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Spectroscopic studies and molecular structure investigation on 2-chloro-4-(trifluoromethyl) pyridine: A combined experimental and DFT analysis

M. Boopathi[1,2], P. Udhayakala[2*], G. R. Ramkumaar[3], T. V. Rajendiran[4] and S. Gunasekaran[5]

[1]*Department of physics, Pachaiyappas College for Men, Kanchipuram, India*
[2]*Department of Chemistry, Dr. M. G. R. Educational and Research Institute, University, Chennai, India*
[3]*Department of Physics, C. Kandaswami Naidu College for Men, Chennai, India*
[4]*Department of Chemistry, Pachaiyappa's College, Chennai, India*
[5]*St. Peters Institute of Higher Education and Research, Avadi, Chennai, India*

ABSTRACT

In the present study, the vibrational spectral analysis of 2-chloro-4-(trifluoromethyl) pyridine (2CTFMP) were carried out by Fourier-transform Infrared (FT-IR) and Fourier-transform Raman (FT-Raman) in the region 4000–400cm^{-1} and 3500–100cm^{-1} respectively. ^{13}C and ^{1}H NMR chemical shifts were calculated by using the gauge-independent atomic orbital (GIAO) method. The molecular structure and fundamental vibrational frequencies have been obtained from density functional theory (DFT) B3LYP and LSDA methods with 6-311++G(d,p) basis set calculations. The Non-Linear Optical (NLO) behaviour of the title compound has been studied by determining the electric dipole moment (μ) and hyperpolarizability (β) using B3LYP / 6-311++G(d,p) method. Molecular electrostatic potential (MEP) of the title compound was calculated to predict the static charges in the molecule. The thermodynamic properties at different temperatures were calculated revealing the correlations between standard heat capacities, entropy and enthalpy changes with temperatures.

Keywords: DFT calculations, 2-chloro-4-(trifluoromethyl) pyridine, vibrational analysis, First order hyperpolarizability and MEP.

INTRODUCTION

Pyridine and its derivatives have attracted a lot of attention due to its applications mainly in biological, agricultural and pharmaceutical importance. Literature survey reveals that substituted pyridine derivatives exhibits antibacterial [1],antifungal[2], herbicidal[3] and anticancer activity[4]. The electronic spectra of pyridines and substituted pyridines have been studied by many researchers [5,6]. Green *et al.*, reported the vibrational spectra of some halogeno pyridines [7]. Vibrational spectra of 3,5 and 2,6–dichloropyridines were recorded and reported by Tripathi [8]. A comparative DFT study of 2-(hydroxymethyl)pyridine and 3-(hydroxymethyl)pyridine was carried out by Arjunan *et al.*,[9]. In our earlier study we have reported FT-IR,FT-Raman, NMR and DFT study on 2-methoxy-3-(trifluoromethyl) pyridine [10]. DFT method of calculating electronic structure of molecules predicts great accuracy in producing molecular geometry, vibrational frequencies and thermodynamic properties [11]. Literature survey reveals that to the best of our knowledge, neither quantum chemical calculations, nor the vibrational spectroscopic analysis have been reported for the compound under study 2CTFMP. To fulfil the inadequacy observed in the literature and also to understand the in-depth insight of the title molecule, the current investigation of the systematic study on the molecular structure and vibrational spectral analysis based on FT-IR, FT-Raman, NMR chemical shift, first order hyperpolarizability, molecular electrostatic potential map (MEP) and thermo dynamical functions have been carried out.

MATERIALS AND METHODS

The compound under investigation namely 2CTFMP was procured from Sigma–Aldrich chemicals, U.S.A with a stated purity of greater than 98%. The compound was used as such without further purification. The FT-IR spectrum of 2CTFMP was recorded in the region 4000-400cm^{-1} on a Perkin Elmer FT-IR Spectrophotometer. The FT-Raman spectrum of the title compound was recorded in the Bruker FRA 106/S instrument equipped with Nd:YAG laser source operating at 1064 nm line widths in the range of 4000–100cm^{-1}. The chemical shift of ^{1}H and ^{13}C NMR spectra was recorded on Bruker Avance III NMR spectrometer using DMSO as a solvent and reported in ppm relative to tetramethylsilane (TMS). The spectral measurements were carried out at Sophisticated Analytical Instrument Facility, IIT, Chennai, India.

1. Computational Procedures

The gas phase geometry of the compound under investigation 2CTFMP in the ground state was optimized by using DFT/B3LYP(Becke3–Lee–Yang–Parr) and LSDA(Local Spin Density Approximation) level with the standard basis set 6-311++G(d,p) using Gaussian 09W [12] program package, invoking gradient geometry optimization [13]. The scaling factors have to be used to obtain considerably better agreement with experimental data. The computed harmonic frequencies at B3LYP/6-311++G(d,p) level of basis set were scaled by 0.981 for frequencies less than 1700cm^{-1} and 0.9615 for higher frequencies[14]. The scaled values used in DFT/LSDA/6-311++G(d,p) were 0.9937 for frequencies less than 1700cm^{-1} and 0.9865 for higher frequencies. ^{13}C and ^{1}H NMR were calculated in dimethylsulfoxide (DMSO) by using the gauge- independent atomic orbital (GIAO) method [15] with B3LYP /6-311++G(d,p) basis set level. Molecular electrostatic potential (MEP) map have been plotted to visualize the variably charged regions of a molecule in terms of colour grading and also to determine the electrophilic and nucleophilic attacking sites. On the basis of theoretical frequencies obtained from density functional calculations at B3LYP/6-311++G(d,p) level, the statistical standard thermodynamic parameters like entropy (S), Heat capacity (C) and enthalpy (H) were calculated.

2. Prediction of Hyperpolarizability

First order hyperpolarizability determine not only the strength of molecular interactions as well as the cross-sections of different scattering and collision processes, but also the non-linear optical properties (NLO) of the system [16]. Density functional theory (DFT) calculations with various functional are excellent methods in the design of NLO molecules and they help predict properties of the new materials, such as molecular dipole moments and hyperpolarizabilities [17,18]. The significance of first hyperpolarizability of molecular system is dependent on the efficiency of electronic communication between acceptor and the donor groups as that will be the key to intra molecular charge transfer [19]. First hyperpolarizability is a third rank tensor that can be described by a 3 x 3 x 3matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [20]. It can be given in the lower tetrahedral format. In the present study, the electric dipole moment and hyperpolarizability of the title compound were investigated. The hyperpolarizability tensors (β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{yzz}, β_{zzz}) can be obtained by a frequency calculation output file of Gaussian. Domination of particular components indicates on a substantial delocalization of charges in those directions. The β values of Gaussian output are in atomic unit(a.u.), so the calculated values have been converted in to electrostatic units (1a.u.=8.6393 x 10^{-30} esu). The static dipole moment μ and first order hyperpolarizability β_{tot} using x,y,z components are defined as follows.

$$\beta_{tot} = (\beta_x^2+\beta_y^2+\beta_z^2)^{1/2} \qquad (1)$$
$$\beta_x = \beta_{xxx}+\beta_{xyy}+\beta_{xzz} \qquad (2)$$
$$\beta_y = \beta_{yyy}+\beta_{xxy}+\beta_{yzz} \qquad (3)$$
$$\beta_z = \beta_{zzz}+\beta_{xxz}+\beta_{yyz} \qquad (4)$$

Total dipole moment can be calculated using the following equation:

$$\mu = (\mu_x^2+\mu_y^2+\mu_z^2)^{1/2} \qquad (5)$$

The calculated dipole moment value is 1.3844Debye (D). The highest value of dipole moment is observed for component μ_y. In this direction, the value is equal to 1.1322D. For direction *x* and *z*, these values are equal to −0.7923D and -0.0835D respectively. The calculated first order hyperpolarizability (βtot = 1.698 x 10^{-30} esu) of title molecule, which is nearly four and half times more than βtot of urea (0.3728 x 10^{-30}esu) indicates that the molecule 2CTFMP possess nonlinear optical properties and may be a potential applicant in the development of NLO materials. Urea is one of the prototypical molecule used in the study of NLO properties and also used as a threshold value for comparative purposes. The calculated dipole moment(μ) and first-order hyperpolarizability (β) are shown in Table 1.

Table 1. The B3LYP/6-311++G(d,p)calculated electric dipole moment μ(D) and first order hyperpolarizability β_{tot} (x10^{-30}esu) of 2CTFMP

Parameters	B3LYP/ 6-311++G(d,p)
μ_x	-0.7923
μ_y	1.1322
μ_z	-0.0835
μ	1.3844
β_{xxx}	-44.4728
β_{xxy}	115.9156
β_{xyy}	-51.9805
β_{yyy}	44.3241
β_{xxz}	-3.6321
β_{xyz}	-0.4771
β_{yyz}	1.800
β_{xzz}	15.5466
β_{yzz}	18.5386
β_{zzz}	-9.6468
β_{tot}	1.698

RESULTS AND DISCUSSION

5.1 Molecular geometry

The optimized molecular structure along with the numbering of atoms of 2-chloro-4-(trifluoromethyl) pyridine (2CTFMP), obtained from Gauss View program is shown in Fig.1. The global minimum energy obtained by the DFT/ B3LYP/6-311++G(d,p) for the optimized structure of the title compound is -1045.121a.u. and showed that the molecule belongs to C*s* symmetry points group.

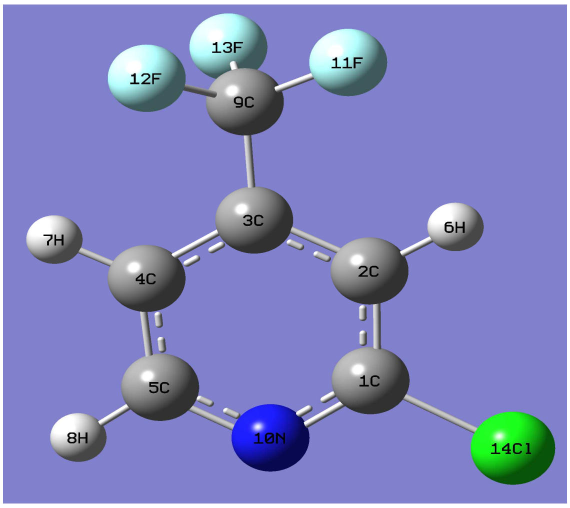


Fig.1 Optimized molecular Structure of 2-Chloro-4-(triflurometһyl) pyridine(2CTFMP)

5.2 Vibrational spectral analysis

The compound under investigation 2CTFMP belongs to Cs symmetry consists of 14 atoms having 36 modes of vibration active in IR and Raman spectra. The detailed vibrational assignments of fundamental modes of 2CTFMP along with observed and calculated frequencies are reported in Table 2. The calculated and experimental FT-Raman and FT-IR spectra are shown in Figs. 2 and 3, respectively.

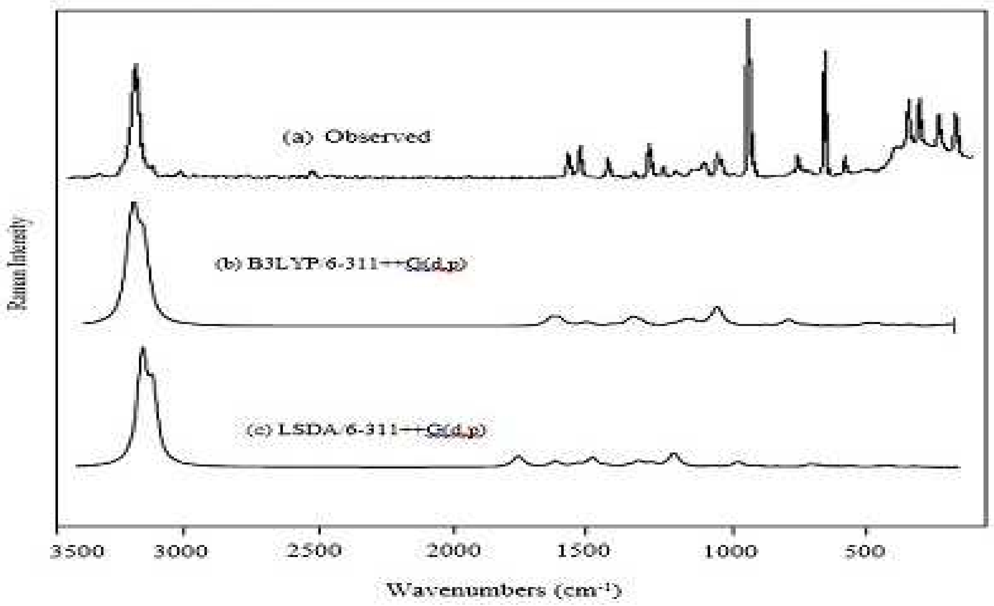


Fig. 2 Observed and calculated FT-Raman spectra of 2-chloro-4-(trifluoromethyl) pyridine (2CTFMP)

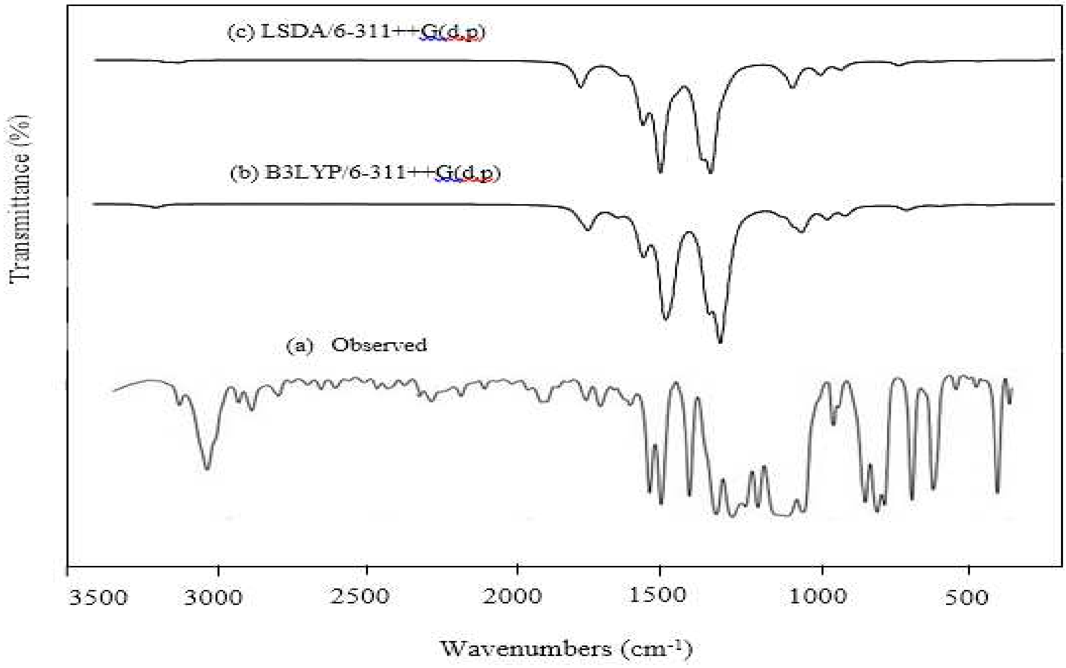


Fig. 3 Observed and calculated FT-IR spectra of 2-chloro-4-(trifluoromethyl) pyridine (2CTFMP)

C-C Vibration

The carbon-carbon stretching vibration is very much prominent in the spectrum of pyridine and its derivatives and is highly characteristic of the aromatic ring itself [21]. Normally the bands between 1400–1650 cm^{-1} in pyridine derivatives are assigned to C- C stretching modes [22]. The experimental bands observed at 1563,1601cm^{-1} in FT-IR and 1565,1605cm^{-1} in FT-Raman spectra is assigned to C-C stretching vibrations. The theoretically computed C- C stretching vibrations by B3LYP/6-311++G(d,p) at 1574,1603cm^{-1} and 1600,1611cm^{-1} by LSDA/6-311++G(d,p) method shows good agreement with experimental as well as literature data. The breathing mode carbon is sensitive to the presence of substituents. In our present study the calculated value at 988cm^{-1} by B3LYP method and at 982cm^{-1} in LSDA method is well correlated with the experimental FT-IR band at 989cm^{-1} and FT-Raman band at 992cm^{-1} is assigned to C-C-C ring breathing mode. This assignment is supported by the literature data [23]. The band observed at 607cm^{-1} in FT-IR and 601cm^{-1} in FT-Raman spectra is assigned to C-C planar ring deformation modes of vibration. The theoretically computed value at 644 and 643cm^{-1} by both the methods is in agreement with the experimental as well as the literature data [24]. The frequency calculated at 734,727cm^{-1} by theoretically calculated methods well agreed with the experimental bands observed at 730cm^{-1} and 732cm^{-1} in FT-IR and FT-Raman is assigned to the non-planar deformation.

C-H vibrations

The characteristic region for C-H stretching vibrations in hetero-aromatic structures in the region of 3150–3000 cm^{-1} [25]. The nature of the substitutions do not influence the bands in this region appreciably. In the present investigation, the bands observed at 2994,3074,3148cm^{-1} in FT-IR and 3023, 3078, 3147cm^{-1} in the FT-Raman spectrum is assigned to C-H stretching vibrations. The theoretically calculated frequencies by B3LYP method at 3040, 3075 and 3092cm^{-1} and 3052, 3092 and 3099cm^{-1} by LSDA method is well agreed with the experimental observations. The C-H in-plane bending vibrations which occur in the region 1400 to 1200cm^{-1} are useful for characterization purpose [26]. The calculated values by B3LYP method at 1268, 1278cm^{-1} and by LSDA method at 1251,1310cm^{-1} is well correlated with the experimental FT-IR bands at 1259, 1281cm^{-1} and FT-Raman bands at 1257,1280cm^{-1} which is assigned to C-H in plane bending mode of vibration. The C-H out-of plane bending vibrations are determined by the number of adjacent atoms on the ring and not very much affected by the nature of substitution [27], normally these vibrations occur in the region 1000-700cm^{-1}. In the present study, the FT-IR bands observed at 730,847cm^{-1} and FT-Raman band at 732, 860cm^{-1} is assigned to C-H- out of plane bending vibration. The calculated wavenumbers at 734,843cm^{-1} by B3LYP method and 727,827cm^{-1} by LSDA methods show good agreement with the experimental wavenumbers.

C-N Vibrations

In pyridine derivatives, the C-N stretching vibration is always mixed with other bands and regularly assigned in the region 1382 - 1266 cm^{-1} [28,29]. The C-N stretching vibration of the title molecule 2CTFMP is observed strongly at 1259,1257cm^{-1} in experimental FT-IR and FT-Raman spectra. This is well correlated with the theoretically predicted frequencies at 1268,1251cm^{-1} by B3LYP and LSDA methods. This frequency is lower than the expected range due to the attachment of electronegative chlorine atom in the ring carbon (C1) and also lie in the region of C-H bending vibration. This view is also supported by the literature data [30]. The band observed at 730cm^{-1} in FT-IR and 732cm^{-1} in FT-Raman spectra is assigned to C-N out-of-plane bending vibration which is well correlated with the theoretically calculated frequencies by B3LYP and LSDA methods at 743 and 727cm^{-1}. The computed frequency wavenumbers at 644, 643cm^{-1} by B3LYP and LSDA methods is agreed with the bands observed at 607,601cm^{-1} in FT-IR and FT-Raman spectra which is assigned to C-N in-plane bending mode of vibration. These assignments are on par with the literature data [31].

C- Cl Vibration

In the present investigation, due to the presence of heavy atoms (Chlorine and Fluorine) on the periphery of the molecule mixing of vibrations are possible. Mooney [32] assigned vibrations of C X group (X = Cl, Br, I) in the frequency range of 1129–480 cm^{-1}. The C-Cl stretching vibrations of the title compound is assigned by the presence of a band at 702 cm^{-1} and an intense band at 822, 823cm^{-1} both in FT-IR and FT-Raman spectra. The computed values at 721,724cm^{-1} and 810, 819cm^{-1} by B3LYP and LSDA methods is well correlated with the experimental observations. This is also supported by the literature data [33]. The band observed at 190cm^{-1} in FT-Raman spectra is assigned to C-Cl out-of-plane bending vibration. The computed value at 175,170cm^{-1} in B3LYP and LSDA methods is well correlated with the experimental observations. C-Cl in-plane- bending mode at 420, 408cm^{-1} in experimental FT-IR and FT-Raman is assigned to C-Cl in-plane-bending mode which is well correlated with the wavenumbers calculated by B3LYP and LSDA methods at 433cm^{-1}. The experimental and theoretical results are in good agreement.

CF_3 Vibration

The title molecule 2CTFMP under consideration possess one CF_3 group in the 4th position of the ring. The computed values at 1148, 1161cm^{-1} by B3LYP and LSDA methods is well correlated with the experimental bands at 1144cm^{-1}

in FT-IR is assigned to CF_3 asymmetric stretching vibration. The bands observed at 1110cm^{-1} in FT-IR is well correlated with the computed values at 1103,1123cm^{-1} by B3LYP and LSDA methods is assigned to symmetric C-F stretching vibration. This is in good agreement with the literature data [34]. The C–F deformation vibration usually occur in the regions 640–580 cm^{-1} and 590–490 cm^{-1} [35]. The experimental peaks at 504 and 660 cm^{-1} in FT-IR and 537 and 664cm^{-1} in FT-Raman spectra of the title compound confirm the presence of out of plane and in-plane bending vibrations of CF_3. The calculated wavenumbers by B3LYP and LSDA methods at 508,507cm^{-1} and 656, 650cm^{-1} is well correlated with experimental as well as the literature data. CF_3 rocking mode usually appears in the ranges of 450–350 cm^{-1} and 350–260 cm^{-1} [36]. The computed value at 433cm^{-1} by both B3LYP and LSDA methods is assigned to CF_3 in-plane rocking which is confirmed by the presence of a strong band observed at 420,408cm^{-1} in FT-IR and FT-Raman spectra. The peak observed at 283cm^{-1} in FT-Raman spectra is assigned to CF_3 out of plane rocking. This theoretically calculated values by both the methods at 272,271cm^{-1} is well correlated with the experimental observations. It is difficult to observe the torsional motion in the FT-IR and FT-Raman spectra. This is because of the low wave number and also due to the presence of heavier fluoro methyl group. The computed frequencies by both the methods at 13,15cm^{-1} is assigned to C-F_3 torsional mode of vibration.

Table 2. Comparison of experimental (FT-IR and FT-Raman) wavenumbers(cm^{-1}) with the calculated harmonic frequencies of 2CTFMP using LSDA and B3LYP /6-311++G(d,p) basis set

S.No	LSDA/ 6-311++ G(d,p)	B3LYP/ 6-311++ G(d,p)	Experimental		Vibrational assignments
			FT-IR	FT- Raman	
1	15	13			τ(C-F_3)
2	117	120		130	γ (C-F)
3	144	147		152	β(C-C), β (C-Cl)
4	170	175		190	γ(C-C),γ(C-Cl)
5	271	272		283	ωC-F_3
6	314	319		308	γ(C-N), γ(C-H), γ (C-F)
7	337	337		341	Lattice vibration
8	399	397		374	β C-Cl
9	433	433	420	408	β C-Cl, ρ C-F
10	436	444	445	445	γ C-H
11	507	508	504	537	γ C-F, γ C-H
12	571	566	584	566	β C-N, γ C-F, ν_{as} C-F
13	643	644	607	601	β C-N, γ C-C, ν_{as} C-F,α-ring
14	650	656	660	664	β C-F,ring stretching
15	724	721	702	702	ν C-Cl, ν_s C-F, ring breathing
16	727	734	730	732	γ C-H, γ C-N , φ- ring
17	819	810	822	823	ν_s C-Cl, ν_sC-CF_3, ν ring
18	827	843	847	860	γ C-H
19	863	890	870	879	γ C-H
20	947	975	978	943	γ C-H
21	982	988	989	992	ν C-N, ring breathing
22	1062	1076	1088	1083	β C-H, νC-F
23	1081	1092		1096	ν_s C-F, βC-H
24	1123	1103	1110		ν C-F, βC-H
25	1127	1121			ν_s C-F, νC-Cl
26	1161	1148	1144		ν_{as} C-F, ν C-C
27	1251	1268	1259	1257	ν C-N, ν C-C, βC-H
28	1310	1278	1281	1280	β C-H, νC-CF_3
29	1367	1303	1326	1328	β C-H, νC-CF_3
30	1375	1379	1378	1357	β C-H, ν C-C
31	1458	1472	1468	1470	β C-H, νC-C, ν C-N
32	1600	1574	1563	1565	ν C-N, ν C-C, β C-H
33	1611	1603	1601	1605	νC-C, β C-H
34	3052	3040	2994	3023	ν C-H
35	3092	3075	3074	3078	ν C-H
36	3099	3092	3148	3147	ν C-H

5.3 NMR Calculations

Nuclear magnetic resonance (NMR) spectroscopy has evolved as one of the most powerful analytical technique that is used in many disciplines of scientific research, medicine, various industries and also visualization of atoms and molecules in various media in solution as well as in cold state. Due to their higher sensitivity, they are valuable for structural investigations. The combined use of NMR and computer simulation methods offers a powerful way to interpret and predict the structure of large biomolecules [37]. For reliable calculations of magnetic properties, accurate predictions of molecular geometries are essential. The optimized structure of 2CTFMP is used to calculate the NMR spectra using the hybrid B3LYP as well as by the LSDA method with 6-311++G(d,p)basis set. Then gauge- independent atomic orbital (GIAO) ^{1}H and ^{13}C chemical shift calculations of the compound was done by same methods in IEFPCM/DMSO solution [38]. Relative chemical shifts were estimated by using the corresponding TMS shielding calculated in advance at the same theoretical level as the reference. The isotropic shielding values were used to calculate the isotropic chemical shifts with respect to the TMS. The value of σ^{TMS} is 182.46 and 31.88 ppm for ^{13}C and ^{1}H respectively.

Usually the range of ^{13}C NMR chemical shifts for a similar organic molecules occur larger than 100 ppm [39]. In our present study, there are six carbon signals calculated theoretically and tabulated in table 3, of which five carbon were located in aromatic region. All the aromatic carbons atom give signals in overlapped areas of the spectrum with chemical shift values from 100 to 150 ppm. The chemical shift value of carbon C1 is greater than other carbons due to the presence of the resonating effect of chlorine and the adjacent electronegative nitrogen atom. The chemical shift value of C5 is the next higher due to the influence of electronegative nature of nitrogen atom. The observed chemical shift value of atoms C3 and C9 is almost same. It may be due to the influence of fluorine atoms. The C2 and 4C have the smallest chemical shift values. The observed and calculated chemical shift values show correlation with each other.

The proton chemical shift (^{1}H NMR) of organic molecules generally varies greatly with the electronic environment of the proton. Usually, hydrogen attached to or nearby electron- withdrawing atom or group can decrease the shielding and move the resonance of attached proton towards a higher frequency, whereas electron-donating atom or group increases the shielding and moves the resonance towards a lower frequency [40]. In our present investigation, the molecule under study contains three hydrogen atoms and all are in the ring. All the three atoms show the chemical shift in both experimental and theoretical methods. The chemical shift value of proton numbered H8 is higher than the other protons due to the influence of electron withdrawing nature of nitrogen atom. The other two protons (6H and 7H) have the chemical shift value 7.82 and 7.72 ppm. Among the computed values, the values calculated by B3LYP/6-311++G(d,p) method is in good agreement with the observed values than the LSDA method. The correlation graph between the experimental and calculated ^{13}C NMR and ^{1}H NMR chemical shifts of title molecule are represented in Fig.4. The experimental chemical shift of ^{13}C and ^{1}H NMR of title molecule is represented in Fig.5. The relations between the calculated and experimental chemical shifts are usually linear and described by the following equation:

$$\delta_{cal} = 1.14889\delta_{exp} - 17.57079 \ {}^{13}C \qquad (R^2=0.918)$$
$$\delta_{cal} = 1.06438\delta_{exp} - 0.15647 \ {}^{1}H \qquad (R^2=0.9985)$$

Table 3. Experimental and theoretical B3LYP and LSDA ^{13}C and ^{1}H isotropic chemical shift of 2CTFMP (with respect to TMS) in DMSO (all values in ppm)

Atom	Experimental	Calculated		Atom	Experimental	Calculated	
		B3LYP	LSDA			B3LYP	LSDA
1C	160.87	165.73	165.23	8H	8.68	8.72	9.45
5C	150.42	156.48	158.27	6H	7.82	7.83	8.65
3C	136.27	147.49	147.22	7H	7.72	7.68	8.45
9C	136.16	132.47	136.02				
2C	126.22	126.05	127.19				
4C	124.06	124.53	125.72				

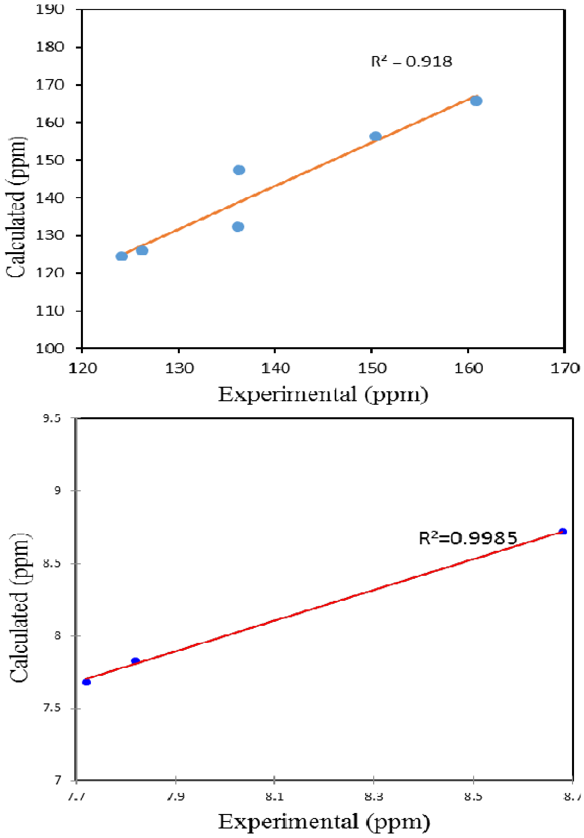
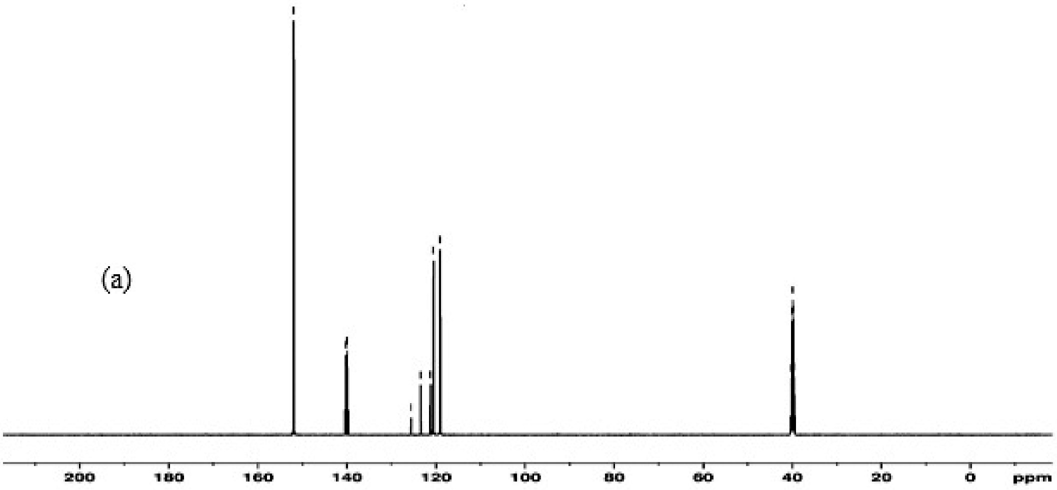


Fig. 4 Correlation graph between calculated (B3LYP/6-311++G(d,p)) and experimental chemical shifts (a) ^{13}C and (b) ^{1}H NMR of 2CTFMP



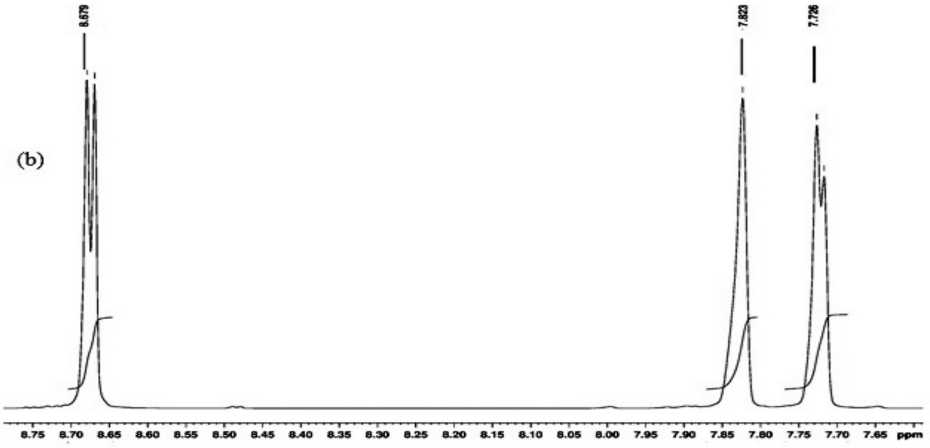


Fig. 5 Experimental chemical shifts of (a) ^{13}C and (b) ^{1}H NMR of 2CTFMP

5.4 The Molecular Electrostatic Potential

The molecular electrostatic potential (MEP) [41] mainly explores the molecular interactions within the molecule. It also provides the correlations between the molecular properties like chemical reactivity and electronegativity of molecules [42,43]. The negative and positive potential regions of the MEP are expected to be the sites of nucleophilic and elctrophilic region where chemical reactions are expected to occur.

MEP surface diagram shown in Fig.6 is used to visualize variably charged regions of a molecule in terms of colour grading. The red region refers to greatest electron density while the blue region is characterized by electron poor region. The green region in MEP refers to the neutral region of electron density. The electrostatic potential increases in the order red < orange < yellow < green < blue [44]. The colour code of the maps in the range -3.718 a.u.(deepest red) to 3.718 a.u.(deepest blue) in the title molecule, where the blue colour indicates the strongest attraction and the red colour indicates the strongest repulsion. In the MEP map of the title compound the maximum negative regions V(r) are associated with the lone pair Nitrogen(N_{10}) atom having value of -0.33013 a.u. The maximum positive regions localized on the H_7 atom in the ring have the value of +0.02781 a.u. From this result, we can conclude that the nitrogen atom indicates the strongest repulsion and H atoms indicate the strongest attraction.

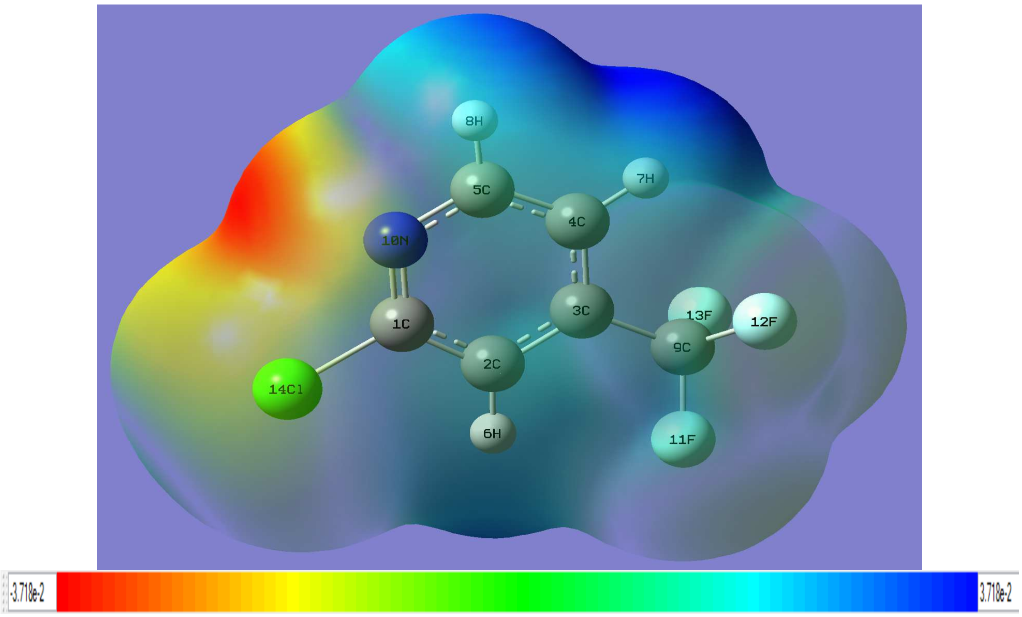


Fig. 6 3D-representation of the electrostatic potential around the molecule 2CTFMP using the DFT /B3LYP level of theory at 6-311++G(d,p) basis set

5.5 Thermodynamic properties

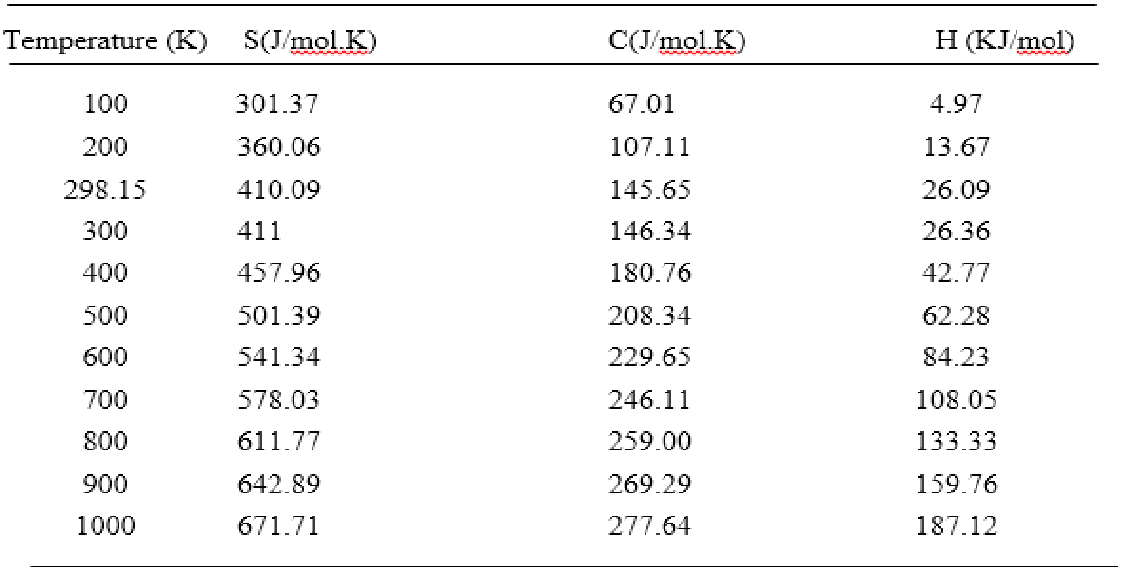
Theoretically computed thermodynamic parameters such as energies(a.u), zero point vibrational energies (kcal mol^{-1}), rotational constants (GHZ), entropies (cal mol^{-1}) and dipole moment of 2CTFMP by DFT/B3LYP/6-311++G(d,p) method are listed in Table 4. On the basis of theoretical frequencies obtained from density functional calculations perl script THERMO. PL [45] is used to calculate the statistical standard thermodynamic parameters like entropy (S), Heat capacity (C) and enthalpy (H) and listed in table 5. It can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1200 K due to the fact that the molecular vibrational intensities increase with temperature [46,47]. While performing the calculation, the molecule was considered to be at room temperature of 298.15 K and one atmospheric pressure. The correlation equations between entropy, heat capacity and enthalpy changes and temperatures were fitted by quadratic formulas, and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9999, 0.9994 and 0.9994 respectively. The corresponding fitting equations are as follows and the correlation graph of those shown in Fig 7.

$S = 245.99743+0.59774T-1.7x10^{-4}\ T^2 \quad (R^2 = 0.9999)$
$C = 20.67682+0.48820T -2.3x10^{-4}\ T^2 \quad (R2=0.9994)$
$H= 6.76327+0.08130T + 1.1x10^{-4}\ T^2 \quad (R^2 = 0.9994)$

Table 4. Theoretically computed energies (a.u.), zero point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal $mol^{-1}\ K^{-1}$) of 2CTFMP employing B3LYP/ 6–311++G(d,p) methods

Parameters	B3LYP/6-311++G(d,p)
Total energy(a.u)	-1045.121
Zero point energy	52.15871
Rotational Constant	1.88545 0.55401 0.46336
Entropy	
Total	57.803
Translational	0.889
Rotational	0.889
Vibrational	56.025

Table 5. Thermodynamic properties of 2CTFMP at different temperatures at B3LYP/ 6-311++G(d,p) level



Temperature (K)	S(J/mol.K)	C(J/mol.K)	H (KJ/mol)
100	301.37	67.01	4.97
200	360.06	107.11	13.67
298.15	410.09	145.65	26.09
300	411	146.34	26.36
400	457.96	180.76	42.77
500	501.39	208.34	62.28
600	541.34	229.65	84.23
700	578.03	246.11	108.05
800	611.77	259.00	133.33
900	642.89	269.29	159.76
1000	671.71	277.64	187.12

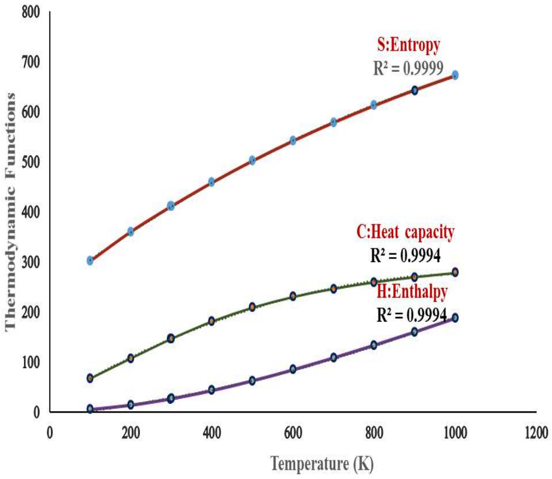


Fig. 7 Correlation graph between temperature and (a) entropy (b) Heat capacity (c) enthalpy of 2CTFMP

CONCLUSION

In the present study, a complete vibrational analysis and electronic properties of 2CTFMP was performed by DFT method (B3LYP) and LSDA at 6-311++G(d,p) basis set level. The computed vibrational wavenumbers were assigned and compared with experimental FT-IR and FT-Raman spectra for the first time. The theoretically constructed FT-IR and FT-Raman spectra shows good correlation with the experimental observations. The difference between the observed and the calculated scaled wavenumbers of most of the fundamentals are very small. The computed first hyperpolarizability value of the title compound is greater than that of urea which indicates that the 2CTFMP is a material for NLO applications. The chemical shift of ^{13}C and ^{1}H of the title compound calculated in DMSO on comparison with the experimental was found to have a linear relation. The MEP map shows the electron rich region around the electronegative lone pair nitrogen atom and the positive potential along the electron deficient hydrogen atoms. The correlations between the statistical thermodynamics and temperature were also obtained. It was ascertained that the heat capacity, entropy and enthalpy increase with the increasing temperature owing to the increase in the intensities of the molecular vibrations with increasing temperature.

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