VIBRATIONAL SPECTRAL INVESTIGATION OF 4-(1-HYDROXYETHYL)BENZENE-1-SULFONAMIDE

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Abstract- The optimization geometry, intramolecular hydrogen bonding and harmonic vibrational wavenumbers of 4-(1-hydroxyethyl)benzene-1-sulfonamide have been investigated with the help of B3LYP density functional theory (DFT) methods. The infrared and Raman spectra were predicted theoretically from the calculated intensities. The various intramolecular interactions have been exposed by natural bond orbital (NBO) analysis. Various reactivity and selectivity descriptors such as chemical hardness, chemical potential, softness, electrophilicity, nucleophilicity and the appropriate local quantities employing natural population analysis (NPA) are calculated.
Keywords – DFT, NBO, NPA

I. INTRODUCTION

Benzenesulfonamide derivatives find wide applications for the synthesis of pharmaceutical products and the synthesis of high molecular weight substances. The chemistry of sulfonamides has been known as synthons in the preparation of various valuable biologically active[1] compounds used as an antibacterial[2], protease inhibitor[3], antitumor[4] and hypoglycaremic[5]. Because of the wide variety of the biological importance of the sulfonamides, the synthesis of several substituted sulfonamides, the study of their crystal structure and other physical, chemical and bioactivity studies have become interesting field in research. The title compound 4-(Hydroxyethyl)benzene-1-sulfonamide (4-HBS) is one such organic compound that belongs to the sulfonamide family. The density functional theory (DFT) method has become a powerful tool for the investigation of molecular structure and vibrational analysis. In the case of sulfonamides, the electron-withdrawing group is the sulfonamide group[6,7]. Literature survey shows that neither spectroscopic characterizations nor computational studies have been done so far on the title compound. In the present study geometry optimization, NBO analysis and HOMO-LUMO analysis are reported.

II. COMPUTATIONAL DETAILS

The DFT computation of 4-HBS was performed using Gaussian '09 program package[8] at DFT level. The computed wavenumbers are scaled by an empirical scaling factor of 0.9682 to fit with the experimental wavenumbers. The Raman activities (S_i) calculated by Gaussian '09 are converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [9]:

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[1 - exp\left(\frac{-hcv_i}{kT}\right)\right]}$$

in order to investigate the optimized geometry corresponding to hydrogen bonding. The hyperconjugative interaction energy was deduced from where v_o is the exciting wavenumber, v_i is the vibrational wavenumber of the ith normal mode, h,c and k are the universal constants and f is the suitably chosen common scaling factor for all peak intensities. The natural bonding orbital (NBO) analysis was performed the second-order perturbation approach [10]:

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$$E^{(2)} = -n_\sigma \frac{\langle \sigma | F | \sigma \rangle^2}{\varepsilon_{\sigma*} - \varepsilon_\sigma} = -n_\sigma \frac{F_{ij}^2}{\Delta E}$$

where $\langle \sigma | F | \sigma \rangle^2$ or F_{ij}^2 is the Fock matrix element between the *ith* and *jth* NBOs, ε_σ and $\varepsilon_{\sigma*}$ are the energies of σ and $\sigma*$ and n_σ is the population of the donor σ orbital. The HOMO-LUMO energy gap have been computed and analyzed.

III. OPTIMIZED GEOMETRY

The optimized geometry of 4HBS molecule was obtained at B3LYP level and shown in figure 1. In the benzene ring C_1-C_6 bond length slightly elongated due to the substitution of hydroxy ethyl group at C_1 position and the hindrance between H_7 and H_{20} atom. The highest bond length observed in this molecule is C_4-S_{11} (1.794 Å). The bond angles C_3-C_4-C_5 (121.2°) and C_2-C_1-C_6 (119.2°) shows variation from 120°, which reveals the interaction between the benzene ring and sulfonamide group as well as hydroxyl ethyl group. This variation in the bond angles also shows the deviation from the aromatic nature of the benzene ring. The atoms around the sulfonamide 'S' atom in the title compound are arranged in slightly distorted tetrahedral configuration.
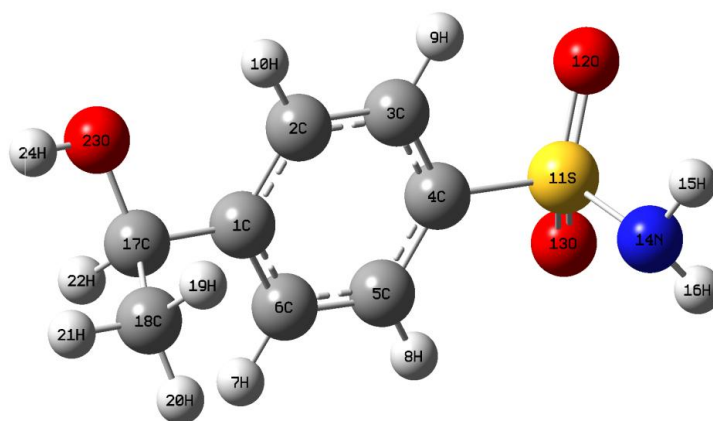

Figure 1 Optimized structure of 4-HBS

The bond angle C_4-S_{11}-N_{14} (107.6°) is smaller than the tetrahedral value of 109° [11]. The torsion angle (C-C-S-N) defining the conformation of the sulfonamide group is reported to lie in the range 60-90° [11].

Table 1 Optimzed parameters

Bond Length	Exp. Value (Å)	Cal. Value (Å)
C1-C2	1.395	1.396
C1-C6	1.395	1.399
C3-H9	1.087	1.083
C4-S11	1.764	1.794
Bond Angle	**Exp. Value (°)**	**Cal. Value (°)**
C1-C2-C3	120	120.5
C2-C3-C4	120	119.2
C3-C4-C5	120	121.2
C4-S11-N14	108	107.6
Dihedral Angle	**Exp. Value (°)**	**Cal. Value (°)**
C1-C2-C3-C4	-0.01	0
C3-C4-C5-H8	-179.9	177.8
C5-C4-S11-N14	-81.6	-83.9
C4-C5-C6-H7	179.4	178.9
C1-C17-C18-H19	-56.3	-58.8

In the title compound the torsion angle $\tau(C_5$-C_4-S_{11}-$N_{14})$ is 83.9°. The hydroxyl ethyl group and sulfonamide group are found out of plane indicated from the torsion angles shown in the table.

IV. CHARGE ANALYSIS

The calculation of effective atomic charges plays an important role in the application of quantum mechanical calculation to molecular systems. The atomic charges of 4HBS molecule is calculated according to the natural population analysis by using B3LYP/6-311G(d,p) method and shown in figure 2.
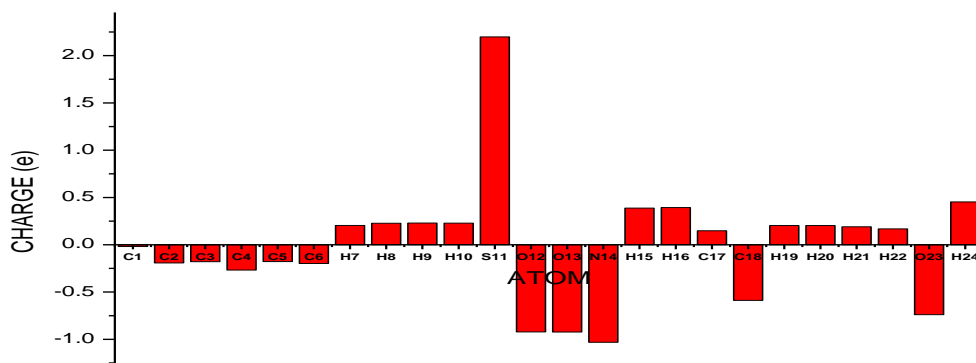

Figure 2. Charge plot of 4-HBS

The positive charge on C_{17} attributes to the presence of hydroxyl group in it and the remaining carbon atoms have negative charges. The S_{11} atom posses a very high positive charge. All oxygen atoms and nitrogen atom of the NH_2 group in the molecules accepted electrons. Charge migration to heavy atoms can be related to molecular interactions.

V. NBO ANALYSIS

The Natural Bond Orbital (NBO) analysis is proved to be an effective tool for chemical interpretation of hyperconjugative interaction and electron density transfer from the filled lone pair electron. The intramolecular interaction are formed by the orbital overlap between σ and π (C-C, C-H and C-N) and σ* and π* (C-C, C-H and C-N) bond orbitals which results intramolecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as increase in electron density (ED) in C-C anti bonding orbital that weakens the respective bonds[12]. The electron density of conjugated double as well as single bond of the aromatic ring clearly demonstrates strong delocalization inside the molecule. The orbital interaction energy between σ (C_1-C_{17}) → σ* (C_5-C_6) and σ (C_4-S_{11}) → σ* (C_5-C_6) are 10.84 and 11.05 kJ/mol respectively. These increasing interaction energies are due to the strong ICT interactions leading to stabilization of the molecule. The magnitude of charges transformed from LP (2) O_{23} → σ* (C_{17}-H_{22}) and LP (2) O_{23} → σ* (C_{18}-H_{20}) show weak intramolecular interactions with stabilization energies 31.67 and 3.05kJ/mol respectively.

VI. VIBRATIONAL ANALYSIS

The experimental FT-IR spectrum is shown in figure 3. The NH2 stretching modes are expected in the region 3260-3390 cm^{-1} [13] and in the present case the stretching bands have split into a doublet 3326, 3242 cm^{-1} in the IR spectrum. The bands observed at 3502, 3397 (DFT) are assigned as NH_2 stretching modes. The rocking/twisting mode of NH_2 is expected in the region 1195 ± 90 cm^{-1} and this mode is observed at 1132 cm^{-1}. The wagging mode of NH_2 is expected in the region 840 ± 55cm^{-1}. For the title compound a medium peak at 808 cm^{-1} is observed and theoretically at 829 cm^{-1}.
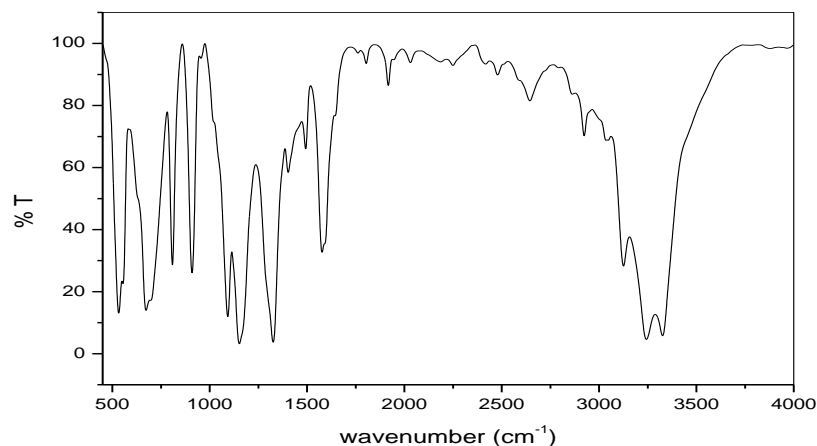
Figure 3 FT-IR spectrum of 4-HBS

The phenyl CH stretching modes occur above 3000 cm^{-1}. In this region, the bands are not affected appreciably by the nature of the substituents[14,15]. For the title compound, the DFT calculations give C-H stretching modes of the benzene ring in the range 3132-3057 cm^{-1}. The bands observed at 3125 cm^{-1} and 3035 cm^{-1} in the IR spectrum were assigned as CH stretching modes of the phenyl ring. The aromatic C-H in plane bending modes of benzene and its derivatives are observed in the region 1000-1300 cm^{-1} with week intensity in the vibrational spectra. In the present case also, the C-H in plane or out of plane bending vibrations are marked by other strong vibrational modes.

Table 2 Modes of vibration

FT-IR		IR intensity	Assignments with PED%
Exp. Wavenumber(cm[-1])	Cal. Wavenumber (cm^{-1})		
3326	3398	43	ν(N14-H15)100
3125	3102	1	ν(C5-H8)96
1577	1566	1	ν(C1-C2)31+β(C1-C2-C3)11
1326	1372	24	β(H22-C17-O23)20
808	816	29	τ(H9-C3-C4-S11)42

The C-H asymmetric stretching vibration of the methyl group appears between 3060 cm^{-1} and 2984 cm^{-1}. For the title compound the asymmetric C-H stretching is observed at 2990 cm^{-1} with PED 97%. The symmetric C-H stretching band of methyl group is observed at 2923 cm^{-1} and 2862 cm^{-1} in the IR spectrum. The other fundamental CH_3 group vibrations which are CH_3 bending , CH_3 rocking appear in the wave number region of 792 cm^{-1} – 1461 cm^{-1}.

The asymmetric and symmetric stretching modes of SO_2 group appears in the region 1310 – 1360 cm^{-1} and 1135 – 1165 cm^{-1} [16].The very strong bands observed at 1326 cm^{-1} and 1152 cm^{-1} are assigned as SO_2 stretching modes. The SO_2 scissoring and wagging vibrations occur in the range 570 ± 60 cm^{-1} and 520 ± 40 cm^{-1}. The corresponding bands are observed for the title compound at 554 cm^{-1} and 532 cm^{-1} in the FT-IR spectrum, calculated as 549 cm^{-1} and 484 cm^{-1} respectively. The SN and CS stretching modes are observed at 833 cm^{-1} for sulfonamide derivatives. The C-S stretching vibration is assigned at 672 cm^{-1} (IR) and at 657 cm^{-1} (DFT).

VII. HOMO – LUMO analysis

The frontier molecular orbitals play an important role in the electric and optical properties as well as the chemical reaction[17]. The energy gap between highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals has been used to prove the bioactivity from intramolecular charge transfer. The energies of HOMO and LUMO orbitals relates the energies of ionization potential and electron affinity of the molecule and characterizes the susceptibility of molecules towards the attack of electrophiles and nucleophiles. The concept of hard and soft

nucleophiles have a low and high energy HOMO respectively while the hard and soft electrophiles have a high and low energy LUMO respectively.
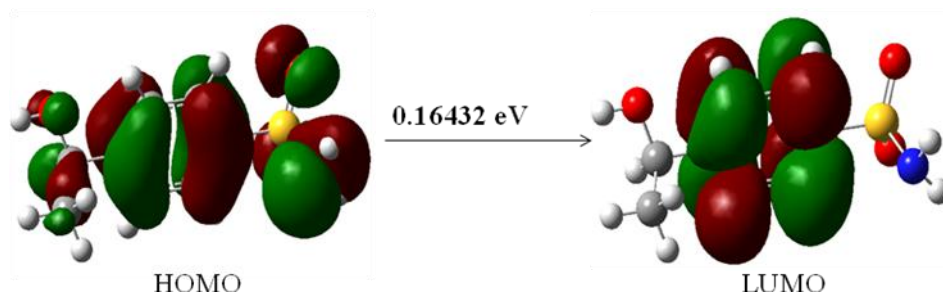

Figure 3 The Frontier Molecular Orbitals of 4-HBS

According to Koopmann[18] the HOMO energy is related to ionization potential and the LUMO energy is used to estimate the electron affinity and their average energy is related to electronegativity and the calculated HOMO-LUMO energy gap is closer to the first electronic excitation energy. The frontier orbitals gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule. The HOMO and LUMO energy are calculated by B3LYP/6-311G(D,P) method and are listed in table 3. For the title compound HOMO orbitals are mainly localized on the sulfonamide and hydroxy ethyl group. LUMO orbitals are localized on the phenyl ring, hence the electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ are expected. The energies of HOMO and LUMO are -0.34790 eV and -0.18358 eV respectively.

Table 3 Calculated energy value of 4HBS molecule

Parameter	B3LYP/6-311 G(D,P)
HOMO (eV)	-0.34790
LUMO (eV)	-0.18358
Energy gap (eV)	0.16432
Chemical hardness (η)	0.08216
Chemical potential (μ)	-0.26574
Electrophilicity Index (ω)	0.42969

VIII. CONCLUSION

The structure of 4-(Hydroxyethyl)benzene-1-sulfonamide is optimized with B3LYP method using 6-311G(D,P) basis set. The vibrational wavenumbers were calculated using DFT method. FT-IR spectrum of the title compound was recorded and analyzed. NBO result reflects the charge transfer mainly due to the sulfonamide group. The charge transfer also depends on the HOMO-LUMO energy gap. The energy gap between HOMO and LUMO is 0.16432 eV. The atoms in the sulfonamide group are more prone to nucleophilic attack. Thus the present investigation provides a complete and reliable structural, vibrational and structure-activity relations of the compound.

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