useful in the interpretation of trends in charge-transfer transition energies ($h\nu_{CT}$) of a series of *o*-chloranil-phenol EDA complexes, the study on which has been described in Part II. The works done in the experimental portion (Part II) of the thesis may be summarised as follows.

5. The electron donor-acceptor (EDA) interaction 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 the 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_{δ} and $k_{C-\delta}$) 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. Details of such calculation by graph theory, where the method of construction of CP developed in (1) has been used, is described in the relevant chapter (Chapter 6).

6. The reaction between 2,3-dichloro 1,4-naphthoquinone and N,N'-diphenylthiourea in acetonitrile medium, which yields two products, viz., 2,3-(N,N'-diphenylthioureylene)-naphtho-1,4-quinone and 2,3-(N-phenyl-[2',3'] benzo epimino) naphtho-1,4-quinone, has been found to take place in two ways – thermal and photochemical. The thermal (dark) reaction occurs through an electron donor-acceptor (EDA) adduct as intermediate with evolution of HCl and kinetic data fit into the scheme



Formation constant of the EDA adduct and the rate constant of the slow process have been determined at four different temperatures from which enthalpy of formation of AB and activation energy of its decay into products have been determined. The photochemical reaction has been studied under diffused sunlight and also at $\lambda = 360$ nm ordinary light; the same has been studied with 365 nm and 370 nm laser beams. Use of laser causes about 10^3 times increase in the rate of the reaction but does not affect the quantum yield. The final products have been isolated and characterised by elemental analysis, ^1H and ^{13}C NMR, IR spectroscopy and mass spectrometry.

7. 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.

8. [60]fullerene has been shown to have a very high quenching effect on the fluorescence of anthracene at room temperature in n-hexane. However, no deviation from linearity in the Stern-Volmer plot was observed, and so this quenching cannot be attributed to EDA complex formation between C_{60} and anthracene. Formation of such a complex is not possible owing to the very low concentration used in the study ($\sim 10^{-5}$ mol dm^{-3} in each of C_{60} and anthracene).