

Abstract of Ph.D. Thesis

Experimental and Theoretical Investigations of Electronic Spectra of Hydroxy and Amino Derivatives of Anthraquinone

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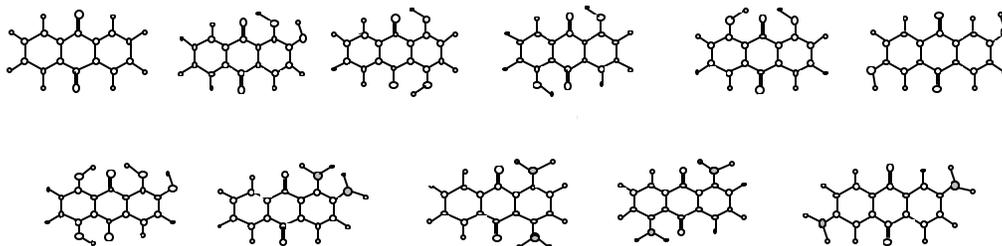
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Anthraquinone (AQ) and its hydroxy and amino derivatives are of considerable practical significance in pharmacology, biochemistry and dye industry. Due to the wide-ranging applications that hydroxy and amino substituted anthraquinones possess we have carried out a detailed and systematic study of the electronic spectra of 9,10-anthraquinone (A) and its hydroxy and amino substituted systems. The following disubstituted derivatives of AQ are included in the study: 1,2-dihydroxy-9,10-anthraquinone (B), 1,4-dihydroxy-9,10-anthraquinone (C), 1,5-dihydroxy-9,10-anthraquinone (D), 1,8-dihydroxy-9,10-anthraquinone (E), 2,6-dihydroxy-9,10-anthraquinone (F), 1,2,5,8-tetrahydroxy-9,10-anthraquinone (G), 1,2-diamino-9,10-anthraquinone (H), 1,4-diamino-9,10-anthraquinone (I), 1,5-diamino-9,10-anthraquinone (J), and 2,6-diamino-9,10-anthraquinone (K).



Electronic Spectra: The electronic absorption spectra are measured in a variety of non-polar and polar solvents at room temperature in the spectral range 190 nm – 900 nm. The effect of amino and hydroxy group on the spectra is also studied and two correlations are derived to estimate the shifts in the wavelength maxima of the lowest $\pi\pi^*$ transitions of anthraquinone derivatives. The wavenumber maxima of the lowest $\pi\pi^*$ state of the anthraquinone derivatives calculated using these empirical relations correlate well with the experimental values and that the correlation is found to be perfectly linear.

Optimization of Molecular Geometries: An important feature of the present work is the optimization of the molecular geometries of the anthraquinones using the ZINDO/1 (*Zerner's Intermediate Neglect of Differential Overlap*) and AM1 (*Austin Model 1*) methods. The Optimized geometrical parameters of ground state molecular structures

thus obtained are in accord with the available X-ray data. In particular, the molecular geometries predicted with the AM1 method are found to be in better agreement with the experiment. The geometry optimizations based on the AM1 method carried out for different tautomers and rotomers of hydroxy derivatives reveal that except for the 2,6-dihydroxy-9,10-anthraquinone, the ground state structures with of the molecular systems under investigation are the most stable ones. The strengths of the *intramolecular hydrogen bond(s)* (IHBs) in the hydroxy derivatives are also estimated computationally using the AM1 method and are found to be in perfect agreement with the values reported earlier.

Interpretation of Electronic Spectra of AQs using ZINDO/S and AM1 Methods: The ZINDO/S and AM1 calculations using configuration interaction are carried for the first time to calculate the electronic spectra of anthraquinone and its hydroxy and amino derivatives. Based on the information from these calculations, the assignments of the electronic transitions are successfully made. The assignments of the electronic bands of the hydroxy substituted systems except for 1,4-dihydroxy-9,10-anthraquinone are entirely new.

Solvent Effect on Electronic Spectra: Study of the effect of solvents on the electronic absorption spectra of anthraquinones forms an important theme of our investigation for which experiments are carried out using twenty four solvents of different polarity. The spectral shifts in various solvents indicate that the value of the spectral shift mainly depend on the strength of the intermolecular hydrogen bond(s) between the substituent groups and the solvent molecules and whether the intramolecular hydrogen bonds are present or not. For the molecular systems with either no intramolecular hydrogen bond (IHB) or an active hydroxyl or amino group that is not involved in the IHB the spectral shifts are quite sensitive to the solvent polarity. It is found that the CT bands ($\pi \rightarrow \pi^*$ transitions) in these molecules are shifted bathochromically with the increase in the solvent polarity, the bathochromic shift being attributed to hydrogen-bonding interaction between the solute molecule and the solvent molecule. On the other hand, spectral shifts in the molecular systems with intramolecular hydrogen bonds (IHBs) are very small. In the absence of the intermolecular hydrogen bonds in all the intramolecular hydrogen bonded systems, the solvent shifts are well interpreted by the solvent polarity function .

Interpretation of Electronic Spectra of Radical Cations of Methyl Substituted Hydrocarbons: In addition to the study of electronic spectra of anthraquinones, we have also carried out the ZINDO/S calculations on the electronic absorption spectra of radical cations of naphthalene, anthracene, phenanthrene and their methyl-substituted systems. On the basis of these calculations, we have for the first time successfully assigned the electronic bands of the above-mentioned molecular systems. Such molecular species are of considerable importance in astrophysics as aromatic hydrocarbons with side chains have been suggested as the possible carriers of the *diffuse interstellar bands* (DIBs). In the nutshell, this work presents a systematic and comprehensive study of electronic spectra of anthraquinone and its hydroxy and amino derivatives.

Keywords: Electronic absorption spectra, Amino-anthraquinones, Hydroxy-anthraquinones, ZINDO/S Calculations, AM1 Calculations, Solvent effect.