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VIBRATIONAL AND THEORETICAL STUDY OF A NEW ORGANIC COMPOUND: 4-NITROTOLUENE-2-SULPHONIC ACID DIHYDRATE

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Abstract:

The complete physicochemical properties of the compound 4-nitrotoluene-2-sulphonic acid dihydrate have been reported by using Density Functional Theory. Quantum chemical calculations of 4-nitrotoluene-2-sulphonic acid dihydrate has been carried out by using DFT/B3LYP/6-31+G(d,p) method. The investigation of HOMO-LUMO gap helps to give information about the molecular stability. From the NBO analysis the inter and intra-molecular interactions and the transfer of charge taking place within the molecule are clearly studied. Molecular electrostatic potential maps (MEPs) help to determine the charge distribution interactions and in the determination of the nature of the chemical bond.

Key Words: Computational DFT, HOMO-LUMO Energy Gap, NLO, MEP & NBO

1. Introduction:

Computer-aided molecular design (CAMD) provides a means for determining molecules having a desirable set of physicochemical properties and is essential for the development of medicinal chemistry [1]. The theoretical methods based on density functional theory (DFT) are playing an increasingly prominent role in many applications of computational chemistry and for NLO applications. In industries the role of computer-aided molecular design is developed into a powerful set of methods involving the calculation of molecular properties. DFT-based calculations are also used to solve the electronic structure of the molecule and design new molecules with various specific properties**.** The thermodynamic and kinetic properties of molecules have been predicted by means of theoretical chemistry which is implemented on fast computers. CAMD is an essential method for industrial applications too and **s**tructure-based methods are also used in a variety of computational chemistry methods [2]. In consideration to the above theoretical approach the compound 4-nitrotoluene-2-sulphonic acid dihydrate has been studied for various applications.

2. Computational Details:

The entire quantum chemical computations are performed using the Gaussian 09 software [3] and GaussView [4] on a personal computer. The vibrational frequencies are determined on the basis of the corresponding PEDs by using VEDA program [5]. The geometry of the title molecule 4-nitrotoluene-2-sulphonic acid dihydrate is fully optimized using B3LYP functional with 6-31+ G (d,p) basis set. The molecular structure is optimized and used to simulate the FTIR and FT-Raman calculations. The other properties such as HOMO–LUMO and NBO have been calculated using time-dependent TD-DFT - B3LYP method.

3. Result and Discussion:

3.1 Optimized Molecular Structure: A complete geometrical optimization has been performed at DFT/B3LYP/6-31+G** level within the C_1 point group symmetry and the most stable optimized molecular structure of NTSAD is shown in Fig.1.

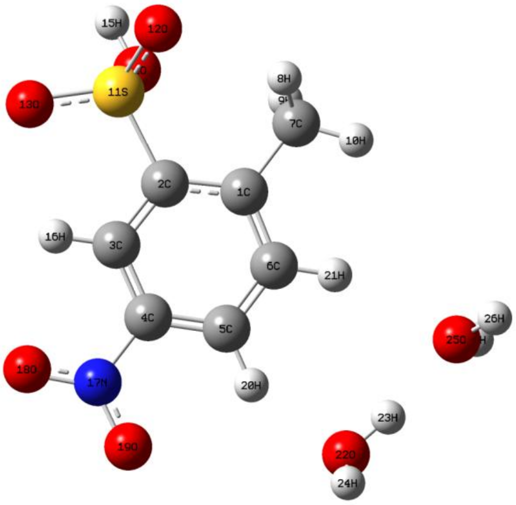
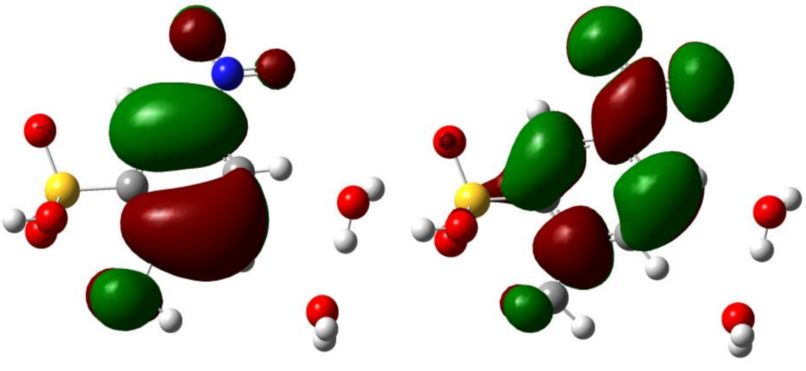


Figure 1: Molecular Structure of NTSAD

3.2 Vibrational Analysis: NTSAD consists of 27 atoms and it has 75 normal vibrational modes. The point group for the title molecule is C_1 point group with 75 degrees of freedom. All the vibrations are active in both IR and Raman. The band at 3713 cm^{-1} in FTIR and 3701 cm^{-1} in Raman spectrum confirms the strong hydrogen bonding interaction taking place in NTSAD. The band simulated at 3116 cm^{-1} are attributed to C-H stretching vibrations. The calculated wave numbers established at1572, 1554, and 1435 cm^{-1} are allotted to C-C stretching vibrations. The band computed at 3002 and 2980 cm^{-1} are assigned to -CH_3 stretching mode. The bands appeared at 1272 cm^{-1} are allotted to –SO_3stretching vibration.

3.3 HOMO- LUMO Analysis: The electronic absorption corresponds to a transition from the ground state to the excited state and is evident by one electron excitation i.e. from HOMO to the LUMO. The frontier molecular orbitals are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), play an important role in the electric and optical properties for molecular systems [6]. The frontier orbital surfaces have been drawn to understand the bonding scheme of NTSAD compound and it is shown in Fig. 2.The HOMO-LUMO energy gap for NTSAD is found as -1.6799 eV. The soft molecules are more polarisable than the hard ones as they need only small energy to get excited. From the pictorial plot of the HOMO-LUMO, the red colour corresponds to the positive phase and green colour depicts the negative phase.



HOMO LUMO

Figure 2: Frontier molecular orbitals of NTSAD

3.4 Analysis of Molecular Electrostatic Potential Surface: The MEP act as an information tool of chemistry to describe different physical and chemical features, including non-covalent interactions in complex biological system [7]. Analysis of MEP predicts the reactive sites of electrophilic and nucleophilic attack and is visualized in Fig.3. In Fig.3, electrophilic reactivity are assigned to the negative (red and yellow) regions of MEP and the positive (blue) regions are connected to nucleophilic reactivity. The electrostatic potential increases in the order red<orange<yellow<green<blue. The color code of the maps is in the range between -0.112 a.u. (deepest red) and 0.112 a.u. (deepest blue) in the title compound. From the molecular surface map, red colour clearly depicts the negative regions localized over the oxygen atoms of the nitro group and which denotes a possible site for electrophilic attack. The hydrogen atoms in the case of methyl group with blue shade indicate the nucleophilic centre.

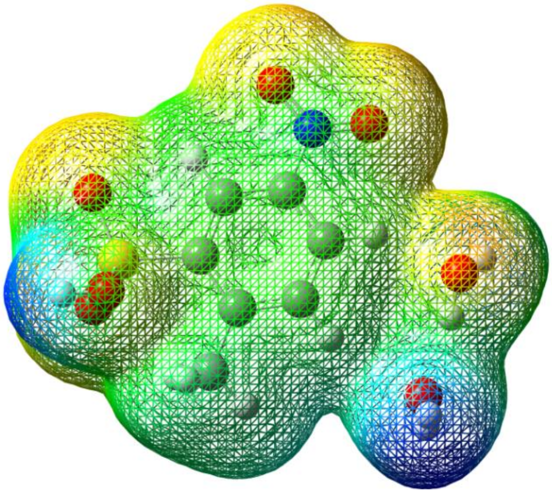


Figure 3: Molecular Electrostatic Potential of NTSAD

3.5 Natural Bond Orbital Analysis:

Natural bond orbital (NBO) analysis is a proficient method to investigate the intra-molecular, inter-molecular bonding and the interaction among bonds [8]. The stabilization energy is attributed to n→π* taking place between n (O13) to π* (S11-O12) with the energy 44.32 KJ/mol. The strong interactions that occur in the title molecule having π→π* transition from lone pair O19 with that of antibonding N17-O18 and the lone pair O12 with that of antibonding S11-O14 results in the stabilization of 144.52 kj/mol and 35.54 kj/mol respectively, which donates larger delocalization. The maximum energy is transfer from O19 and O12 to N17-O18 and S11-O13. Conjugation to the anti-bonding orbital causing n→ σ* transition from (O18)→(N17-O19) contributes maximum stabilization energy of 27.62 and 25.52 kcal/mol respectively.

4. Conclusion:

The geometrical parameters have been investigated by means of optimization of the title molecule. The vibrational nature of the functional groups present in the molecule is investigated by analyzing the vibrational spectrum. The calculated HOMO and LUMO energies authenticate the charge transfer occurs in the molecule when it is excited. Molecular electrostatic potential maps (MEPs) depicts the electrophilic and nucleophilic regions. The hyper conjucative calculations are determined from the NBO analysis.

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