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## Spectroscopic (FT-IR, FT-Raman), first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis of 5-tert-Butyl-6-chloro-N-[(4-(trifluoromethyl)phenyl)pyrazine-2-carboxamide



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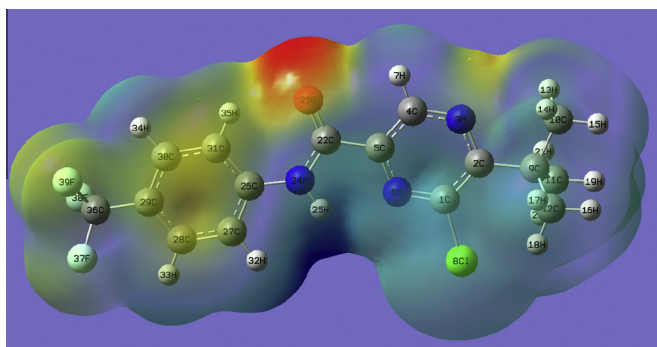
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### HIGHLIGHTS

- IR, Raman spectra and NBO analysis were reported.
- The wavenumbers are calculated theoretically using Gaussian09 software.
- The wavenumbers are assigned using PED analysis.
- The geometrical parameters are in agreement with reported literature.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The optimized molecular structure, vibrational frequencies, corresponding vibrational assignments of 5-tert-Butyl-6-chloro-N-[(4-(trifluoromethyl)phenyl)pyrazine-2-carboxamide] have been investigated experimentally and theoretically using Gaussian09 software package. Potential energy distribution of normal modes of vibrations was done using GAR2PED program. The HOMO and LUMO analysis is used to determine the charge transfer within the molecule. The stability of the molecule arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. From the NBO analysis it is evident that the increased electron density at the nitrogen, carbon atoms leads to the elongation of respective bond length and a lowering of the corresponding stretching wave number. The calculated geometrical parameters are in agreement with that of similar derivatives. The calculated first hyperpolarizability is high and the calculated data suggest an extended  $\pi$ -electron delocalization over the pyrazine ring and carboxamide moiety which is responsible for the nonlinearity of the molecule.

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## Introduction

The diazine rings are building blocks of many important natural and synthetic compounds, e.g., nucleotides. Pyrazine and its derivatives form an important class of compounds present in several natural flavors and complex organic molecules [1]. The 2-methylpyrazine is used in flavors in food, baccy. It is the intermediate of aldinamide and hydrazog. Besides, the 2-methylpyrazine is an insecticide, photo medicine and pigment, sensitizer; polymer catalyst of ethylene and other unsaturated compounds, the curing agent of epoxy resins, curing agent of halogen polymers, metal chelating agent and separating agent, brightener of copper plating. Dimethylpyrazines are added to impart or help a taste or aroma in food. The 2,5-dimethylpyrazine is found in beef, blackberry, corn, grape fruit juice and used in breakfast cereal. The 2,6-dimethylpyrazine mainly used to confect the essence of cocoa, coffee, meat or potato flavor. 2-Chloropyrazine and 2,6-dichloropyrazine are mainly found as medical and agricultural drug intermediates [1]. The incidence of tuberculosis in both developing and industrialized countries, have seen increased and the wide spread emergence of drug-resistant strains and a deadly synergy with human immune deficiency virus [2,3]. Akuzuz et al. [4] reported the vibrational spectroscopic study of two dimensional polymer compounds of pyrazinamide. The dynamical pattern of the 2-aminopyrazine-3-carboxylic acid molecule by inelastic and incoherent neutron scattering, Raman spectroscopy and ab initio calculations was reported by Pawlukoje et al. [5]. Billes et al. [6] calculated the vibrational frequencies of the three parent diazines (pyrazine, pyridazine and pyrimidine) applying ab initio quantum chemical methods, Moller–Pleassett perturbation and local density function methods. Various compounds possessing —NHCO— groups, e.g. substituted amides, acyl and thioacyl anilides, benzanilides, phenyl carbamates, etc., were found to inhibit photo synthetic electron transport [7,8].

Ab initio quantum mechanical method is at present widely used for simulating infrared spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them and time-dependent DFT (TD-DFT) calculations have also been used for the analysis of the electronic spectrum and spectroscopic properties. The energies, degrees of hybridization, populations of the lone electron pairs, energies of their interaction with the anti-bonding  $\pi^*$  orbital of the benzene ring, electron density (ED) distributions and  $E(2)$  energies have been calculated by NBO analysis using DFT method to give clear evidence of stabilization originating from the hyper conjugation of various intra-molecular interactions. In this work, infrared, Raman spectra and  $^1\text{H}$  NMR parameters of the title compound are reported both experimentally and theoretically. The HOMO and LUMO analysis have been used to elucidate information regarding charge transfer within the molecule. 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 compounds showing high hyperpolarizability are those containing an electron donating group or an electron withdrawing group interacting through a system of conjugated double bonds. In this case, the electron withdrawing group —C=O, —CF<sub>3</sub> are present in the title compound.

## Experimental details

The 5-tert-Butyl-6-chloro-pyrazine-2-carboxylic acid [9] (50.0 mmol) and thionyl chloride (5.5 mL, 75.0 mmol) in dry

toluene (20 mL) was refluxed for about 1 h. Excess of thionyl chloride was removed by repeated evaporation with dry toluene in vacuo. The crude acyl chloride dissolved in dry acetone (50 mL) was added drop wise to a stirred solution of the 4-trifluoromethylamine (50.0 mmol) and pyridine (50.0 mmol) in dry acetone (50 mL) kept at room temperature. After the addition was complete, stirring continued for 30 min, then the reaction mixture was poured into cold water (100 mL) and the crude amide was collected and re-crystallized from aqueous ethanol. Yield: 67%. Anal. Calcd. for C<sub>16</sub>H<sub>15</sub>ClF<sub>3</sub>N<sub>3</sub>O (357.8), 53.72% C, 4.23% H, 11.75% N; Found: 53.70% C, 4.34% H, 11.67% N; MP 81.7 °C. The FT-IR spectrum (Fig. 1) was recorded using KBr pellets on a DR/Jasco FT-IR 6300 spectrometer in KBr pellets. The spectral resolution was 2 cm<sup>-1</sup>. The FT-Raman spectrum (Fig. 2) was obtained on a Bruker RFS 100/s, Germany. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, measurement on solid sample. The spectral resolution after apodization was 2 cm<sup>-1</sup>.

## Computational details

Calculations of the title compound are carried out with Gaussian09 program [10] using the HF/6-31G(6D, 7F) and B3LYP/6-31G(6D, 7F) basis sets to predict the molecular structure and vibrational wave numbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wave numbers are calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The wave number values computed at the Hartree–Fock level contain known systematic errors due to the negligence of electron correlation [11]. We therefore, have used the scaling factor value of 0.8929 for HF and 0.9613 for DFT methods. Then frequency calculations were employed to confirm the structure as minimum points in energy. Parameters corresponding to optimized geometry (DFT) of the title compound (Fig. 3) are given in Table 1. The absence of imaginary wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignments of the calculated wave numbers are aided by the animation option of GAUSSVIEW program, which gives a visual presentation of the vibrational modes [12]. The potential energy distribution (PED) is calculated with the help of GAR2PED software package [13]. The  $^1\text{H}$  NMR data were obtained from the DFT method using

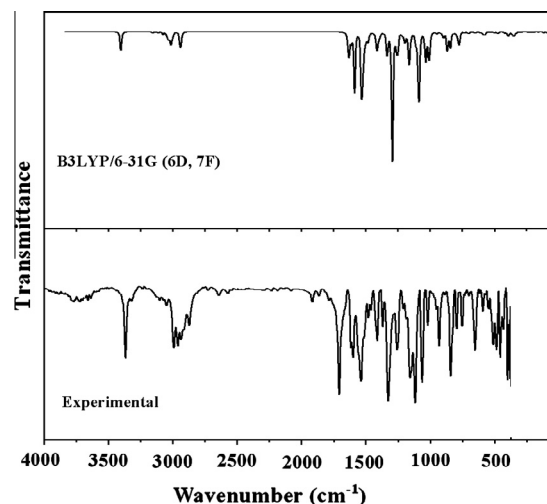


Fig. 1. FT-IR spectrum of 5-tert-Butyl-6-chloro-N-[(4-(trifluoromethyl)phenyl)pyrazine-2-carboxamide].

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