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Vibrational analyses of Molecular structure and NMR chemical shielding anisotropy (CSA) parameters of methyl 2-chloronicotinate

P. Dinesh

Department of Physics, Salem Sowdeswari College (Govt. Aided), Salem-10, India.

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ABSTRACT

In this work, FT-IR and FT-Raman spectra are recorded on the solid phase of methyl 2-chloronicotinate in the regions 4000–400 cm^{-1} and 3500–100 cm^{-1} respectively. The geometrical parameters, vibrational assignments, HOMO–LUMO energies and NBO calculations are obtained for the monomer and dimer of methyl 2-chloronicotinate from DFT (B3LYP) with 6-311++G (d, p) basis set calculations. Second order perturbation energies and electron density (ED) transfer from filled lone pairs of Lewis base to unfilled Lewis acid sites of methyl 2-chloronicotinate are discussed on the basis of NBO analysis. give the evidence for the formation of dimer entities in the title molecule. The theoretically calculated harmonic frequencies are scaled by common scale factor. The observed and the calculated frequencies are found to be in good agreement. The thermodynamic functions were obtained for the range of temperature 100–1000 K. The polarizability, first hyperpolarizability, anisotropy polarizability invariant has been computed using quantum chemical calculations. The chemical parameters were calculated from the HOMO and LUMO values. The NMR chemical shielding anisotropy (CSA) parameters were also computed for the title molecule.

Introduction

The biological importance of Chloronicotinate and their complexes have shown notable bioactivity as medicinal, physicochemical, chelating therapeutics and biological properties. They are found in nature [1, 2] and they can also be obtained by means of diverse synthesis procedures [3]. Chloronicotinate derivatives act as powerful inhibitors of the anthelmintic and vitamins. We found out that the treatment of alkylidene cyanoacetates with the Vilsmeier Haack reagent [4]. It is known that the therapeutically administered drugs are a subject of considerable interest. But little is known about modification of the activities of most drugs that are potential ligands. The methyl 2-chloronicotinate derivate are mainly of great pharmacological and medicinal interest because they exhibit a wide range of anticancer activity [5-14], A recent study has linked such as hypnotic, anti-tubercular [15], analgesic [16], antiviral [17], anti-bacterial[18-22], anti-diabetic, anti-inflammatory and antitumor agents [23-26], and the mechanism of action attributed to each derivative are strongly depending on the type of modifications of methyl 2-chloronicotinate [27-31]. To the best of our knowledge, no detailed spectroscopic investigation has been made on the title compound consideration of the above factors motivated us to undertake this detailed spectroscopic investigation.

Considering the above mentioned aspects and the resulting demand of methyl 2-chloronicotinate has led to search for commercially attractive and flexible compounds and to investigate the entire properties. To the best of our knowledge, FTIR and FT-Raman vibrational studies on the fundamental modes and electronic property investigations by NBO analysis, frontier molecular orbitals (FMOs) and thermodynamic properties on methyl 2-chloronicotinate are inadequate in the literature. This inadequacy observed in the literature motivated us to investigate on methyl 2-chloronicotinate by experimental techniques and theoretical methods. Thus, a detailed investigation have been attempted using DFT/B3LYP method with 6-311++G (d,p) basis set to provide more satisfactory and valuable information on electronic structure, molecular orbitals and potential energy distribution. The optimized geometry, FMO's and their energy gaps, molecular electrostatic potential contour (MESP), total density region and electro static potential contour (MESP) map have been constructed at B3LYP/6-311++G(d,p) level, in order to understand the electronic properties, electrophilic and nucleophilic active centers of methyl 2-chloronicotinate.

2. Experimental Details

The methyl 2-chloronicotinate in the liquid (Clear - Slightly pale yellow - reddish yellow) were purchased from Lancaster Chemical Company, UK which is of spectroscopic grade and hence used for recording the spectra as such without any further purification to record FTIR and FT-Raman spectra. The FTIR compounds were recorded by KBr pellet method in the region 4000 - 400cm^{-1} using BROKER IFS 66V spectrometer with a Globar source, Ge/KBr beam splitter and a MCT detector. The frequencies for all sharp bands are accurate to 2 cm^{-1}. The FT-Raman spectra were also recorded in the range 3500-50-cm^{-1} by the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source with 200mW power operating at 1064nm. A liquid nitrogen cooled-Ge detector was used. The spectral resolution is 2 cm^{-1}.

Tele: +91 94881 12792.

E-mail address: pgdineshp6@gmail.com

Table 1. Optimized geometrical parameters of methyl 2-chloronicotinate obtained by B3LYP/6311++G(d,p) level calculations

Bond Length	Value (◦)	Bond angle	Value (◦)	Dihedral Angle	Value (◦)
N1-C2	1.32	C2-N1-C6	118.71	C6-N1-C2-C3	-0.36
N1-C6	1.34	N1-C2-C3	123.75	C6-N1-C2-Cl7	176.76
C2-C3	1.41	N1-C2-Cl7	114.38	C2-N1-C6-C5	-1.65
C2-Cl7	1.76	C3-C2-Cl7	121.80	C2-N1-C6-H17	178.96
C3-C4	1.40	C2-C3-C4	116.36	N1-C2-C3-C4	2.39
C3-C8	1.50	C2-C3-C8	127.66	N1-C2-C3-C8	-178.90
C4-C5	1.39	C4-C3-C8	115.97	Cl7-C2-C3-C4	-174.53
C4-H15	1.08	C3-C4-C5	120.34	Cl7-C2-C3-C8	4.17
C5-C6	1.39	C3-C4-H15	118.21	C2-C3-C4-C5	-2.48
C5-H16	1.08	C5-C4-H15	121.45	C2-C3-C4-H15	177.71
C6-H17	1.09	C4-C5-C6	117.81	C8-C3-C4-C5	178.66
C8-O9	1.21	C4-C5-H16	121.36	C8-C3-C4-H15	-1.15
C8-O10	1.34	C6-C5-H16	120.83	C2-C3-C8-O9	-148.57
O10-C11	1.44	N1-C6-C5	122.96	C2-C3-C8-O10	34.37
C11-H12	1.09	N1-C6-H17	115.84	C4-C3-C8-O9	30.14
C11-H13	1.09	C5-C6-H17	121.20	C4-C3-C8-O10	-146.92
C11-H14	1.09	C3-C8-O9	122.54	C3-C4-C5-C6	0.71
		C3-C8-O10	113.46	C3-C4-C5-H16	-179.24
		O9-C8-O10	123.94	H15-C4-C5-C6	-179.49
		C8-O10-C11	116.12	H15-C4-C5-H16	0.56
		O10-C11-H12	110.27	C4-C5-C6-N1	1.46
		O10-C11-H13	105.21	C4-C5-C6-H17	-179.17
		O10-C11-H14	110.33	H16-C5-C6-N1	-178.58
		H12-C11-H13	110.80	H16-C5-C6-H17	0.78
		H12-C11-H14	109.36	C3-C8-O10-C11	179.70
		H13-C11-H14	110.82	O9-C8-O10-C11	2.69
				C8-O10-C11-H12	59.74
				C8-O10-C11-H13	179.25
				C8-O10-C11-H14	-61.17

3. Computational Details

Quantum chemical calculation were used for methyl 2-chloronicotinate to carry out the optimized geometry and vibrational wavenumbers with the 2009 version of the Gaussian suite [32] using the DFT-B3LYP methods [33, 34] supplemented with standard 6-311++G(d,p) basis sets. The stability of the optimized geometries was confirmed by wavenumber calculations, which gave positive values for all the obtained wavenumbers. The vibrational modes were assigned by means of visual inspection using GAUSSVIEW 5.0.8 program [35]. A comparison is made between the theoretically calculated frequencies and the experimentally measured frequencies. In this investigation we observed that the calculated frequencies were slightly greater than the fundamental frequencies. To improve the agreement between the predicted and observed frequencies, the computed harmonic frequencies are usually scaled for comparison. In this work the force field was scaled according to the SQM procedure [36], the Cartesian representation of the force constants were transferred to a non-redundant set of local symmetry coordinates, chosen in accordance to the recommendations of Pulay et al. [37]. Calculation of the potential energy distribution (PED) and the prediction of IR intensities and Raman activities were done on a PC with the VEDA 4 program [38]. The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (Si) calculated by Gaussian 09W and adjusted during scaling procedure with VEDA 4 program were converted to relative Raman intensity (Ii) using the following relation from the basic theory of Raman scattering [39, 40].

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i[1 - \exp(-hcv_i / kT)]}$$

wavenumber of the i[th] normal mode, *h*, *c* and *k* are universal constants, and f is the suitably chosen common scaling factor for all the peak intensities. Finally, the thermodynamic properties of the optimized structures were obtained theoretically from the harmonic vibrations.

4. Result and discussion

Structural descriptions

The optimized geometry of methyl 2-chloronicotinate, using B3LYP/6-311++G (d,p) methods for various possible calculations. The structure optimization have shown that of Fig. 1 have produced the energy E= -935.91257(A.U.). The most optimized structural parameters were also calculated by DFT method with different basis sets are depicted in Table 1. The optimized structural parameters were used to compute the vibrational frequencies of methyl 2-chloronicotinate at the B3LYP/6-311 + +G (d,p) level of calculations.

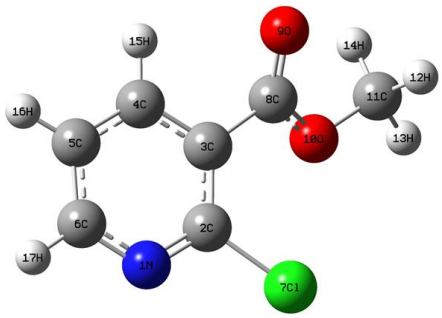

Fig. 1.Optimized molecular structure of methyl-2-chloronicotinate.

Vibrational assignments

The geometry of the molecules under investigation is considered by possessing C_1 point group symmetry and the optimized molecular structure is obtained from GAUSSAN 09W and GAUSSVIEW programs as shown in Fig. 1.

Table 2. Detailed assignment of fundamental vibrations of methyl 2-chloronicotinate by normal mode analysis based on scaled quantum Mechanical force field

No.	Observed frequency (cm^{-1})		Calculated frequency (cm^{-1})					Characterization of normal modes with PED(%)
	FT-IR	FT-Raman	B3LYP/6-311++G(d,p)					
			Unscaled	Scaled	IR Activity	Raman Activity	Raman Intensity	
1	3209	3216	3206	3215	5.80	188.60	333.72	CH (99)
2	3180	-	3193	3185	2.91	166.73	345.01	CH (99)
3	-	3160	3164	3162	12.16	123.00	227.11	CH (99)
4	-	3102	3164	3104	9.67	77.33	138.65	CH_{3ips} (99)
5	3048	-	3129	3048	15.46	62.06	114.62	CH_{3ss} (99)
6	3005	-	3054	3004	30.90	57.33	705.93	CH_{3ops} (99)
7	1740	-	1763	1739	307.33	53.24	101.97	C=O (93)
8	1614	1621	1622	1616	90.49	40.90	406.35	CC (84), bCN (13)
9	1516	-	1590	1516	32.49	35.93	1190.56	CC (85), bCH (12)
10	-	1498	1496	1490	9.08	31.50	650.00	$CH3_{ipb}$ (89)
11	1490	-	1484	1495	9.88	13.73	177.75	bCH (65), Rtrigd (19)
12	-	1487	1477	1486	26.67	12.76	2942.31	$CH3_{sb}$ (96)
13	1460		1466	1460	3.91	10.80	166.37	$CH3_{opb}$ (96)
14	1352	1340	1431	1351	130.96	9.90	154.13	CN (79), bCC (19)
15	1306	-	1317	1306	355.54	9.67	322.80	bOH (80), bCO (17)
16	1277	1280	1289	1278	3.28	9.46	261.65	CC(81), Rasymd(15)
17	1248	-	1252	1248	56.12	7.37	172.05	CC(70), CO(17),CH(13)
18	-	1230	1214	1228	31.52	7.36	159.97	CH_{3ipr}(78)
19	1192	-	1170	1190	1.02	6.89	397.51	CH_{3opr}(77)
20	-	1178	1166	1176	115.83	6.50	98.06	CC(77), CC(21)
21	1144	-	1143	1143	25.09	4.70	488.46	CC(74), Rsymd(17)
22	-	1095	1080	1094	38.48	4.45	186.85	bC=O(73), bCC(13)
23	1066	-	1077	1068	42.77	3.71	62.52	CN(60),CC(25),Rtrigd(15)
24	1028	-	1002	1026	0.34	3.40	253.83	bCC(72), CO(13)
25	-	978	981	976	2.44	3.04	88.23	bCH(85), CC(12)
26	958	-	975	956	9.30	2.60	71.40	CO(82)
27	834	872	849	835	13.91	2.46	61.73	bC=O(73), bCC(13)
28	-	778	835	773	14.15	1.90	896.27	bCH(63), CC(23)
29	766	-	779	766	44.73	1.85	76.79	bCO(72), bCC(13)
30	743	755	757	742	26.37	1.66	26.39	bCH(65), Rtrigd(19)
31	-	740	737	741	2.51	1.65	103.72	bCC(63), bCO(17)
32	646	665	652	665	4.70	1.49	943.23	Rsymd(69), Rasymd(21)
33	534	-	547	547	3.25	1.41	134.59	bCC(65), Rtrigd(19)
34	-	492	494	492	1.43	1.33	720.16	bCC(55), wCC(23)
35		473	451	475	10.27	1.28	502.14	bCL(60), Rtrigd((19)
36	-	436	435	436	4.99	1.28	76.53	wCC(57),tRsym(25)
37	-	385	348	385	17.64	1.05	420.70	wCC(53), wCO(29)
38	-	324	322	320	1.48	0.85	130.08	wCC(55), tRasym(23)
39	-	270	281	270	2.26	0.68	47.53	tRtrig(53), wCl(27)
40	-	-	230	236	1.47	0.68	168.43	wCl(53), wCO(23)
41	-	176	166	172	3.94	0.65	120.05	wCO(51),wCC(23)
42	-	-	132	133	0.20	0.55	103.96	CH_3twist(61)
43	-	-	115	118	3.88	0.54	42.39	tRasym(60), wCO(21)
44	-	95	91	94	0.13	0.30	877.28	tRsym(51), tRasym(21)
45	-	41	31	40	3.12	0.20	7.99	wCO(52), tRing(19)

abbreviations

b-bending; g-out-of-plane bending; t-torsion; R-ring;; asym-assymetic; sym-symmetric; vs-very strong; s-strong; ms-medium strong; m-medium; w-weak; vw-very-weak.

The methyl 2-chloronicotinate consists of 17 atoms hence undergoes 45 fundamental modes of vibrations of each compound are distributed into the irreducible representations under C_1 symmetry as 31 in-plane vibrations of A′ species and 14 out of plane vibrations of A″ species.

$$\Gamma_{vib} = 31A' + 14A''$$

All vibrations are active in both IR and Raman. The title molecule contains fluorine atom and carbonyl group with benzene ring. The experimental FTIR and FT-Raman spectra of methyl 2-chloronicotinate are given in Figs. 2 and 3, respectively. Comparison of the vibrational modes calculated at B3LYP with experimental values (Table 2) reveals that over

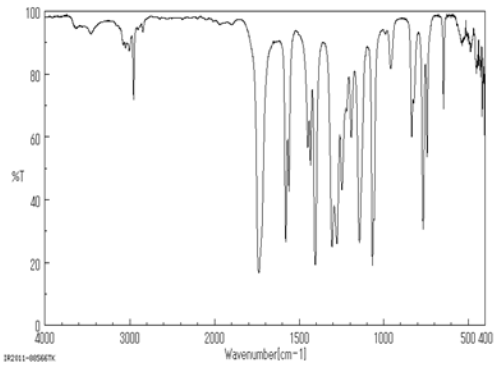

Fig. 2.FT-IR spectrum of methyl-2-chloronicotinate.

estimation of the calculated vibrational modes of anharmonicity in the real system. Inclusion of electron correlation in the 6-311G++(d,p) to a certain wavenumber data. The observed FT-IR and FT-Raman spectra of methyl 2-chloronicotinate are shown in Figs. 2 and 3, respectively. It is convenient to discuss the vibrational spectra of methyl 2-chloronicotinate in terms of characteristic spectral regions as described below.

CH3 group vibrations

The title compound possesses a single CH_3 group in fourth position of the ring. The CH methyl group stretching vibrations are generally observed in the range 3000–2800 cm^{-1} [41, 42]. For the assignments of CH_3 group frequencies one can expect nine fundamentals viz., namely the symmetrical stretching in CH_3 (CH_3 sym. stretch), asymmetrical stretching (CH_3 asym. stretch), symmetrical (CH_3 sym. deform) and asymmetrical (CH_3 asy. deform) deformation modes, in-plane rocking (CH_3 ipr), out-of-plane rocking (CH_3 opr), CH_3 wagging (CH_3 wag.) and twisting (CH_3) modes. Methyl groups are generally referred as an electron donating substitution in the aromatic ring system.

The recorded FT-IR and FT-Raman spectra of methyl 2-chloronicotinate have strong and very weak intensity bands at 3160 and 3102 $cm^{-1}$and they are assigned to CH_3 stretching vibrations of methyl 2-chloronicotinate. The CH_3 ss frequency is established at 3048 cm^{-1} in the FT-Raman spectrum of methyl 2-chloronicotinate. The methyl deformation modes mainly coupled with the in-plane bending vibrations and are also well established. The inplane methyl deformation mode of methyl 2-chloronicotinate is found at 1498 cm^{-1} in FT-IR spectrum. The band at 1460 cm^{-1} in FT-IR is attributed to CH_3 out-of-plane deformation mode of methyl 2-chloronicotinate. The bands obtained at 1230 and 1192 cm^{-1} in FT-IR and FT-Raman spectra are assigned to CH_3 in-plane and out-of-plane rocking modes, respectively. The contributions for all these modes are about 85%. In the present study, they show good agreement with the calculated values.

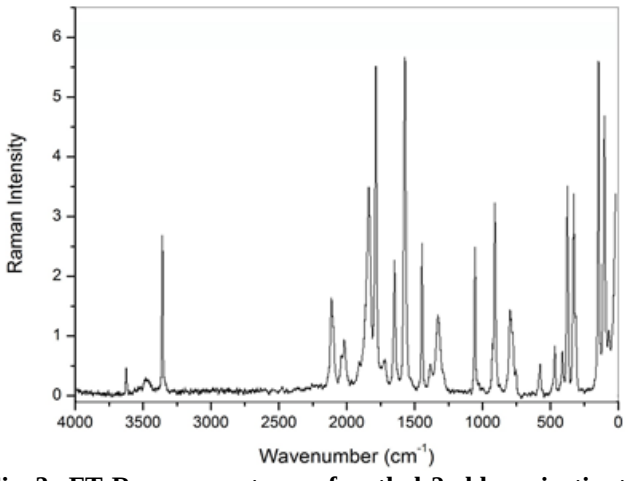

Fig. 3. FT-Raman spectrum of methyl-2-chloronicotinate.

C–N vibrations

The assignment of C–N stretching frequency is a rather difficult task since there are problems in identifying these frequencies from other vibrations. Silverstein et al. [42] assigned C–N stretching vibrations in the region 1382–1266 cm^{-1} for the aromatic amines. The bands obtained at 1352 and 1066 cm^{-1} in FT-Raman spectrum and 1340 cm^{-1} in FT-IR spectra have been assigned to C–N stretching vibrations. The PED contribution results at the last column of Table 2 show that, C–N stretching vibrations (79%) interacting considerably with C–C (19%) stretching mode. In the present work, the observed value at 1095 cm^{-1} in FT-IR spectra is assigned to C–N in-plane bending vibration. In the present study, the theoretically computed values belonging to C–N stretching vibrations are good agreement with spectral data.

C–O vibrations

Generally, the C–O vibrations occur in the region 1260–1000 cm^{-1} [43]. In the present study, the C–O stretching vibrations are assigned at 1248, 958 cm^{-1} in FT-Raman spectrum of methyl 2-chloronicotinate. According to the literature [44], the C–O vibration is pushed to the lower region by the influence of other vibrations, because of the proximity in methyl 2-chloronicotinate C–O in plane bending vibration is found at 958 cm^{-1} in FT-Raman spectrum.

Ring vibrations

In case of methyl 2-chloronicotinate, the carbon atoms coupled together in the hexagonal chain of ring possesses two C–C stretching vibrations at 958, 859 and 978, 872 cm^{-1} in FT-IR and FT-Raman. The in-plane and out-of-plane bending vibrations of the benzene ring are generally observed below 1002 cm^{-1} [45] and these modes are not pure but they contributes drastically from other vibrations and are substituent- sensitive. In the title molecule, the ring in-plane (*b* ring) and out-of plane (*c* ring) bending modes are affected to a great extent by the substituents and produce bands below 547 cm^{-1} . From PED results, the bands present at 270 and 176 cm^{-1} in FT-Raman are assigned to C ring. The scaled theoretical wavenumbers corresponding to all the ring vibrations are found to have a good correlation with their available experimental observations.

5. HOMO–LUMO analysis

In the first hyper polarizability value, there is an inverse relationship between first hyper polarizability and HOMO–LUMO gap, allowing the molecular orbitals to overlap to have a proper electronic communication conjugation, which is a marker of the intramolecular charge transfer from the electron donating group through the p-conjugation system to the electron accepting group [46,47]. Many organic molecules, containing conjugated p-electrons characterized by large values of molecular first hyper polarizabilities were analyzed by means of vibrational spectroscopy [48, 49].

In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. But the intramolecular charge transfer from the donor to acceptor group through a single–double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman intensity strong at the same time. The most important orbitals in a molecule are the frontier molecular orbitals, called HOMO and LUMO. These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [50]. The frontier molecular orbitals play an important role in the electric and optical properties [51]. The conjugated molecules are characterized by a small highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO–LUMO) separation, which is the result of a significant degree of intramolecular charge transfer from the end-capping electron-donor groups to the efficient electron-acceptor groups through p-conjugated path [52].

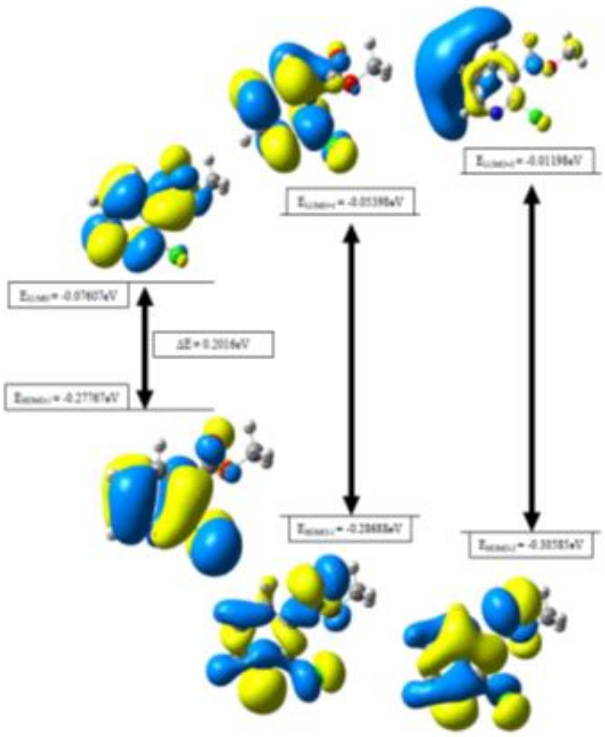

Fig. 4.The atomic orbital compositions of the Frontier Molecular Orbitals for methyl-2-chloronicotinate.

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-311G++(d,p) method is shown below. The energy gap between HOMO and LUMO is shown in Table 3 which shows that charge transfer may be taking place from methyl 2-chloronicotinate atom in Fig. 4. The energy difference between HOMO and LUMO orbital which is called as energy gap is a critical parameter in determining molecular electrical transport properties in DOS Spectrum analysis Fig. 5, because it is a measure electron conductivity calculated -7.5558eV and -2.0700eV for methyl 2-chloronicotinate, respectively.

Table 3. HOMO-LUMO energy and other related properties of methyl 2-chloronicotinate based on B3LYP/6-311++G(d,p) method.

Parameters	B3LYP/6-311++G(d,p)	
	A.U	eV
HOMO-3	-0.3148	-8.5651
HOMO-2	-0.3059	-8.3226
HOMO -1	-0.2869	-7.8064
HOMO	-0.2777	-7.5558
LUMO	-0.0761	-2.0700
LUMO+1	-0.0540	-1.4689
LUMO+2	-0.0120	-0.3260
LUMO+3	-0.0063	-0.1714
LUMO - HOMO (Energy gap)	0.3537	9.6258
Global Hardness (η)	-0.1008	-2.7429
Electronegativity (χ)	-0.1769	-4.8129
Global softness (s)	-9.9206	-269.9544
Chemical potential (μ)	0.1769	4.8129
Global Electrophilicity (ω)	-0.1552	-4.2225
Dipole moment (μ)	2.0696 Debye	
Mean polarizability(α)	-67.8094 x 10^{-30}esu	
Anisotropy of the polarizability (Δα)	598.9310 x 10^{-30}esu	
First hyperpolarizability(β)	1.214 x 10^{-30}esu	
Optimized global minimum Energy	-935.9125(Hartrees)	
RMS	0.00000628 (a.u.)	

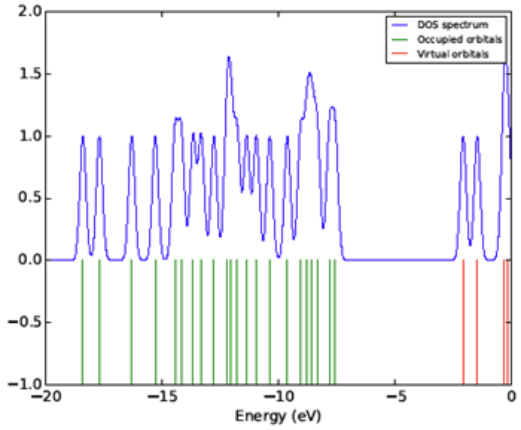

Fig. 5. Density of States (DOS) diagram for methyl-2-chloronicotinate.

Based on density functional descriptors global chemical reactivity descriptors of compounds such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined [53-57, 32]. Pauling introduced the concept of electronegativity as the power of an atom in a compound to attract electrons to it. Hardness (η), chemical potential (μ) and electronegativity (χ) and softness are defined follows.

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)}$$

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)}$$

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)}$$

Where, *E* and *v(r)* are electronic energy and external potential of an N-electron system respectively. Softness is a property of compound that measures the extent of chemical reactivity. It is the reciprocal of hardness.

$$S = \frac{1}{\eta}$$

Using Koop man's theorem for closed-shell compounds η, μ and χ can be defined as

$$\eta = \frac{(1-A)}{2}$$

$$\mu = \frac{-(1+A)}{2}$$

$$\chi = \frac{(1+A)}{2}$$

Where, A and I are the ionization potential and electron affinity of the compounds respectively. Electron affinity refers to the capability of a ligand to accept precisely one electron from a donor. However, in many kinds of bonding viz., covalent hydrogen bonding, and partial charge transfer takes place. Recently Parr et al. [53] have defined a new descriptor to quantify the global electrophilic power of the compound as electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a compound. Parr et al. [53] have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as follows

$$\omega = \frac{\mu^2}{2\eta}$$

The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [32,

58, 59]. The calculated value of electrophilicity index describes the biological activity of methyl 2-chloronicotinate. All the calculated values of hardness, potential, softness and electrophilicity index are shown in Table 3.

6. Natural bond orbital (NBO) analysis

The NBO calculations were performed using NBO 3.1 program as implemented in the Gaussian 09W package at the DFT/B3LYP level in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is the measure of the delocalization or hyper conjugation. By the use of the second-order bond–antibond (donor–acceptor) NBO energetic analysis, insight in the most important delocalization schemes was obtained. The change in electron density (ED) of (σ^*,π^*) antibonding orbitals and E(2) energies have been calculated by natural bond orbital (NBO) analysis [60] using DFT method to give clear evidence of stabilization originating from various molecular interactions. NBO analysis has been performed on methyl 2-chloronicotinate in order to elucidate intramolecular hydrogen bonding, intramolecular charge transfer (ICT) interactions and delocalization of p-electrons of the benzene ring. The hyperconjugative interaction energy was deduced from the second-order perturbation approach [61]. For each donor (i) and acceptor (j), the stabilization energy E2 associated with the delocalization i→j is estimated as

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

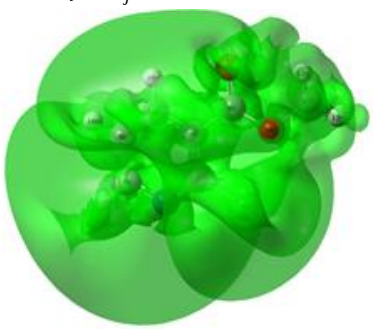

Fig. 6. Electron density spin magnitude density contours for methyl-2-chloronicotinate.

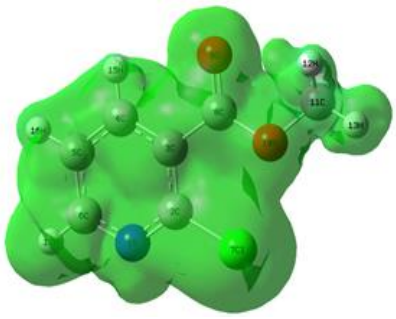

Fig. 7. Electron density form magnitude of magnetically induced current density for methyl-2-chloronicotinate.

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. The most important interactions between Lewis and non-Lewis orbitals with oxygen lone pairs are the second order perturbation energy values, E(2), corresponding to these interactions, and the overlap integral of each orbital pair. The second order perturbation theory analysis of Fock matrix in NBO basis of methyl 2-chloronicotinate (Table 4-5) also indicates intramolecular interactions due to the orbital overlap of **π** (C3 - C4) and **π*** (C2 - C3), resulting in high electron density (approx. 0.069e) of anti-bonding **π** orbitals

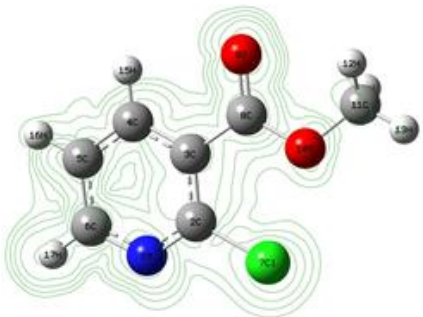

Fig. 8. Electron density form magnitude of magnetically induced current density contours for methyl-2-chloronicotinate.

The intra-molecular charge transfer from O atom of the CO-CH3 group to the C-C bond of benzene ring is also apparent from the MEP plot in Fig. [6,7,8]. The orbital overlap between **π**(C4- C5) and **π***(C3 - C8) results in intramolecular charge transfer causing stabilization of the system. The charge transfer from σ (C4 - C5) to σ *(N1 - C6) amounts to the stabilization of 28.89 kcal/mol. The magnitude of charge transfer from the lone pairs of O9 to antibonding σ (C2 - C3) and σ *(C4 - C5), σ orbitals amount to stabilization of 20.78 and 19.39 kcal/mol, respectively.

7. Molecular electrostatic potentials (MEP)

Molecular electrostatic potential used extensively for interpreting potentials have been and predicting the reactive behavior of a wide variety of chemical system in both electrophilic and nucleophilic reactions, the study of biological recognition processes and hydrogen bonding interactions [62]. V(r), at a given point r(x, y, z) in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and positive test charge (a proton) located at r. Unlike many of the other quantities used at present and earlier as indices of reactivity, V(r) is a real physical property that can be determined experimentally by diffraction or by computational methods. For the systems studied the MEP values were calculated as described previously, using the following equation [63]:

$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr'$$

Where, the summation runs over all the nuclei A in the molecule and polarization and reorganization effects are neglected. Z_A is the charge of the nucleus A, located at R_A and q(r0) is the electron density function of the molecule.

To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, the MEP at the B3LYP/6-311++G(d,p) optimized geometry was calculated. In the present study, the electrostatic potential (ESP), electron density (ED) and the molecular electrostatic potential (MEP)

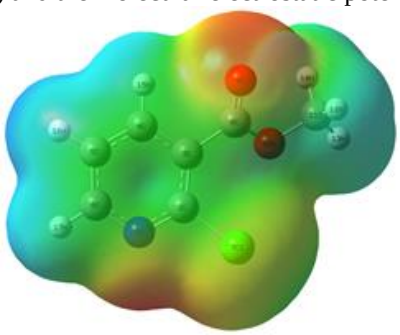

Fig. 9. Molecular electrostatic potential for methyl-2-chloronicotinate.

Table 4. Second order perturbation theory of fock matrix in NBO basis using B3LYP/6-311++G(d,p) basis set for 5-chloro-2-hydroxypyridine.

Donor NBO (i)	Acceptor NBO (j)	E(2) j K/mol	E(j) – E(i) a.u.	F(i, j) a.u.
π (N1 - C6)	π* (C2 -Cl7)	4.36	0.97	0.058
σ (N1 - C6)	σ * (C4 - C5)	12.31	0.32	0.056
σ (C2 - C3)	σ * (N1 - C6)	16.37	0.28	0.06
σ (C2 - C3)	σ * (C4 - C5)	20.78	0.3	0.072
σ (C2 - C3)	σ * (C8 - O9)	16.86	0.27	0.063
π (C3 - C4)	π* (C2 - C3)	4.77	1.26	0.069
π (C3 - C4)	π* (C2 -Cl7)	4.21	0.86	0.054
π (C3 - C8)	π* (N1 - C2)	3.02	1.16	0.053
π (C4 - C5)	π* (C3 - C8)	3.81	1.07	0.058
σ (C4 - C5)	σ * (N1 - C6)	28.89	0.26	0.077
σ (C4 - C5)	σ * (C2 - C3)	19.39	0.26	0.064
π (C4 - H15)	π* (C2 - C3)	4.08	1.07	0.059
π (C5 - H16)	π* (C3 - C4)	3.45	1.09	0.055
π (C6 - H17)	π* (N1 - C2)	4.49	1.05	0.062
π (C6 - H17)	π* (C4 - C5)	3.37	1.1	0.055
σ (C8 - O9)	σ * (C2 - C3)	4.17	0.37	0.039

Table 5. The angular properties of natural hybrid orbitals (NHO) of methyl 2-chloronicotinate using B3LYP at 6-311++G(d,p) basis set.

NBO	Line of Centers		Hybrid 1			Hybrid 2		
	Theta	Phi	Theta	Phi	Dev	Theta	Phi	Dev
σ(N1 - C6)	87.9	227.2	--	--	--	92.3	44.5	2.7
π(N1 - C6)	87.9	227.2	176.4	172.2	90.1	3.7	352.7	90
σ(C2 - C3)	91.7	289	91.8	291.7	2.7	88.4	107.7	1.4
π(C2 - C3)	91.7	289	3.9	352	89.9	4.2	352.5	90.2
σ(C2 -Cl7)	92.1	48.9	92	50.2	1.3	--	--	--
σ(C3 - C8)	93.7	348.8	94.1	349.9	1.2	87.3	166.8	2.2
π(C4 - C5)	86.3	167.3	176.2	172.2	89.9	176.3	172.6	89.9
σ(C5 - C6)	88.5	106.6	--	--	--	91.6	288.8	2.2
σ(C6 - H17)	86.3	166.9	86.3	165.4	1.5	--	--	--
σ(C8 - O9)	91.7	288.7	92.1	290.5	1.8	--	--	--
π(C8 - O9)	91.7	288.7	3.7	341.5	89.4	177.1	183.2	90.9
σ(C8 - O10)	92.1	48.8	90.9	45.2	3.8	87.4	227.6	1.4
σ(O10 - C11)	65.5	341.3	64.4	341.2	1.1	114.1	163.7	2.2
σ(C11 - H12)	120.2	294.8	121.6	293.8	1.7	--	--	--
σ(C11 - H13)	92.1	48.8	92.8	51	2.3	--	--	--
σ(C11 - H14)	17.7	238.5	18.5	231.1	2.5	--	--	--
π*(N1 - C6)	87.9	227.2	176.4	172.2	90.1	3.7	352.7	90
π*(C2 - C3)	91.7	289	3.9	352	89.9	4.2	352.5	90.2
π*(C4 - C5)	86.3	167.3	176.2	172.2	89.9	176.3	172.6	89.9
π*(C8 - O9)	91.7	288.7	3.7	341.5	89.4	177.1	183.2	90.9
σ*(C8 - O10)	92.1	48.8	90.9	45.2	3.8	87.4	227.6	1.4

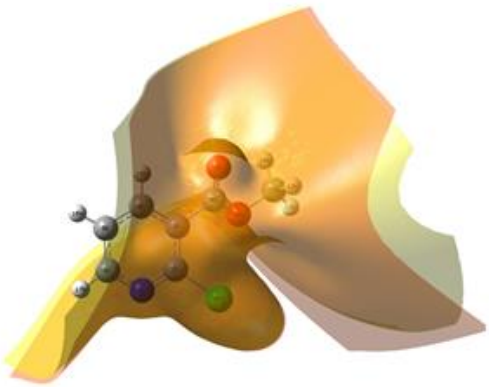

Fig. 10. Electrostatic potential surface for methyl-2-chloronicotinate.

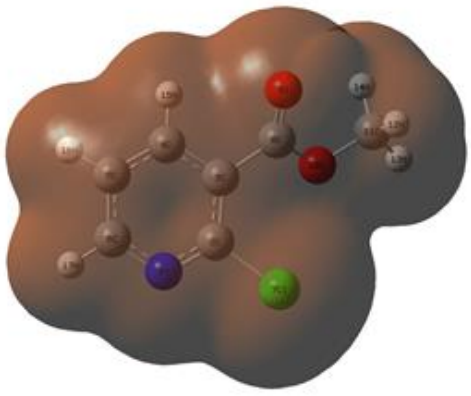

Fig. 11. The total alpha density surface for methyl-2-chloronicotinate.

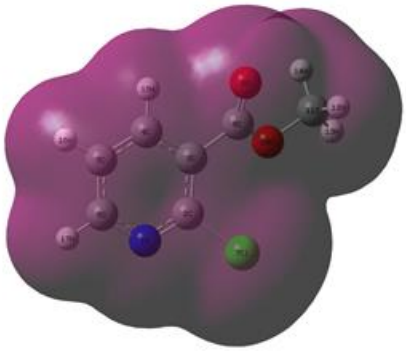

Fig. 12. The total electron density surface for methyl-2-chloronicotinate.

map figures for methyl 2-chloronicotinate are shown in Fig. [9-14]. The ED plots for title molecule show a uniform distribution. However, it can be seen from the ESP figures, that while the negative ESP is localized more over the oxygen atom and fluorine atoms and is reflected as a yellowish blob,

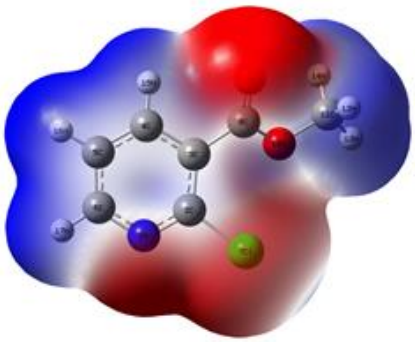

Fig. 13. The total alpha density surface for methyl-2-chloronicotinate.

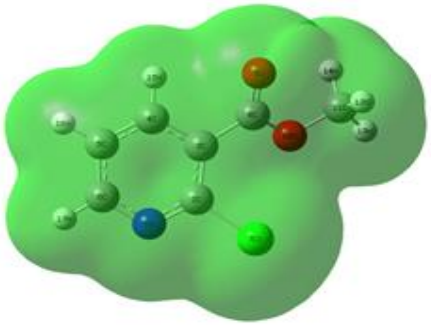

Fig. 14. Electrostatic potential isoval surface for methyl-2-chloronicotinate.

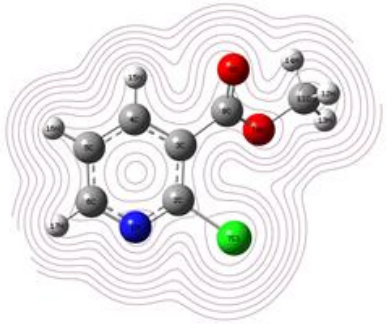

Fig. 15. Electron density contour surface for methyl-2-chloronicotinate.

the positive ESP is localized on the rest of the molecule. This result is expected, because ESP correlates with electro negativity and partial charges. In the majority of the MEPs, while the maximum negative region which preferred site for electrophilic attack indications as red color, the maximum positive region which preferred site for nucleophilic attack symptoms as blue color. The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading and is very useful in research of molecular structure with its physiochemical property relationship. The resulting surface simultaneously displays molecular size and shape and electrostatic potential value. In the present study, 3D plots of molecular electrostatic potential (MEP) of methyl 2-chloronicotinate has been draw in Fig. [15, 16]. The MEP is a plot of electrostatic potential mapped onto the constant electron density surface. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red <orange < yellow < green < blue. The negative (red1 and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity, as shown in Fig. 9.

8. Thermodynamic properties

On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity ($C^{o}_{p,m}$), enthalpy changes (ΔH^{o}_{m}) and entropy (S^{o}_{m}) for the title molecule were obtained from the theoretical harmonic frequencies and listed in Table 6. From Table 6, it can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increases with temperature expect Gibb's free energy. The correlation equations between heat capacity, entropy, enthalpy changes, Gibb's free energy and temperatures were fitted by quadratic formulas and the corresponding fitting factors (R2) for these thermodynamic properties are 0.996, 0.9997 and 0.9995, respectively. The corresponding fitting equations are as follows and the correlation graphics of those shown in Fig. 17.

Table 6. Temperature dependence of the thermodynamic properties of methyl 2-chloronicotinate determined by DFT/B3LYP 6-311++G(d, p) method

T(K)	methyl 2-chloronicotinate		
	S ($J.mol^{-1}.K^{-1}$)	Cp ($J.mol^{-1}.K^{-1}$)	$\Delta H_0 \rightarrow T$ ($kJ.mol^{-1}$)
100	72.04588906	18.61615678	1.3026
200	87.92065004	28.14053536	3.6472
298.15	100.8867112	37.45697895	6.8642
300	101.1185468	37.63145313	6.9336
400	113.2146271	46.73757167	11.1616
500	124.5124282	54.56261947	16.2380
600	135.045411	60.94168257	22.0244
700	144.8398661	66.09464623	28.3843
800	153.9483747	70.29397701	35.2127
900	162.4354684	73.75717013	42.4187
1000	170.3585085	76.64674948	49.9450

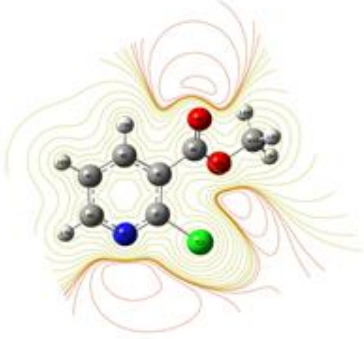

Fig. 16. Electrostatic Potential MEP for methyl-2-chloronicotinate.

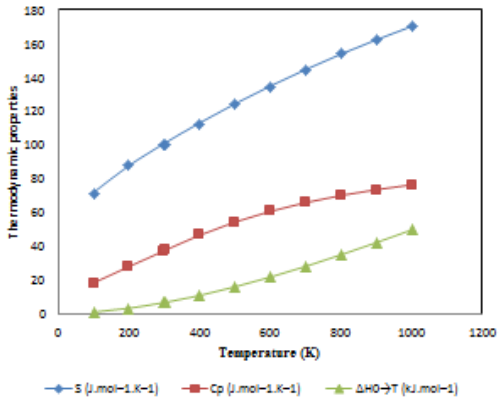

Fig. 17. Correlation graph of thermodynamic parameters for methyl-2-chloronicotinate.

$$C^{o}_{p,m} = -5.0244 + 0.12021 + 6.5247 \times 10^{-5} T^{2} (R^{2} = 0.9996)$$

$$S^{o}_{m} = -4.2741 + 0.1544\,T + 58.0862\ (R^{2} = 0.9997)$$

$$\Delta H^{o}_{m} = 3.2610 + 0.0192\,T - 1.4532\ (R^{2} = 0.9995)$$

All the thermodynamic data supply helpful information for the further study on the methyl 2-chloronicotinate. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamic theoretical harmonic frequencies and listed in Table 7.

Table 7. Theoretically computed zero point vibrational energy (kcal mol^{-1}), rotational constant (GHz), rotational temperature (kelvin), thermal energy (kcal mol^{-1}), molar capacity at constant volume (cal mol^{-1} kelvin^{-1}), entropy (cal mol^{-1} kelvin^{-1}), vibrational temperature (kelvin) of methyl 2-chloronicotinate by B3LYP/6-311++G(d,p) method.

Parameter	B3LYP/6-311++G(d,p)
Zero point vibrational energy	75.99076
Rotational constant	1.46582 0.81413 0.54415
Rotational temperatures	0.07035 0.03907 0.02612
Energy	
Total	82.263
Translation	0.889
Rotational	0.889
Vibrational	80.485
Molar capacity at constant volume	
Total	35.469
Translational	2.981
Rotational	2.981
Vibrational	29.508
Entropy	
Total	100.860
Translational	41.317
Rotational	30.583
Vibrational	28.960

9. Chemical shielding anisotropy (CSA) parameters

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the structure determination of large molecules. The NMR technique is based on the sensitively of magnetic properties, typically isotropic chemical shielding (ICS), to the chemical environment of the nuclei. The full NMR shielding tensor in Fig. 18 (a) is nonsymmetrical and of rank 2, containing nine independent quantities are used to predict the CSA parameters defined by Czinki et al. [64] as follows. The isotropic chemical shielding, α_{iso} one of the scalar invariants of the tensor, is given by 1/3 of the trace of (α).

$$\alpha_{iso} = (1/3) Tr\sigma = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3 = (\sigma_1 + \sigma_2 + \sigma_3)/3$$

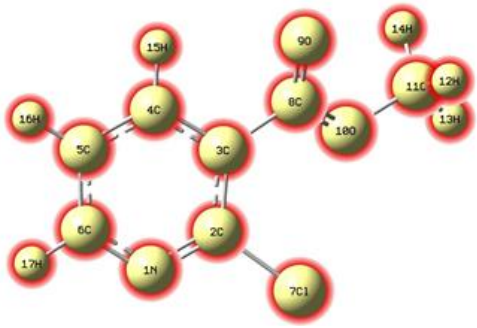

Fig. 18. The NMR Spin-Spin shielding surfaces for methyl-2-chloronicotinate.

In NMR spectroscopy the concept of anisotropy was advanced from the theory of axially symmetric tensors, where two principal components have the same value. The anisotropy (Δ) is the difference of the two distinct components in this generalization,

$$\Delta = \sigma_3 - (\sigma_1 + \sigma_2)/2 = 3(\sigma_3 - \sigma_{iso})/2$$

The asymmetry (η) was intended to show the deviation from the axially symmetric tensor,

$$\eta = (\sigma_2 - \sigma_1)/(\sigma_3 - \sigma_{iso})$$

In the case of an axially symmetric tensor, η = 0 The CSA parameters, span (Ω) and skew (k) of the shielding tensor are in Fig. 19,

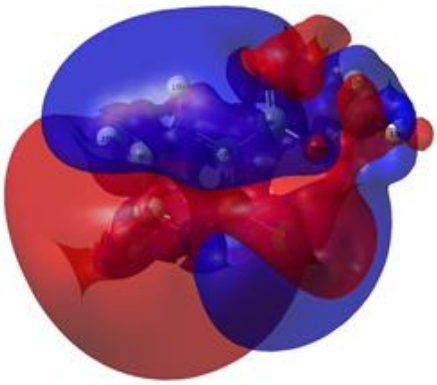

Fig. 19. The NMR shielding surfaces for methyl-2-chloronicotinate.

$$\Omega = \sigma_3 - \sigma_1 (\Omega \geq 0)$$

and

$$k = 3(\sigma_2 - \sigma_{iso})/\Omega = (2\sigma_2 - \sigma_1 - \sigma_3)/\Omega (-1 \leq k \leq +1)$$

where the principal components (Eigen values of σ^{s}) are labeled according to $(-1 \leq k \leq +1)$

The symmetric Eigen values are obtained from the following relations,

$$\sigma_1 = \sigma_{iso} - \Omega(k+3)/6$$

$$\sigma_2 = \sigma_{iso} + \Omega k/3$$

$$\sigma_3 = \sigma_{iso} - \Omega(k-3)/6$$

The CSA parameters (ρ) and (τ) describe the magnitude and orientation of the anisotropy, respectively

$$(\rho) = sqrt([(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2]/2)$$

and

$$(3\tau) = k\pi + (-1)^{(k+1)} \arcsin (\text{mod e}(\sigma))$$

Table 8. NMR −Chemical Shielding Anisotropy parameters of methyl 2-chloronicotinatebased on B3LYP/6-311++G(d,p) method.

Atom	σ 1(ppm)	σ 2(ppm)	σ 3(ppm)	σ_{iso} (ppm)	σ_{aniso} (ppm)	η	Ω(ppm)	k	ρ(ppm)	mode(σ)	τ(rad)
C^{13}											
C2	-74.2355	21.2688	83.3609	10.1314	109.8443	1.3042	157.5964	0.2120	137.5011	-0.3573	-0.1218
C3	-34.3375	42.8281	140.5838	49.6915	136.3385	0.8490	174.9213	-0.1177	151.8357	0.2022	0.0679
C4	-68.6534	12.6634	175.7384	39.9161	203.7334	0.5987	244.3918	-0.3345	215.5612	0.5416	0.1908
C5	-58.9559	47.7238	172.2178	53.6619	177.8339	0.8998	231.1737	-0.0771	200.4003	0.1330	0.0445
C6	-92.0904	24.0265	137.2428	23.0596	171.2748	1.0169	229.3332	0.0126	198.6137	-0.0219	-0.0073
C8	-122.2801	29.7131	46.7513	-15.2719	93.0348	2.4506	169.0314	0.7984	161.1891	-0.9624	-0.4319
C11	102.5479	111.6423	182.0077	132.0660	74.9126	0.1821	79.4598	-0.7711	75.3255	0.9510	0.4188
H^{1}											
H12	23.5114	26.5953	32.6199	27.5755	7.5666	0.6114	9.1085	-0.3229	8.0241	0.5251	0.1843
H13	25.35	27.2687	33.5624	28.7270	7.2530	0.3968	8.2124	-0.5327	7.4410	0.7803	0.2984
H14	25.3303	27.0956	35.4488	29.2916	9.2359	0.2867	10.1185	-0.6511	9.3615	0.8813	0.3596
H15	19.8949	22.2636	28.3657	23.5081	7.2865	0.4876	8.4708	-0.4407	7.5697	0.6798	0.2492
H16	22.4316	23.5586	28.4813	24.8238	5.4862	0.3081	6.0497	-0.6274	5.5723	0.8637	0.3475
H17	19.9554	21.8196	27.3769	23.0506	6.4894	0.4309	7.4215	-0.4976	6.6872	0.7442	0.2798

σ 1, σ 2, σ 3 - Eigen values of the symmetrized shielding tensor η- asymmetry Ω-span k- skew

σ_{iso} - isotropic shielding tensor σaniso - Shielding Anisotropy ρ- magnitude of anisotropy τ- orientation if anisotropy

Table 9. Magnetic susceptibility of methyl 2-chloronicotinate by B3LYP/6-311++G (d, p).

Temperature	Magnetic susceptibility	1/Susceptibility	1/Temperature
50	1.01752E-06	982779.7335	0.02
100	5.08761E-07	1965559.467	0.01
150	3.39174E-07	2948339.201	0.006667
200	2.54381E-07	3931118.934	0.005
250	2.03504E-07	4913898.668	0.004
273	1.86359E-07	5365977.345	0.003663
298.15	1.70639E-07	5860315.551	0.003354
300	1.69587E-07	5896678.401	0.003333
350	1.4536E-07	6879458.135	0.002857
400	1.2719E-07	7862237.868	0.0025
450	1.13058E-07	8845017.602	0.002222
500	1.01752E-07	9827797.335	0.002

Table 10. Natural atomic charge distribution of methyl 2-chloronicotinate based on B3LYP/6-311++G(d,p) methods.

Atoms	Atomic Charges	
	Mulliken	NPA
N1	0.14475	-0.46282
C2	-1.353087	0.22305
C3	1.458359	-0.20511
C4	-0.16791	-0.1159
C5	-0.105227	-0.23396
C6	-0.180639	0.08875
Cl7	0.464069	0.06527
C8	-0.854993	0.80572
O9	-0.236987	-0.59637
O10	-0.046049	-0.55945
C11	-0.267399	-0.20508
H12	0.190207	0.19064
H13	0.158669	0.18452
H14	0.178544	0.17186
H15	0.211491	0.23849
H16	0.195114	0.21458
H17	0.211087	0.19581

$(k = 0, \pm 1, \pm 2, \pm 3)$

The CSA parameters (ρ) and (τ) are also expressed in terms of span (Ω) and skew (k) are as follows

$$(\rho, \tau) = \left(\left(\frac{\Omega}{2} \sqrt{3 + k^2} \right), \arcsin \left[\frac{k(9 - k^2)}{(3 + k^2)^{\frac{3}{2}}} \right] \right)$$

Using the above said relations the complete nuclear magnetic resonance (NMR) chemical-shielding tensors, r, have been computed at density functional theory (DFT) and chloronicotinate. The CSA parameters of the carbon nitrogen and hydrogen atoms of the molecule both in monomer and dimer are calculated in DFT method with the level of B3LYP/6-311++G (d, p) and presented in Table 8.

10. Magnetic susceptibility

Atoms, molecules, free radicals or ions which contain one or more unpaired electron will possess permanent magnetic dipole moment, that arises from the residual spin and angular momentum of the unpaired electrons. All substances having permanent magnetic moment display paramagnetic behavior in nature. When a paramagnetic substance is placed in a magnetic field, they will align themselves in the direction of

the field and thus produces positive magnetic susceptibility, which depends on the temperature; since thermal agitation will oppose the alignment of the magnetic dipoles. The effectiveness of the field diminishes with increase in temperature. The magnetic susceptibility (χ_m) of the molecules for various temperatures are predicted with knowledge of unpaired electron [65] and presented in Table 9. The graphical representation of (χ_m) with 1/T (temperature^{-1}) is shown in Fig. [20-22]. The effective magnetic moment is found to be a constant, which is 1.7063 x10^{-5} (BM) and the Curie constant is obtained from the magnetic moment (μ_m) and is found to be 3.39174x10^{-5}.

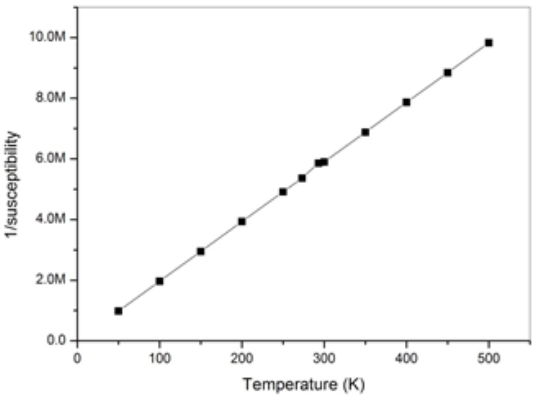

Fig 20. The magnetic 1/susceptibility for methyl-2-chloronicotinate.

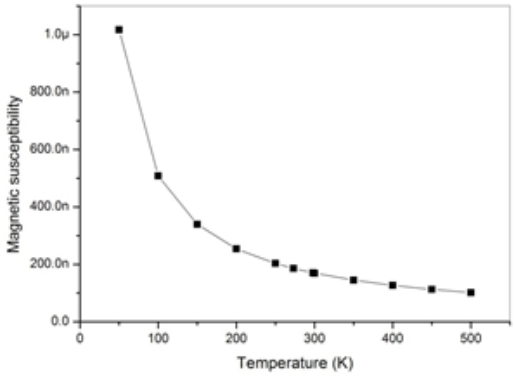

Fig 21. The magnetic susceptibility for methyl-2-chloronicotinate.

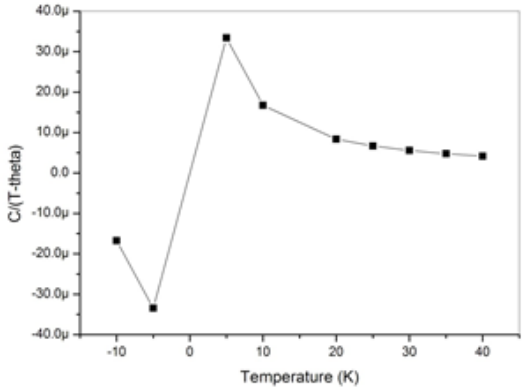

Fig 22. The magnetic C / (T-theta) for methyl-2-chloronicotinate.

11. Natural Charges

The total atomic charges of methyl 2-chloronicotinate molecule are obtained by Mulliken population analysis with B3LYP/6−311++G (d, p) basis set are listed in Table 10. From the results, it is clear that the substitution in methyl 2-chloronicotinate leads to the redistribution of electron density. The σ electron with drawing character of the Cl7 atom in methyl 2-chloronicotinate is demonstrated by the decrease in electron density on C3 atom. In methyl 2-chloronicotinate the C8 atom is more acidic due to more positive charge. The Mulliken atomic charges of the methyl group hydrogen atoms are lesser than hydrogen atom. The graphical representation of atomic charges of the atoms obtained by B3LYP for methyl 2-chloronicotinate is shown in Fig. [23, 24].

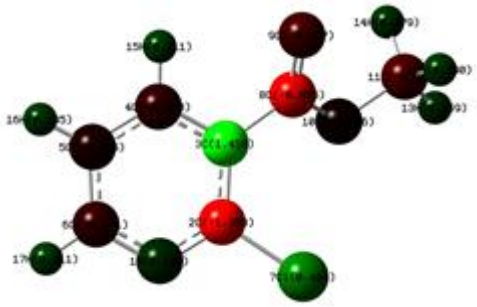

Fig 23. The Mulliken charges distribution for methyl-2-chloronicotinate.

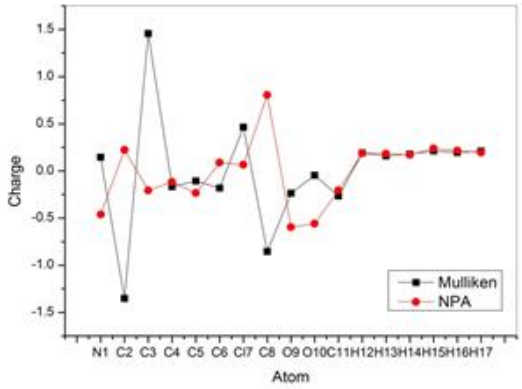

Fig 24. Mulliken atomic charge and Natural Population Analysis Plot for methyl-2-chloronicotinate.

Since the charge distribution on the molecule has an important influence on the vibrational spectra, the net charge distribution of methyl 2-chloronicotinate was calculated by the natural population analysis (NPA) method with B3LYP/6-311G++(d,p) basis sets and the charges are listed in Table 10. The corresponding NPA plot is shown in Fig. 24. The atomic charges of methyl 2-chloronicotinate calculated by NPA analysis using B3LYP methods with 6-311++G(d,p) basis sets are presented in Table 10. Among the carbon atoms C3 and C5 have positive charge while C8 have negative charge.

12. Conclusion

FT-IR and FT-Raman spectroscopies and were performed on methyl 2-chloronicotinate in order to identify its structural and spectroscopic properties. A complete vibrational analysis of methyl 2-chloronicotinate was performed using the basis of *ab initio* DFT calculation based on B3LYP level with the standard basis sets 6- 311++G (d, p). Comparison between the calculated and experimental structural parameters indicated that B3LYP was in good agreement with experimental observations. Complete vibrational analysis of methyl 2-chloronicotinate has been investigated by FT-IR and FT-Raman spectroscopy. The intermolecular hydrogen bond in dimer structure was also analyzed. The effects of hydrogen bond due to dimerization were discussed with the natural atomic hybridization. The role of nitro and carboxylic group in the vibrational frequencies of the title compound has been studied. NBO analysis has also been performed on methyl 2-chloronicotinate molecule, in order to elucidate intermolecular hydrogen bonding, intermolecular charge transfer, rehybridization and delocalization of electron density. Thermodynamic parameters were calculated theoretically for the range 100–1000 K. The electric dipole moments and the

first order hyperpolarizability of the compound have been calculated by DFT method. Quantum chemical parameters such as HOMO, LUMO, energy gap, hardness (η), softness (S), electron affinity (A), ionization potential (I), absolute electronegativity (χ) and electrophilicity (ω) were calculated. The NMR-chemical shielding anisotropy (CSA) parameters of methyl 2-chloronicotinate have been computed.

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