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FT-IR, FT-Raman spectroscopy and computational study of *N*-carbamimidoyl-4-{[(E)-((2-hydroxyphenyl)methylidene]amino} benzenesulfonamide

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ABSTRACT

The infrared and Raman spectra of *N*-carbamimidoyl-4-((2-hydroxybenzylidene) amino) benzenesulfonamide have been recorded and analyzed. Geometry and harmonic vibrational wavenumbers were calculated theoretically using Gaussian 03 set of quantum chemistry codes. Calculations were performed at the DFT (B3LYP) and MP2(SDD) levels of theory. The calculated wavenumbers (MP2) agree well with the observed wavenumbers. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands found in infrared and Raman spectra of the studied molecule. The red-shift of the N–H stretching band in the infrared spectrum from the computed wavenumber indicates the weakening of the N–H bond. The N–H stretching bands has split into a doublet, 3453, 3427 and 3355, 3225 cm^{-1} in the IR spectrum owing to the Davydov coupling between neighboring units. The geometrical parameters of the title compound are in agreement with the reported similar derivatives. Calculated infrared intensities, Raman activities and the first hyperpolarizability are reported. The calculated first hyperpolarizability is comparable with the reported value of similar structures and may be an attractive object for further studies on non linear optics.

1. Introduction

Sulfonamides represent an important class of medicinally important compounds which are extensively used as bacteriostatic agent. It is well documented [1–4] that toxicological and pharmacological properties are enhanced when sulfonamides are administered in the form of their metal complexes [5–8]. Carta et al. [9] reported the synthesis of a series of diazenylbenzenesulfonamides, azo-dye derivatives of sulfanilamide or metanilamide incorporating phenol and amine moieties and were tested for inhibition of the tumor associated isozymes carbonic anhydrase. In analytical area, sulfonamides have been investigated as reagents for the separation, concentration, and selective determination of many of the first row transition metal cations [10–12]. Yilmaz et al. [13] reported the synthesis, spectra and crystal structure of 2-({[3-(methyl){3-[(2-hydroxybenzylidene)amino]propyl}amino)propyl] imino}methyl) phenol copper (II) complex. There has been growing interest in using organic materials for nonlinear optical (NLO) devices, functioning as second harmonic generators, frequency converters, electro-optical modulators, etc. because of the large second order electric susceptibilities of organic materials. Since the second order electric susceptibility is related to first hyperpolarizability, the search for organic chromophores with large first hyperpolarizability is fully justified. The organic compound showing high hyperpolarizability are those containing an electron-donating group and an electron withdrawing group interacting through a system of conjugated double bonds. In the case of sulfonamides, the electron withdrawing group is the sulfonyl group [14,15]. To our knowledge, no theoretical density functional theory (DFT) or MP2(SDD) calculations, or detailed vibrational infrared and Raman analyses, have been performed on the title compound. A detailed quantum chemical study will aid in understanding the

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vibrational modes of the title compound and clarifying the experimental data available for this molecule. DFT and MP2 calculations are known to provide excellent vibrational wavenumbers of organic compounds if the calculated wavenumbers are scaled to compensate for the approximate treatment of electron, correlation, for basis set deficiencies, and for the anharmonicity effects [16,17]. In this work, by using B3LYP and MP2(SDD) methods, we calculated the vibrational wavenumbers of the title compound in the ground state to distinguish the fundamentals from the many experimental vibrational wavenumbers and geometric parameters. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

2. Experimental

All the chemicals were procured from Sigma–Aldrich, USA. 0.5 mg of sulphaguanidine and 0.3 ml salicylaldehyde in 20 ml ethanol is refluxed 3 hrs. The yellowish orange precipitate was filtered off, washed with ethanol and then dried. Elemental analysis: found/calculated (%): C 52.53/52.83; N 17.9/17.6; S 10.0/10.06; H 4.9/4.7. The FT-IR spectrum (Fig. 1) was recorded using a Bruker IFS 28 spectrometer in KBr pellets, number of scans 16, resolution 2 cm^{-1}. The FT-Raman spectrum (Fig. 1) was obtained on a Bruker Equinox 55/s spectrometer with FRA Raman socket, 106/s. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, laser power 250 mW, resolution 2 cm^{-1}, number of scans 128, measurement on solid sample.

3. Computational details

Calculations of the title compound were carried out with Gaussian03 software program [18] using the B3LYP/6-31G* and MP2/SDD (Moller–Plesset second perturbation) basis sets to predict the molecular structure and vibrational wavenumbers. Calculations were carried out with Becke's three parameter hybrid model using the Lee–Yang–Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface. The Stuttagard/Dresden effective core potential basis set (SDD) [19] was chosen particularly because of its advantage of doing faster calculations with relatively better accuracy and structures [20]. Then frequency calculations were employed to confirm the structure as minimum points in energy. At the optimized structure (Fig. 2) of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The DFT hybrid B3LYP functional and MP2 methods tend to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data [21]. The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. The obtained geometrical parameters (MP2) are given as Supplementary material in Table S1. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes [22,23]. Potential energy surface scan studies has been carried out to understand the stability of planar and non-planar structures of the molecule. The profiles of potential energy surface for torsion angle N_{23}–C_{21}–C_6–C_5 and bond angle C_{31}–N_{29}–S_{26} are given in Figs. 3 and 4. The energy is minimum for 168.6° (−1384.68927 Hartree) and 127° (−1378.6688 Hartree), for the torsion angle and bond angle scans.

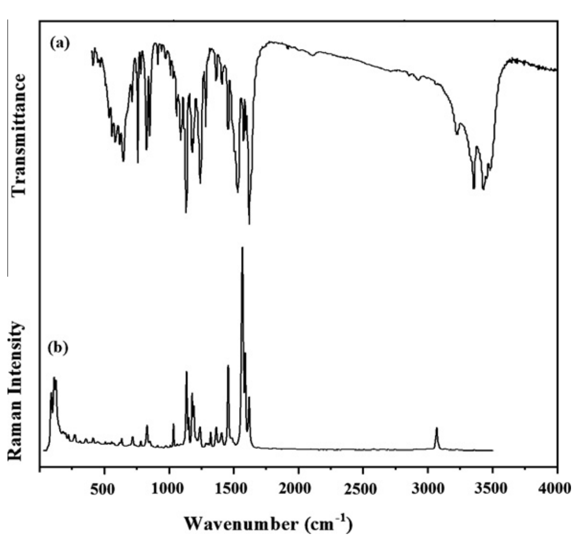

Fig. 1. FT-IR and FT-Raman spectra of *N*-carbamimidoyl-4-{[(E)-((2-hydroxyphenyl) methylidene]amino}benzenesulfonamide.

4. Results and discussion

4.1. IR and Raman spectra

The observed IR and Raman bands with their relative intensities and calculated (scaled) wavenumbers and assignments are given in Table 1.

The NH_2 stretching modes of guanidine are expected in the region 3260–3390 cm^{-1} [24] and in the present case bands observed at 3484 cm^{-1} in the IR spectrum and bands at 3480, 3401 cm^{-1} (MP2) are assigned as NH_2 stretching modes. Topacli and Topacli [25] reported the calculated wavenumbers in the range 3670–3920 cm^{-1} for NH_2 stretching modes. The bands corresponding to the δNH_2 vibrations are expected in the region 1610 ± 30 cm^{-1} [24]. In the IR and Raman spectra δNH_2 is observed at 1573 and 1566 cm^{-1}. The calculated value is 1554 cm^{-1}. The rocking/twisting mode of NH_2 is expected in the region 1195 ± 90 cm^{-1} and the MP2 calculations give this mode at 1218 cm^{-1}. The wagging mode of NH_2 is expected in the range 840 ± 55 cm^{-1} [24]. The MP2 calculations give this mode at 774 cm^{-1}. The torsional NH_2 mode is expected in the range 355 ± 65 cm^{-1} [24] and the band at 285 cm^{-1} (MP2) is assigned as this mode. For sulfonamide derivatives, the NH_2 modes are reported at 3390, 3395, 3399 cm^{-1} and NH modes at 3253, 3230, 3255 cm^{-1} [26].

The antisymmetric and symmetric stretching modes of SO_2 group appear in the region 1360–1310 and 1165–1135 cm^{-1}, respectively [24]. The observed bands at 1321 cm^{-1} in the Raman spectrum and 1132 (IR), 1132 cm^{-1} (Raman) were assigned to the SO_2 stretching modes. The MP2 calculations give the antisymmetric and symmetric stretching modes at 1322 and 1120 cm^{-1}. The symmetric SO_2 stretching mode is not pure, but contains contributions from other modes also. Although the region of the SO_2 scissors (560 ± 40 cm^{-1}) and that of SO_2 wagging vibration (500 ± 55 cm^{-1}) partly overlap, the two vibrations appear separately [24]. The scissoring mode is observed at 536 cm^{-1} in the IR spectrum and at 537 cm^{-1} in the Raman spectrum. The wagging mode is not observed experimentally. The MP2 calculations give these modes at 530 and 498 cm^{-1}. Hangen et al. [27] reported the SO_2 stretching vibrations at 1314, 1308, 1274, 1157, 1147, 1133 cm^{-1} and SN stretching modes at 917, 920, 932, 948 cm^{-1} for sulfonamide derivatives. Chotan et al. [28] reported SO_2 stretching modes at 1345, 1110 cm^{-1} and SN and C–S stretching