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Vibrational (FT-IR and FT-Raman) spectra and quantum chemical studies on the molecular orbital calculations, chemical reactivity and thermodynamic parameters of 2-chloro-5-(trifluoromethyl) aniline

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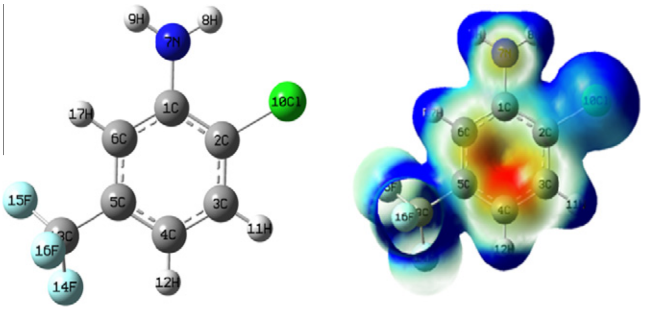
HIGHLIGHTS

- Vibrational spectroscopic studies of 2-chloro-5-(trifluoromethyl) aniline were carried out.
- HOMO–LUMO energy gap, electrostatic potential and thermodynamic parameters were performed.
- NBO analysis provides information about delocalization of charge and electron density of atoms.
- Theoretical spectrograms were simulated and compared with the experimental FT-IR and FT-Raman.
- Correlations of temperature dependence thermodynamic parameters were studied.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the vibrational characteristics of 2-chloro-5-(trifluoromethyl) aniline have been investigated and both the experimental and theoretical vibrational data indicate the presence of various functional groups within the title molecule. The influence of chlorine substituent on the vibrational wavenumbers of a molecule in comparison with aniline and trifluoromethyl aniline has been discussed in detail. The density functional theoretical (DFT) computations were performed at the B3LYP/6-31++G(3df,3pd)/6-31G(3df,3pd) levels to derive the optimized geometry, vibrational wavenumbers with IR and Raman intensities. Furthermore, the molecular orbital calculations such as; natural bond orbitals (NBOs) and HOMO–LUMO energy gap and mapped molecular electrostatic potential (MEP) surfaces were also performed with the same level of DFT. The temperature dependence thermodynamic parameters of a molecule were illustrated on the basis of their correlation graphs. The detailed interpretation of the vibrational spectra has been carried out with the aid of potential energy distribution (PED) results obtained from MOLVIB program. The delocalization of electron density in various constituents of the molecule has been discussed with the aid of NBO and HOMO–LUMO energy gap analysis.

Introduction

Recently, the study of vibrational characteristics of substituted aniline compounds are of great deal of interest among the spec-

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troscopists due to their chemical and physical properties. Furthermore, aniline and its derivatives are used in the production of dyes, pesticides and antioxidants [1,2]. In the aniline compounds, amino group affects the planarity of the molecule and inclusion of an additional substituent group in aniline leads to further changes in the charge distribution of a molecule, and consequently affects the structural and vibrational parameters [2]. In particular, trifluoromethyl and chlorinated trifluoromethyl aniline compounds have attracted a special attention in the field of vibrational spectroscopy for many reasons. Trifluoromethyl and chlorinated trifluoromethyl aniline are used as an intermediate in the production of the herbicides fluometuron and norflurazon and are also used as intermediates and pesticides in medicinal industry [3]. The vibrational assignments of *p*-trifluoromethyl aniline were proposed by Yadav and Singh [4]. Arjunan et al. investigated the vibrational and non-linear optical properties of 2-(trifluoromethyl) aniline and 3-(trifluoromethyl) aniline [5]. Recently chlorinated trifluoromethyl aniline was taken for elucidating vibrational characteristics by Arivazhagan et al. [6].

In the present study, we have proposed the vibrational assignments of 2-chloro-5-(trifluoromethyl) aniline according to the characteristic group frequencies observed in FT-IR and FT-Raman spectra. Furthermore, we interpreted the calculated spectra in terms of potential energy distributions (PEDs) and also made the vibrational assignments based on these PED results. The Natural population analysis (NPA) performed in this study enhanced us to know about the delocalization of charge and electron density of atoms of a molecule and thus leads to an explanation of molecular geometrical gradients in comparison with the planar benzene. In addition to that the molecular species which are responsible for chemical stability and chemical reactivity of the molecule were also identified by NBO and MEP surface analysis, respectively. Furthermore, the intensities of molecular vibrations at different temperatures were examined on basis of correlation graphs between the temperature and thermodynamic parameters. To the best of our knowledge, there have been no other significant studies reported for considering 2-chloro-5-(trifluoromethyl) aniline so far. This inadequacy observed in the literature encouraged us to make the aforementioned studies in this work.

Experimental techniques and computational methods

Experimental techniques

The newly synthesized compound 2-chloro-5-(trifluoromethyl) aniline at Lancaster Chemicals Ltd., UK was purchased and used it for spectral measurements without any further purification. The mid-Infrared (MIR) spectra of the title compound in KBr pellets has been recorded with a NEXUS 670 model of spectrophotometer equipped Mercury-Cadmium-Telluride (MCT-B) as a detector and signal to noise ratio <10. This recorded MIR spectrum in the region 4000–400 cm^{-1} has taken for the vibrational assignments of characteristic group frequencies.

Since some of the peaks are IR inactive, we have taken Raman spectra of a molecule in the region 3500–100 cm^{-1} on a NEXUS 670 model of spectrophotometer equipped with Indium-Gallium-Arsenide (InGaAs) detector. While taking FT-Raman, the Nd:YAG laser is used as an excitation source in the FT-Raman module. It emits continuous-wave laser energy at wavelength of 1064 nm and it has a power level of 0.9W at the sample.

Computational methods

For a supportive evidence to the experimental observations, the density functional theory computations were performed with the aid of GAUSSIAN 09W software package [7] with internally stored B3LYP/6-31G(3df,3pd) and B3LYP/6-31++G(3df,3pd) basis set methods. At first, the global minimum energy structure of the title molecule was optimized by both the aforesaid basis set methods. Subsequently, the vibrational normal mode wavenumbers in association with the molecule were derived along with their IR intensity and Raman activity.

In our calculations, there were some deviations persist between the observed and calculated wavenumbers due to the neglect of anharmonic effect at the beginning of frequency calculation and basis set deficiencies. In the present study, these deviations were overcome by a selective scaling procedure in the natural internal coordinate representation followed by Refs. [8,9]. Transformations of the force field and the subsequent normal coordinate analysis including the least squares refinement of the scaling factors, calculation of potential energy distribution (PED) and IR and Raman intensities were done on a PC with the MOLVIB program (Version V7.0-G77) written by Sundius [10–12]. The PED elements provide a measure of each internal coordinate's contribution to the normal coordinate. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1} and the modified Raman activities during scaling procedure with MOLVIB were converted to relative Raman intensities using the following relationship derived from the basic theory of Raman scattering [13–15]. Finally, the converted Raman intensities and the calculated infrared intensities were modified by assigning the highest intensity peak to 100%.

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 S_i}{\upsilon_i\left[1 - \exp\left(\frac{hc\upsilon_i}{K_b T}\right)\right]} \tag{1}$$

where υ_0 is the exciting wavenumber (1064 nm = 9398 cm^{-1}) of laser light source used while recording Raman spectra, υ_i the vibrational wavenumber of the *i*th normal mode. *h*, *c* and K_b fundamental constants, and *f* is a suitably chosen common normalization factor for all peak intensities of the Raman spectrum of the title molecule.

In order to predict the reactive behavior of the molecule, we have plotted MEP surface and derived electrostatic potential values and point charges at B3LYP/6-31++G(3df,3pd) basis set. The population of atomic charges on individual atoms and the distribution of atomic charges on the core, valance and Rydberg sub-shells of the atomic orbitals were also derived using NBO calculations in GAUSSIAN 09W. From the computed NBO results, the stabilization energies of molecular species which are most responsible for the stability of molecule were identified. Furthermore, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were predicted to interpret the orbital overlapping and the possibility of charge transfer within the molecule using B3LYP method with 6-31++G(3df,3pd) basis set combination. Apart from the aforesaid calculations, certain thermodynamic properties were computed at B3LYP/6-31++G(3df,3pd) method to examine the thermal stability of a molecule at higher temperatures.

Results and discussion

Optimized geometrical parameters and Natural atomic orbitals

The crystallography data of the title compound has not yet been determined, the optimized structure parameters of 2-chloro-5-(trifluoromethyl) aniline calculated at density functional B3LYP method with 6-31G(3df,3pd) and 6-31++G(3df,3pd) basis sets are being compared with experimentally available X-ray data for aniline [16] in Table 1 in accordance with the atom numbering scheme given in