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Theoretical Molecular Structures and Vibrational Analysis of Monohalogenated Thiophenols

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Thiophenol (benzenethiol) ArSH as a derivative of phenol belongs to the sulfur-containing compounds whose importance in atmospheric, environmental, biological, and medical areas can hardly be overestimated. Moreover, the recent huge activity in nanoscience and nanotechnology has renewed the interest in these compounds, particularly in thiophenols and its derivatives, because of the ability of sulfur to bind metallic clusters [1-3]. As yet, geometrical parameters and frequency assignment of halothiophenols are unknown. In this work the effect of -F, -Cl, and -Br substitutions upon the geometry, vibrational frequency, and infrared intensities of thiophenol is discussed. We also examined the intramolecular hydrogen bonding of ortho-substituted thiophenols and compared with that of phenols. In this study, the equilibrium geometry and vibrational frequency of titled compounds were computed with the GAUSSIAN 03 software program by using a selection of modern density functional, using B3LYP level. Natural bond orbital analysis [4] was carried out using 6-311++G** basis set. The influence of solvent on compounds was studied using the Onsager model. The optimized geometry parameters and harmonic vibrational frequencies of halogenated thiophenols in the gas phase obtained at Density Functional Theory (B3LYP) level using 6-31G**, 6-311G**, and 6-311++G** basis sets. A comparison of the theoretical spectra of thiophenol with experimental data shows a rather good performance of the B3LYP/6-311++G**. The structural changes of the thiophenol ring are governed mainly by the electronegativity of the halogen atoms and, to a lesser extent, by resonance factors. All the vibrational normal modes of these compounds were assigned completely. The SH stretching, bending and torsional modes occupy a particular place among all the vibrational modes of thiophenol due to their extreme sensitivity to molecular environment. It was observed that the substitution effects on these frequencies. Also the energy differences obtained show that the strength of hydrogen bonding in the ortho-halothiophenols depends on type of substituted halogen atom and environmental conditions.

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NLO Properties of Aza-platinabenzene-Based Chromophores: A theoretical Study

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The hyperpolarizabilities for a series of substituted Aza-platinabenzene -based nonlinear optical (NLO) chromophores were determined. The effects on the hyperpolarizabilities of various donor and acceptor substituents (NH₂, OH, Me, H, F, COOH, CN, NO₂) were studied. To understand this phenomenon in the context of molecular orbital picture, we examined the molecular HOMOs and molecular LUMOs generated. The effects of the intramolecular charge transfer (ICT) from the donor to the acceptor groups on the molecular geometry and atomic charge distribution of this NLO-phore are minimum-energy structure and Natural Population Analysis.

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Spectrophotometric and thermodynamic studies on complex formation of thallium (I) ion with uracil at different temperatures

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Research results have clearly demonstrated that certain metal ions play a basic role in directing a number of biochemical processes. Thallium has been recognized as a toxic element for many years. Since thallium(I) shows marked similarities to that of potassium cation, its interaction with nucleotides, the monomeric units of DNA and RNA, in aqueous solution would be of a major biochemical interest [1]. In the living cell, there are found nucleoproteins. These compounds control heredity on the molecular level [2]. This revealed the need for comprehensive studies of metal ion-bioligand interactions, as model systems. Spectroscopic methods are in general highly sensitive and are frequently used to analyze chemical equilibria in solution [1-5]. In 1971 Lawton and Sylvestre introduced chemometric methods for spectral analysis. In the present work, the formation constant of thallium (I) ion with the heterocyclic base of uracil in aqueous solution was studied using a combination of potentiometric and spectrophotometric methods at different temperatures and constant ionic strength by means of computer fitting of the pH-absorbance data with appropriate mass balance equations. A sophisticated method based on chemometrical concepts was applied in order to determine formation constants. For this purpose, the computer program equispec was used to extract the desired information from the spectral data. The effect of temperature on the formation constants were studied and thermodynamic functions have been obtained for the complexes of thallium (I) with heterocyclic base. Uracil and thallium (I) nitrate were of analytical reagent grade (Merck). These chemicals were used without further purification. All solutions were prepared in deionized water with specific conductance equal to $(1.8 \pm 0.1) \mu\Omega^{-1} \text{ cm}^{-1}$. A HORIBA M-12 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated at pH 3.00 and 9.00 [2]. A HP-8453 spectrophotometer controlled by a computer was used for UV-Vis spectra acquisition. The data were transferred to a computer for subsequent analysis using MATLAB software, version 6.5 and for