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Density functional theory studies on the molecular structure, vibrational spectral analysis of 4-chloro-3-(trifluoromethyl)aniline

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ABSTRACT

Primarily, the vibrational spectroscopic signature of 4-chloro-3-(trifluoromethyl)aniline has been studied experimentally by means of FT-IR and FT-Raman techniques. The electron donating and electron withdrawing effects on the structure of aniline and effects of substituent positions on the vibrational spectra of the title molecule in comparison with similar kind of molecules have also been illustrated. The details about hyperconjugative interactions, HOMO-LUMO energy gap, and molecular electrostatic potential (MEP) surface analysis have been predicted with the help of theoretical density functional theory computations.

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Introduction

In the recent decade, the study of vibrational spectroscopic investigation of substituted aniline derivatives are of great deal of interest among the spectroscopists 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 case of aniline, the 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 it also 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 [3–7]. Trifluoromethyl and chlorinated trifluoromethyl aniline are used as intermediates 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 et al [4]. Arjunan et al. investigated the vibrational and non-linear optical properties of 2-(trifluoromethyl) aniline and 3-(trifluoromethyl) aniline [5].

In our previous work, we have analyzed the vibrational FT-IR and FT-Raman spectra and also performed quantum chemical studies on the molecular orbitals, chemical reactivity and thermodynamic parameters of 2-chloro-5-(trifluoromethyl) aniline [6]. Vibrational spectroscopic studies, first order hyperpolarizability and HOMO-LUMO studies have been performed on 4-chloro-2-(trifluoromethyl) aniline by Arivazhagan et al [7]. In the present study, we have proposed the vibrational assignments of 4-chloro-3-(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 4-chloro-3-(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 4-chloro-3-(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[8] with internally

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stored B3LYP/6-31G(d,p) basis set. 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 the reference [9,10]. Transformations of the force field and the subsequent normal coordinate analysis including the least squares refinement of the scaling factors, and the calculation of Potential energy distribution (PED) were done on a PC with the MOLVIB program (Version V7.0-G77) written by Sundius [11–13]. The PED elements provide a measure of each internal coordinate's contribution to the normal coordinate.

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/6-31G(d,p) basis set. The population of atomic charges on individual atoms and the distribution of atomic charges on the core, valence 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 6-31G(d,p) basis set combination.

Results and discussion

Optimized geometrical parameters and Natural atomic orbitals

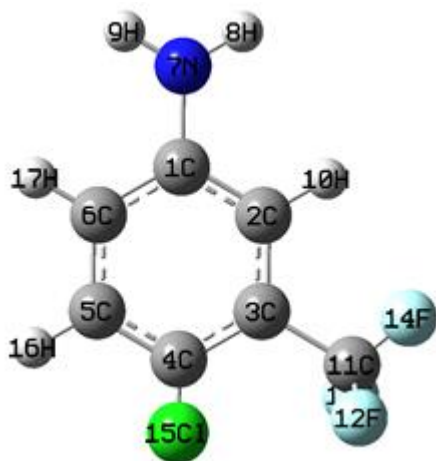


Fig 1. Optimized molecular structure of 4-chloro-3-(trifluoromethyl)aniline

The crystallography data of the title compound has not yet been determined, the optimized structure parameters of 4-chloro-3-(trifluoromethyl) aniline calculated at density functional B3LYP method with 6-31G(d,p) basis set is compared with experimentally available X-ray data for aniline [14] in Table 1 in accordance with the atom numbering scheme given in Fig. 1. The absence of imaginary frequencies as well as the negative eigen values of second-derivative matrix confirmed that the stationary point obtained in this study corresponds to a minima of potential energy hyper surfaces. The local minima of

optimized structure of the title molecule is found to be -1084.2305 a.u by B3LYP/6-31G(d,p) method. One can suggest that the chlorine substituent induces a rather minor variation in interatomic distances and angles in the phenyl moiety across chlorinated congeners.

Notably, the phenyl ring distances such as (C1–C2, C2–C3, C3–C4, C4–C5, C5–C6, C6–C1) change appreciably in reference to the aniline; especially in congeners with one or both ortho positions are occupied by electron donating chlorine atoms [15]. The calculated values of C1–N7 bond length and C2–C1–C6 bond angle appear shortens in reference to the experimental observation of unsubstituted aniline and the calculated values are in agreement with the reference [15] too. However in aniline, the nitrogen is pyramidal, with the dihedral angle between the NH₂ plane and the plane of the aromatic ring being 37.5° [15]. Substitution on the aniline ring has been found to change this angle and also affects the degree of pyramidalisation by resonance effects than inductive effects [16–18]. In the title molecule, the dihedral angle between the NH₂ plane and the plane of the aromatic ring is found to be 33.8° .

Kydd et al. suggested that the electron withdrawing CF₃ group substitution enhances the delocalization of electron density (ED) from the nitrogen lone pair into the ring [18]. In order to prove this enhancement of CF₃ group, the natural atomic orbital (NAO) occupancies and their energies of 4-chloro-3-(trifluoromethyl) aniline are computed at B3LYP/6-31G(d,p) basis set method. For comparative purpose, the theoretically computed NAO occupancies and the energies of lone pair and anti-bonding orbitals of aniline are also depicted in Table 2.

An atomic orbital of a lone pair nitrogen atom of the title molecule is occupied by 1.8866 e while for aniline; it is occupied by 1.8453 e. On the other hand, the energy corresponding to the atomic orbital n(N₇) of the title molecule is reported as -0.3962 a.u which is lower than that of aniline. As expected, the calculated values of occupancies and energies of most of the anti-bonding molecular orbitals of the title molecule do not coincide with that of unsubstituted aniline. From the results, we may conclude that the delocalization of electron density between the aromatic carbon and the substituent can cause a change in the planarity or the degree of pyramidal NH₂ moiety.

Natural population analysis

The natural population analysis [19] performed for the title molecule clearly depicts the distribution of charges in the various sub-shells (core, valence, Rydberg) in the molecular orbital. The accumulation of natural charges on individual atom of the title molecule is given in Table 3. It shows that an atom N₇ has the most electronegative charge and C₁₃ has the most electropositive charge. Likewise, F₁₄, F₁₅, F₁₆, C₆ and C₄ atoms have considerable electro negativity and they tend to donate an electron. Conversely, the H₈ and H₉ atoms have considerable electropositive and they tend to acquire an electron. Further, the natural population analysis showed that 146 electrons in the title molecule are distributed on the sub shells as follows:

Core	:	31.98784 (99.9620% of 32)
Valence	:	65.83768 (99.7541% of 66)
Rydberg	:	0.17448 (0.1780% of 98)

Natural bond orbital analysis

The natural bond orbital (NBO) [20] analysis of 4-chloro-3-(trifluoromethyl) aniline are being performed to estimate the delocalization pattern of electron density (ED) between the principal occupied Lewis-type (bond or lone pair) orbitals and unoccupied non-Lewis (antibond or Rydberg) orbitals. Table 4

lists the occupancies and energies of most interacting NBO's along with their percentage of hybrid atomic orbital contribution.

The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy $E(2)$ associated with the delocalization $i \rightarrow j$ is estimated as

$$E(2) = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_j - \varepsilon_i} \quad \dots\dots\dots (1)$$

Where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements and $F(i, j)$ is the off diagonal NBO Fock matrix element. NBO analysis provides an efficient method for studying intra- and intermolecular bonding and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [21]. The predominant contribution to the hybrid atomic orbitals of lone pair nitrogen atom is set to p-type and a lone pair chlorine atom Cl_{15} and lone pair Fluorine atoms (F_{12} , F_{13} , F_{14}) are contributed to s-type atomic orbital. On the other hand, all the antibonding orbitals which involved in the interactions are mostly contributed to p-type orbitals.

The possibilities of ED delocalization between the lone pair donor atoms to antibonding acceptor atoms of the title molecule are depicted in Table 5. It is evident from the stabilization energy that a very strong electron transition is observed between the lone electron pair of N_7 and neighboring antibonding orbital of $\pi^*(C_1-C_6)$. In other words, the delocalization of ED through donor to the acceptor of this type contributed predominantly to the stabilization of entire molecular system. This is due to the fact that greater the value of $E(2)$, the more intensive is the interaction between electron donors and electron acceptors. Other significant contributions for the molecular stabilization are further given by the lone pairs of chlorine and fluorine atoms through the orbital overlap with the C-C and C-F antibonding orbitals. In the title molecule is concerned, the lone pair Fluorine atoms delocalize themselves and it provides more stability than molecules of similar kind [5,6].

The hybrid directionality and bond bending analysis of the natural hybrid orbitals (NHOs) of the phenyl ring in the title molecule provide an excellent evidence for the substituent and steric effect. The angular properties of NHOs are very much influenced by the type of substituent that causes conjugative effect or steric effect [22]. In Table 4, the bending angles of different bonds are expressed in terms of angle of deviation from the direction of line joining two nuclei centers. The C_1 and C_2 atoms are more bent away from the line of centers by 4.8° and 3.3° respectively, which results in a strong charge transfer path towards C-NH₂. Similarly, a little bending effect is also noticed at the bonds where the electron donating Cl is substituted. According to the results, we can say that the degree of pyramidalisation has affected by Cl and CF₃ substituents.

Analysis of Molecular electrostatic potential (MEP) surface and Frontier molecular orbitals (FMOs)

The MEP surface generally provides information regarding the chemical reactivity of a molecule. The electrostatic potential generated in space around a molecule by the charge distribution is helpful to understand the electrophilic and nucleophilic regions in the title molecule. The electrostatic potential $V(\vec{r})$ at any point in space around a molecule by charge distribution is given by

$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} dr' \quad \dots\dots\dots (3)$$

where $\rho(\vec{r}')$ is the electron density function of a molecule, Z_A is the charge on the nucleus A located at \vec{R}_A and \vec{r} is the dummy integration variable. $V(\vec{r})$ is a real physical property, which can be determined either computationally or experimentally by diffraction methods [23].

Fig. 2 shows the plot of molecular electrostatic potential surface of 4-chloro-3-(trifluoromethyl) aniline along with the computationally derived electrostatic potential and electrostatic point charges on its individual atoms. It is clear from the figure that the atoms N_7 , C_6 and C_2 holds significant electronegative charges and the atoms C_1 , C_{11} , H_8 and H_9 holds significant positive charges. The MEP surface, the negative electrostatic potentials are shown in red colour and the intensity of which is proportional to the absolute value of the potential energy, and positive electrostatic potentials are shown in blue. In view of this, we can say that the delocalization of charge and electron density of atoms primarily takes place within the benzene ring and the electron withdrawing chlorine and Trifluoromethyl substituents increase the chemical reactivity of a molecule.

The analysis of frontier molecular orbitals describes one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The energy of HOMO is directly related to the ionization potential and the energy of LUMO is related to the electron affinity. The HOMO-LUMO energy gap is an important stability index and also it reflects the chemical activity of a molecule [24]. The MOs are defined as eigen functions of the Fock operator, which exhibits the full symmetry of the nuclear point group, and they necessarily form a basis for irreducible representations of full point-group symmetry. In the present study, the energies of HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1 and LUMO+2 and their orbital energy gaps are calculated by B3LYP/6-31G(d,p) method. The pictorial illustration of the frontier molecular orbitals and their respective positive and negative regions are shown in Fig. 3

In the HOMO surface, the bonding π orbitals spreading over the ring carbon atoms are helpful to hold the molecule together. It is worth mentioning here that the molecular orbital lobes which located on the chlorine atom of the HOMO surface is a non-bonding orbital. Hence, the electrons in chlorine atom act little like a lone pair of electrons in a Lewis structure. In contrast, the molecular orbital lobes on C_3-H_{11} and C_6-H_{17} bonds are σ orbitals and they have cylindrical symmetry about the internuclear axis. The same type of σ orbital is also identified on the bond C_4-H_{12} in LUMO+1 surface. The molecular orbital lobes spreading over the HOMO-2 and LUMO+2 surfaces are of antibonding character because it has a node between adjacent nuclei with lobes of opposite sign (shown in different colours) and p-orbital on the chlorine atom is a major contributor of HOMO-2, LUMO+2 surfaces. The energy gap between HOMO and LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity of a molecule. In the case of 4-chloro-3-(trifluoromethyl) aniline, the smallest energy gap of $\Delta E_1 = -0.1867$ a.u is identified between the HOMO and LUMO with the help of B3LYP/6-31++G(d,p) method.

V(r)	Point charges (e)
C1	0.3939
C2	-0.2739
C3	0.0382
C4	-0.0006
C5	-0.0291
C6	-0.2669
N7	-0.8061
H8	0.3517
H9	0.3455
H10	0.1421
C11	0.4726
F12	-0.1777
F13	-0.1617
F14	-0.1630
C15	-0.1080
H16	0.0955
H17	0.1475

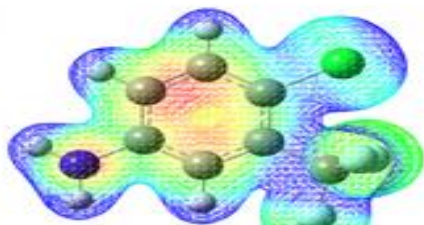


Fig. 7 Molecular electrostatic potential surface of 4-chloro-3-(trifluoromethyl) aniline

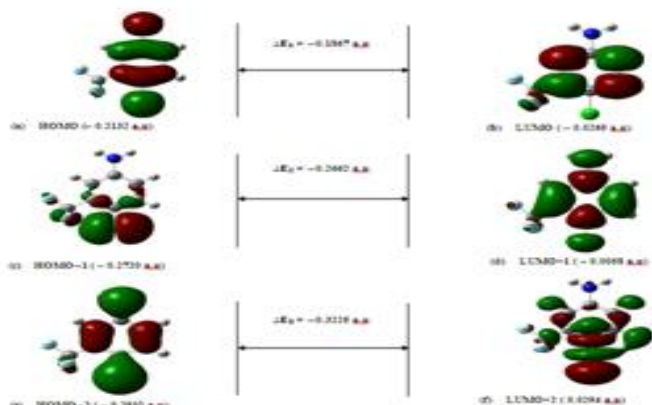


Fig. 8 Electron density surface map of molecular orbitals of 4-chloro-3-(trifluoromethyl) aniline

Vibrational frequency analysis

In the present study, the spectroscopic signature of 4-chloro-3-(trifluoromethyl) aniline has been analyzed by the both experimental and theoretical IR and Raman spectra. The title compound consists of 17 atoms, thus it has 45 vibrational degrees of freedom under C₁ point group symmetry. In the present study, all the 45 normal modes of vibrations have been assigned according to the detailed PED results obtained from the MOLVIB program. The two distinct scale factors are used to fit the calculated wavenumbers with the observed experimental wavenumbers. The observed FT-IR and FT-Raman spectra of the title molecule are shown in Figs. 4 and 5. The observed FT-IR, FT-Raman wavenumbers and the calculated wavenumbers using density functional B3LYP method with 6-31G(d,p) basis set along with their relative intensities, probable assignments of the compound are summarized in Table 6

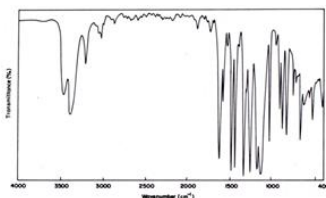


Fig. 4 Fourier Transform infrared spectrum of 4-chloro-3-(trifluoromethyl) aniline

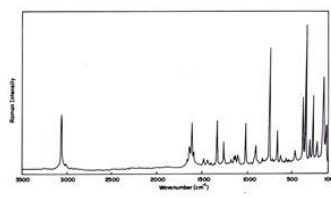


Fig. 5 Fourier Transform Raman spectrum of 4-chloro-3-(trifluoromethyl) aniline

Ring vibrations

Generally, the carbon-carbon stretching modes of the phenyl group are expected to appear in the range from 1650 to 1200 cm⁻¹ [5]. The actual positions of these modes are determined not so much by the nature but by the form of substitution around the ring. The heavy halogens undoubtedly diminish the frequency [25]. In the title molecule, the peaks observed at 1611, 1587, 1490 and 1440 cm⁻¹ in FT-Raman and at 1607, 1481 cm⁻¹ in FT-IR are ascribed to C-C stretching vibrations. The experimentally observed results in this case are consistent with the scaled theoretical wavenumbers. In the case of unsubstituted aniline, the ring C-C stretching vibrational

peaks were identified at 1626, 1492, 1269, 994 and 804 cm⁻¹ in IR spectrum by Coblenz[26]. Also, the peaks observed at 1612, 1499, 1272, 996 and 810 cm⁻¹ in Raman spectrum have been assigned to ring C-C stretching vibrations by Venkateswaran et al [27].

It is evident from the PED results that, the in-plane and out-of-plane bending modes of the phenyl ring are coupled with other vibrations. The ring in-plane bending modes are identified at 569, 534 cm⁻¹ in FT-IR and 565 cm⁻¹ in FT-Raman spectrum. As ring in-plane and out-of-plane bending modes are not much active in FT-IR, the scaled wavenumbers are compared with observed Raman peaks and the major contribution to the percentage of PED results also confirmed these modes.

NH₂ vibrations

The NH₂ group in the title molecule has six vibrations viz. asymmetry stretching, symmetry stretching, scissoring, rocking, wagging and twisting. In primary amines, usually the N-H stretching vibrations occurs in the region 3600–3300 cm⁻¹ [28–30]. In the present study, the N-H asymmetric and symmetric stretching modes are assigned at 3464 and 3360 cm⁻¹ in FT-IR, respectively. As expected, the NH₂ stretching modes are not much affected by the substituents. The reported values of these modes are matched well with that of unsubstituted aniline. For aniline, the more intense depolarized peak at 3423 cm⁻¹ and a highly polarized peak at 3362 cm⁻¹ in Raman spectrum were assigned to NH₂ asymmetric and symmetric stretching modes, respectively [27]. Varsanyi [25] expressed that the frequencies of the amino group appear around 1630–1610 cm⁻¹ for the NH₂ scissoring deformation, and 1090–1060 cm⁻¹ for the NH₂ rocking deformation. In the title molecule, a very strong peak observed at 1634 cm⁻¹ in FT-IR and 1643 cm⁻¹ in FT-Raman are assigned to NH₂ scissoring deformation and the calculated value of 1073 cm⁻¹ is ascribed to NH₂ rocking deformation.

The strong peak identified at 302 cm⁻¹ in FT-Raman and the calculated value of 381 cm⁻¹ by B3LYP/6-31G(d,p) method are assigned to NH₂ wagging and NH₂ twisting modes, respectively. It is noticed from the PED results that NH₂ wagging and NH₂ torsion modes are mixed somewhat with other ring vibrations.

Trifluoromethyl group vibrations

The -CF₃ group wavenumbers of the title molecule make a significant contribution to vibrational spectra. In the case of -CF₃ group, the symmetric stretching is observed at higher wavenumber region (1310–1340 cm⁻¹) than that of asymmetric stretching (1110–1185 cm⁻¹) [25]. The C-F symmetric stretching of the title molecule is not active in both the recorded spectra. A weak intensity peak present at 1148 cm⁻¹ in FT-IR and a peak at 1145 cm⁻¹ in FT-Raman are assigned to C-F asymmetric stretching modes. The Trifluoromethyl deformation modes are also well established and the symmetrical deformation mode of the -CF₃ group is observed at 638 cm⁻¹ in FT-IR and 629 cm⁻¹ in FT-Raman. Due to the absence of asymmetrical methyl deformation, the computed value of 652 cm⁻¹ is ascribed to this mode. The other wavenumbers of the trifluoromethyl group such as; twisting and rocking modes are also assigned and are presented in the Table 6. These assignments are substantiated by the reported literatures of similar kind of molecules [5-7].

Table 1. The structural parameters calculated for 4-chloro-3-(trifluoromethyl) aniline by B3LYP method with 6-31G(d,p)

Parameters	6-31G(d,p)	Experimental ^a	Parameters	6-31G(d,p)	Experimental ^a
Internuclear distance (Å)					
C ₁ -C ₂	1.4035	1.397±0.003	C ₅ -C ₆	1.3899	
C ₁ -C ₆	1.4040		C ₅ -H ₁₆	1.0842	
C ₁ -N ₇	1.3905	1.402±0.002	C ₆ -H ₁₇	1.0865	
C ₂ -C ₃	1.3948	1.394±0.004	N ₇ -H ₈	1.0101	1.001±0.001
C ₂ -H ₁₀	1.0837		N ₇ -H ₉	1.0100	1.001±0.001
C ₃ -C ₄	1.4025	1.396±0.003	C ₁₁ -F ₁₂	1.3492	
C ₃ -C ₁₁	1.5124	1.083±0.002	C ₁₁ -F ₁₃	1.3484	
C ₄ -C ₅	1.3939		C ₁₁ -F ₁₄	1.3540	
C ₄ -Cl ₁₅	1.7565	1.080±0.002			
Bond angles (°)					
C ₂ -C ₁ -C ₆	118.2	119.43	C ₆ -C ₅ -H ₁₆	120.1	
C ₂ -C ₁ -N ₇	120.6		C ₁ -C ₆ -C ₅	120.6	
C ₆ -C ₁ -N ₇	121.1		C ₁ -C ₆ -H ₁₇	119.9	
C ₁ -C ₂ -C ₃	121.5	120.05	C ₅ -C ₆ -H ₁₇	119.5	
C ₁ -C ₂ -H ₁₀	119.8		C ₁ -N ₇ -H ₈	115.8	
C ₃ -C ₂ -H ₁₀	118.7		C ₁ -N ₇ -H ₉	115.8	
C ₂ -C ₃ -C ₄	119.3	120.70	H ₈ -N ₇ -H ₉	112.4	113.1
C ₂ -C ₃ -C ₁₁	118.6	119.60	C ₃ -C ₁₁ -F ₁₂	111.9	
C ₄ -C ₃ -C ₁₁	122.0		C ₃ -C ₁₁ -F ₁₃	111.9	
C ₃ -C ₄ -C ₅	119.6	118.91	C ₃ -C ₁₁ -F ₁₄	111.5	
C ₃ -C ₄ -Cl ₁₅	122.2		F ₁₂ -C ₁₁ -F ₁₃	107.5	
C ₅ -C ₄ -Cl ₁₅	118.2		F ₁₂ -C ₁₁ -F ₁₄	106.8	
C ₄ -C ₅ -C ₆	120.7		F ₁₃ -C ₁₁ -F ₁₄	106.9	
C ₄ -C ₅ -H ₁₆	119.2				

^aValues taken from Ref [14]**Table 2. Comparison of occupancies and energies of atomic orbitals between aniline and 4-chloro-3-(trifluoromethyl) aniline**

Parameters ^a	Aniline		4-chloro-3-(trifluoromethyl) aniline	
	Occupancies (e)	Energies (a.u)	Occupancies (e)	Energies (a.u)
n (N ₇)	1.8453	-0.2956	1.8866	-0.3962
σ* (C ₁ -C ₂)	0.0238	0.5378	0.0186	0.8100
σ* (C ₁ -C ₆)	0.0236	0.5425	0.0185	0.8096
σ* (C ₂ -C ₃)	0.0125	0.5812	0.0209	0.8063
σ* (C ₃ -C ₄)	0.0155	0.5808	0.0316	0.7811
σ* (C ₄ -C ₅)	0.0155	0.5741	0.0233	0.7882
σ* (C ₅ -C ₆)	0.0126	0.5807	0.0157	0.8123
σ* (C ₁ -N ₇)	0.0177	0.4452	0.0156	0.5604
σ* (N ₇ -H ₈)	0.0074	0.4111	0.0023	0.6793
σ* (N ₇ -H ₉)	0.0074	0.4123	0.0022	0.6785
σ* (C ₂ -H ₁₀)	0.0120	0.4666	0.0108	0.7340
σ* (C ₅ -H ₁₆)	0.0122	0.4706	0.0090	0.7377
σ* [C ₆ -H ₁₇ (H ₁₄)] ^b	0.0122	0.4548	0.0095	0.7298

^aFor numbering of atoms refer Fig. 1^bNumbering of hydrogen atom of the aniline geometry is given in the brackets**Table 3. Accumulation of natural charges and electron population of atoms in core, valence, Rydberg orbitals of 4-chloro-3-(trifluoromethyl) aniline**

Atoms ^a	Charge (e)	Natural population (e)			Total (e)	Atoms ^b	Charge (e)	Natural population (e)			Total (e)
		Core	Valence	Rydberg				Core	Valence	Rydberg	
C ₂	-0.2665	1.9986	4.2519	0.0160	6.2665	C ₁	0.2255	1.9985	3.7610	0.0151	5.7745
C ₃	-0.1622	1.9984	4.1506	0.0132	6.1622	H ₈	0.4103	0.0000	0.5890	0.0007	0.5897
C ₄	-0.0906	1.9982	4.0736	0.0188	6.0906	H ₉	0.4099	0.0000	0.5895	0.0007	0.5901
C ₅	-0.1986	1.9986	4.1843	0.0158	6.1986	H ₁₀	0.2655	0.0000	0.7328	0.0018	0.7345
C ₆	-0.2794	1.9986	4.2672	0.0136	6.2794	C ₁₁	1.1634	1.9986	2.7815	0.0565	4.8366
N ₇	-0.8998	1.9993	5.8969	0.0035	7.8998	Cl ₁₅	0.0067	9.9997	6.9806	0.0131	16.993
F ₁₂	-0.3642	1.9998	7.3628	0.0015	9.3642	H ₁₆	0.2649	0.0000	0.7345	0.0007	0.7351
F ₁₃	-0.3640	1.9998	7.3627	0.0015	9.3640	H ₁₇	0.2515	0.0000	0.7479	0.0006	0.7485
F ₁₄	-0.3724	1.9998	7.3711	0.0015	9.3724						

^aAtoms containing negative charges^bAtoms containing positive charges

Table 4. Natural atomic orbital occupancies and energies of most interacting NBO's of 4-chloro-3-(trifluoromethyl) aniline along with their hybrid atomic orbital

Parameters ^a (A-B)	Occupancies (e)	Energies (a.u)	Hybrid	AO(%) ^b	Deviation at A (°)	Deviation at B (°)
$\sigma^*(C_1-C_2)$	0.0186	0.8100	$sp^{1.72}(C_1)$ $sp^{1.89}(C_2)$	$s(36.77) p(63.23)$ $s(34.58) p(65.42)$	4.8	3.3
$\sigma^*(C_1-C_6)$	0.0185	0.8096	$sp^{1.71}(C_1)$ $sp^{1.94}(C_6)$	$s(36.96) p(63.04)$ $s(34.01) p(65.99)$	5.0	3.6
$\sigma^*(C_1-N_7)$	0.0156	0.1353	$sp^{2.83}(C_1)$ $sp^{1.82}(N_7)$	$s(26.14) p(73.86)$ $s(35.50) p(64.50)$	-	-
$\sigma^*(C_2-C_3)$	0.0210	0.8063	$sp^{1.93}(C_2)$ $sp^{1.75}(C_3)$	$s(34.16) p(65.84)$ $s(36.41) p(63.59)$	3.0	2.1
$\sigma^*(C_4-Cl_{15})$	0.0191	0.3160	$sp^{3.23}(C_4)$ $sp^{4.99}(Cl_{15})$	$s(23.63) p(76.37)$ $s(16.70) p(83.30)$	-	-
$\sigma^*(C_3-C_4)$	0.0316	0.7811	$sp^{1.84}(C_3)$ $sp^{1.67}(C_4)$	$s(35.26) p(64.74)$ $s(37.44)$ $p(62.56)$	3.4	5.8
$\sigma^*(C_4-C_5)$	0.0233	0.7882	$sp^{1.57}(C_4)$ $sp^{1.96}(C_5)$	$s(38.97) p(61.03)$ $s(33.76)$ $p(66.24)$	5.6	3.9
$\sigma^*(C_5-C_6)$	0.0157	0.8123	$sp^{1.86}(C_5)$ $sp^{1.87}(C_6)$	$s(34.96)$ $p(65.04)$ $s(34.84)$ $p(65.16)$	2.9	3.0
$\sigma^*(C_3-C_{11})$	0.0573	0.5242	$sp^{2.53}(C_3)$ $sp^{1.98}(C_{11})$	$s(28.34) p(71.66)$ $s(33.51) p(66.49)$	-	-
$n(N_7)$	1.8866	-0.3962	$sp^{1.00}$	$s(0.00) p(100.0)$	-	-
$n(Cl)$	1.9961	-1.1771	$sp^{0.19}$	$s(83.70) p(16.30)$	-	-
$n(F_{12})$	1.98853	-1.45243	$sp^{0.40}$	$s(71.68) p(28.32)$	-	-
$n(F_{13})$	1.98849	-1.4530	$sp^{0.39}$	$s(71.73) p(28.27)$	-	-
$n(F_{14})$	1.98809	-1.4410	$sp^{0.42}$	$s(70.41) p(29.59)$	-	-

^a For numbering of atoms refer Fig. 1

^b Percentage of s-type and p-type subshell of an atomic orbitals are given in their respective brackets

Table 5. Significant second-order interaction energy (E(2), kcal/mol) between donor and acceptor orbitals of 4-chloro-3-(trifluoromethyl) aniline calculated at B3LYP/6-31G(d,p) level of theory

Donor (i) → Acceptor (j)	E(2) ^a kcal/mol	$(\epsilon_j - \epsilon_i)$ a.u	F_{ij} a.u
$n(N_7) \rightarrow \pi^*(C_1-C_6)$	40.13	0.53	0.139
$n(Cl_{15}) \rightarrow \sigma^*(C_3-C_4)$	1.55	1.43	0.042
$n(Cl_{15}) \rightarrow \sigma^*(C_4-C_5)$	2.00	1.47	0.049
$n(F_{12}) \rightarrow \sigma^*(C_2-C_3)$	1.21	0.78	0.030
$n(F_{12}) \rightarrow \sigma^*(C_3-C_{11})$	9.43	1.18	0.094
$n(F_{12}) \rightarrow \sigma^*(C_{11}-F_{13})$	7.38	1.06	0.080
$n(F_{12}) \rightarrow \sigma^*(C_{11}-F_{14})$	5.88	1.05	0.071
$n(F_{13}) \rightarrow \sigma^*(C_2-C_3)$	0.96	0.78	0.027
$n(F_{13}) \rightarrow \sigma^*(C_3-C_{11})$	9.55	1.18	0.095
$n(F_{13}) \rightarrow \sigma^*(C_{11}-F_{13})$	7.46	1.06	0.080
$n(F_{13}) \rightarrow \sigma^*(C_{11}-F_{14})$	5.80	1.05	0.071
$n(F_{14}) \rightarrow \sigma^*(C_1-C_2)$	0.51	1.48	0.025
$n(F_{14}) \rightarrow \sigma^*(C_3-C_4)$	0.83	1.45	0.031
$n(F_{14}) \rightarrow \sigma^*(C_3-C_{11})$	9.71	1.19	0.096
$n(F_{14}) \rightarrow \sigma^*(C_{11}-F_{12})$	7.66	1.07	0.082
$n(F_{14}) \rightarrow \sigma^*(C_{11}-F_{13})$	5.37	1.07	0.069

C–H vibrations

The aromatic C–H stretching vibrations are normally found between 3100 and 3000 cm^{-1} . In this region, the bands are not affected appreciably by the nature of substituents. The aromatic C–H bonds present in the title molecule produce bands at 3070 and 3016 cm^{-1} in FT-Raman and 3025 cm^{-1} in FT-IR. The aromatic C–H in-plane bending modes of benzene and its derivatives are observed in the region 1300–1000 cm^{-1} . These modes are observed in the FT-Raman spectrum of the title molecule at 1258 and 1102 cm^{-1} and 1259 cm^{-1} in FT-IR. The C–H out-of-plane bending mode of benzene derivatives are generally observed in the region 1100–600 cm^{-1} . According to the PED results, the calculated scaled values of 448, 361 and 101 cm^{-1} are assigned to C–H out-of-plane bending. For unsubstituted aniline, the peaks at 938, 888 cm^{-1} in Raman [27] and at 930, 888 cm^{-1} in IR spectrum [26] were assigned to C–H out-of-plane bending vibrations. Moreover, aromatic C–H out of plane bending vibrations of 2TFMA and 3TFMA, which reported by Arjunan et al. [5] are supported well with that of the title molecule.

C–X (X= Cl, NH₂, CF₃) vibrations

The bond between the ring and the halogen atom gives rise to three distinct vibrations. Generally, the broad region obtained in vibration spectrum between 850 and 550 cm^{-1} belongs to C–Cl stretching [31]. In the present study, the peak present at 914 cm^{-1} in FT-IR is designated as C–Cl stretching mode. Due to the absence of C–Cl bending modes in the vibrational spectrum of this compound, the assignments corresponding to these modes are assigned here on the basis of PED results. According to the results, we may notice that, the ring out-of-plane bending modes are coupled with these modes considerably.

The C–NH₂ stretching of primary aromatic amines absorbs strongly in the region 1360–1250 cm^{-1} . In the case of 4-chloro-3-(trifluoromethyl) aniline, a strong peak observed at 1336 cm^{-1} in FT-Raman is assigned to C–N stretching mode. For mono substituted amino benzenes with electron donating substituent. The C–N in-plane bending is observed below 400 cm^{-1} whereas with electron withdrawing substituents in the ring, this band is above 400 cm^{-1} . The C–N in-plane bending mode of a title compound is identified at 460 cm^{-1} in FT-Raman spectrum. The out-of-plane bending mode of C–NH₂ is not active in the infrared spectrum. the theoretically computed value of 292 cm^{-1} (B3LYP/6-31G(d,p)) assigned in this study is in good correlation with the experimental FT-Raman.

Due to the cumulative electron withdrawing effect of fluorine, the force constant of the C–C bond is decreased and the C–CF₃ stretching vibrational frequency is lowered [5]. As said, the calculated value of 1252 cm^{-1} is ascribed to C–CF₃ stretching vibration. In the present study, the C–CF₃ in-plane bending mode is assigned at 670 cm^{-1} in FT-IR and 669 cm^{-1} in FT-Raman spectra.

Conclusion

The vibrational characteristics of 4-chloro-3-(trifluoromethyl) aniline has been investigated by the experimental (FT-IR and FT-Raman) and theoretical DFT quantum chemical methods. Scaled theoretical wavenumbers and PED results were quite useful for the reliable assignments of normal modes of vibrations. Moreover, the optimized geometrical parameters were calculated and the substitution effect of change in the planarity or the degree of pyramidal NH₂ moiety were explained on the basis of natural atomic orbital

studies. The NBO analysis performed in this study enabled us to know about the conjugative interactions and other type of interactions taking place within the molecular species.

The mapped isodensity surfaces for the frontier molecular orbitals were plotted. The smallest energy gap of $\Delta E = -0.1867$ a.u is calculated between HOMO and LUMO orbitals. The derived electrostatic point charges revealed that the atom N₇ is having more electronegative point charge of electron withdrawing nature and the C₁ and C₁₁ are having more positive charge of which being an electron acceptor.

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