Experimental (FT-IR, FT-Raman, NMR) and computational (NLO, FMO, MEPS) investigation of methyl 2, 4-dihydroxy-6-methyl benzoate

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ABSTRACT

Extensive quantum chemical calculations of energy, geometrical structure, harmonic vibrational frequencies and the construction of theoretical spectrograms of IR and Raman spectra of the molecule, methyl 2,4-dihydroxy-6-methyl benzoate(methyl orsellinate) have been carried out by Hartree-Fock (HF) and Density Functional Theory (DFT/B3LYP) method with 6311++G(d, p) basis set. The assignments of normal modes of the vibration of the title molecule along with the observed frequencies (FT-IR and FT-R) and scaled frequencies have been obtained by HF/DFT computation. The simulated NMR spectra are obtained by (GIAO) gauge independent atomic orbital method and their chemical shifts are compared with the experimental ^{13}C NMR and ^{1}H NMR spectra. Molecular geometric parameters, dipole moment, mullikan charge, thermodynamic properties, FMO analysis and NLO properties have also been computed and discussed in a detailed manner.The electrostatic potential surface and the mullikan charge analysis indicates that the oxygen atoms of the molecule act as reactive centers for nucleophilic attack .The temperature dependence of the thermodynamic properties such as entropy (S), enthalpy (H) and heat capacity (Cp) from 50K to 700K were also determined.

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Introduction

The compound chosen for the present work of quantum chemical studies is methyl 2,4-dihydroxy-6-methyl benzoate which is also called as methyl orsellinate (MO) has anti-fungal activity as reported by Xiao-ning et al [1] , antioxidant potential and histamine liberation inhibition as shown by Shuhsien Wu et al [2]. The anti-bacterial activity of the compound was also reported by Alcir Teixeira et al [3]. Because of the wide applications of methyl orsellinate kindled the attention to take over a complete study of the compound. Neither quantum chemical calculations nor the vibrational spectral analysis have been reported in the literature for the molecule, methyl orsellinate and the present study is carried out for the first time.

Experimental Details

The title compound, methyl 2,4-dihydroxy-6-methyl benzoate (methyl orsellinate) was prepared from lecanoric acid by the methanolysis process for the experimental investigations. The room temperature Fourier transform IR spectrum of the chosen compound (solid phase) was measured in 4000-450 cm^{-1} region at a resolution of $\pm$ 2 cm^{-1} using Bruker IFS-66v Fourier transform spectrometer with the KBr pellet technique. The FT-Raman spectrum of MO was recorded on the same instrument equipped with FRA 106 FT–Raman accessories in the region of 4000-50 cm^{-1} with Nd: YAG laser operating at 100 mW (srl=100). ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100MHz) spectra of methyl orsellinate

were recorded in DMSO solution on a Bruker HC400 FT-NMR spectrometer.

Computational details

The optimized geometry of the methyl orsellinate was carried out by 6-311++G(d, p) basis set including polarized and diffused functions at the framework of Hartree-Fock (HF) and Density Functional Theory (DFT) methods on Intel (R) Core (TM) i5-3210M/2.50 GHz processor. For quantum chemical computation, the HF method and the DFT method along with Becke-3-Lee-Yang-Parr (B3LYP) functional [4, 5] were employed with the version 8 of Gaussian 09W (revision B.01) program package [6]. For the construction of simulated IR and Raman spectra, pure Lorentzian band shapes with the band width of 10 cm^{-1} was employed using the Gabedit Version 2.4.5.

Simulated ^{1}H-NMR and ^{13}C-NMR isotropic magnetic shielding of methyl orsellinate were calculated with the gauge independent atomic orbital DFT/GIAO method for the optimized structure of B3LYP/6-311++G (d, p) basis set. The isotropic chemical shifts in DMSO solvent with respect to TMS were calculated (δ_{cal}) by the equation $\delta_{cal}(X)= \sigma_{cal}(X)_{TMS}- \sigma_{cal}(X)$, where δ_{cal} is isotropic chemical shift and σ_{cal} is isotropic shielding constant [7].

Bond parameters such as bond length and bond angles, calculation of IR and Raman frequencies, the correlation between experimental and theoretical IR frequencies, thermodynamic properties, atomic charges, self-consistent

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energy (SCF), energy gap in frontier molecular orbitals, total dipole moment(μ^0), polarizability(σ) and hyperpolarisibility(β) were determined by HF and DFT/B3LYP methods with 6-311++G(d, p)basis set. IR modes of vibration, molecular electro static potential surface mapping (MEPS), contour mapping and HOMO-LUMO orbital energies [8] at DFT/ B3LYP/6-311++G (d, p) level were studied through animation options of Gauss View 5.0.8 visualization program [9].

Results and Discussion

Analysis of geometric parameters

Most stable optimized molecular structure of methyl orsellinate was obtained by B3LYP/6-311++G (d, p) level with C_1 point group symmetry and is shown in Fig 1. The computed bond parameters of methyl orsellinate at HF and DFT levels with 6-311+ +G (d, p) basis set are summarized in the Table 1 along with the experimental parameters [10] for comparative purpose.

Fig 1. Optimized structure of Methyl orsellinate.
The self-consistent field (SCF) energy determined at

B3LYP/ 6-311+ +G (d, p) is found to be relatively low (-650.0884 a.u) when compared to SCF energy calculated at HF method (-646.2829 a.u). Hence optimized geometry derived by B3LYP/6-311++G (d, p) is concluded as the most stable form and the optimized structure of methyl orsellinate reveals the planar structure of benzene ring.

In the theoretical calculation of bond parameters at HF and DFT with 6-311++G (d, p) framework , the bond length of O13-H16 is shown as 1.741Å and 1.652Å respectively and it clearly proves that the presence of intramolecular hydrogen bonding (O-H16---O13) between the hydrogen atom of phenolic group (OH16) and oxygen atom of the carbonyl group (C=O13)in the chosen molecule. Hydrogen bond is a weak type of force that forms a special type of dipole-dipole interaction which occurs when a hydrogen atom bonded to a strongly electronegative atom which exists in the vicinity of another electronegative atom with a lone pair of electrons. The electrostatic dipole-dipole interaction occurs in the range of 1.5 to 2.5 Å [11] and the hydrogen bond length measured by quantum chemical calculations at both HF and DFT levels in the chosen molecule also found to be in the same range.

At DFT method, the calculated bond angles (exo-angles) of C3-C4-C9 and C5- C4- C9 are measured as 116.5° and 125. 2° respectively although both the angles experience the similar situation in the title molecule. The variation in these exo angles is due to the formation of intramolecular hydrogen bonding because of which the lone pair of electrons on O13 is pulled towards electropositive H16 atom and hence the bond angle of C3-C4-C9 is relatively reduced by 8.5 ° which is also supported by the experimental values.

Table 1. Geometric parameters of methyl orsellinate calculated at HF and DFT method with 6-311++G(d, p) level.

Bond length (Å)	HF	DFT	Experimental[a]	Bond angle (°)	HF	DFT	Experimental[a]
C1-C2	1.372	1.384	1.137	C2-C1-C6	120.8	120.7	120.7
C1-C6	1.396	1.400	1.407	C2-C1-O7	122.3	122.5	123.8
C1-O7	1.339	1.361	1.364	C6-C1-O7	116.9	116.8	115.5
C2-C3	1.392	1.397	1.377	C1-C2-C3	119.4	119.5	120.0
C2-H11	1.075	1.084	0.930	C1-C2-H11	122.2	122.2	120.0
C3-C4	1.411	1.428	1.404	C3-C2-H11	118.4	118.4	120.0
C3-O8	1.324	1.341	1.351	C2-C3-C4	121.2	120.9	120.2
C4-C5	1.424	1.429	1.395	C2-C3-O8	115.0	116.0	117.4
C4-C9	1.475	1.468	1.448	C4-C3-O8	123.8	123.0	122.4
C5-C6	1.374	1.386	1.373	C3-C4-C5	118.1	118.3	119.3
C5-C10	1.514	1.512	-	C3-C4-C9	117.1	116.5	119.2
C6-H12	1.073	1.083	0.930	C5-C4-C9	124.8	125.2	121.6
O7-H15	0.942	0.964	0.820	C4-C5-C6	119.6	119.3	120.6
O8-H16	0.952	0.988	0.820	C4-C5-C10	124.1	123.9	-
C9-O13	1.203	1.233	1.231	C6-C5-C10	116.3	116.7	-
C9-O14	1.314	1.343	1.331	C1-C6-C5	120.9	121.2	119.3
C10-H17	1.082	1.091	-	C1-C6-H12	118.2	118.3	120.0
C10-H18	1.082	1.091	-	C5-C6-H12	120.9	120.5	120.0
C10-H19	1.082	1.091	-	C1-O7-H15	111.2	109.9	109.0
O13-H16	1.741	1.651	H-bonding	C3-O8-H16	110.1	107.4	109.0
O14-C20	1.419	1.441	1.451	C4-C9-O13	123.6	123.9	124.5
C20-H21	1.081	1.090	0.960	C4-C9-O14	115.8	116.0	114.9
C20-H22	1.081	1.090	0.960	O13-C9-O14	120.6	120.1	120.7
C20-H23	1.080	1.088	0.960	C5-C10-H17	111.5	112.0	-
				C5-C10-H18	111.5	111.7	-
				C5-C10-H19	109.2	109.6	-
				H17-C10-H18	107.4	106.6	-
				H17-C10-H19	108.6	108.5	-
				H18-C10-H19	108.6	108.5	-
				C9-O14-C20	117.7	116.3	117.5
				O14-C20-H21	110.5	110.5	110.0
				O14-C20-H22	110.5	110.5	110.0
				O14-C20-H23	105.5	105.1	110.0
				H21-C20-H22	109.4	109.2	109
				H21-C20-H23	110.4	110.7	109
				H22-C20-H23	110.4	110.7	109

[a] Values taken from Ref.[10]

Table 2. The experimental FTIR , FT-Raman and calculated scaled frequencies using HF/DFT methods with 6-311++G(d, p) level along with their intensities and probable vibrational assignments of methyl orsellinate.

S. No.	Experimental [a] Frequency (cm-1)				Calculated frequency (cm-1)						Vibrational Assignment [b]
	FT-IR		FTR		HF/6-311++G(d, p)			DFT/B3LYP/6-311++G(d, p)			
					unscaled	scaled	IR-Int	unscaled	scaled	IR-Int	
1	3368	vs			4176	3424	128.81	3827	3731	88.29	ν O-H
2	3312	vs	3311	vw	3929	3222	374.03	3339	3305	419.13	ν O-H
3			3213	vw	3352	3319	4.63	3196	3196	3.47	ν C-H of ring
4	3109	w			3341	3107	4.99	3178	3098	4.15	ν C-H of ring
5			3082	vw	3306	3074	21.30	3157	3078	13.23	ν asy C-H of CH3
6			3054	vw	3291	3061	24.87	3129	3051	16.16	ν asy C-H of CH3
7	3038	m			3266	3037	15.86	3117	3039	19.17	ν asy C-H of CH3
8			3036	vw	3266	3037	25.33	3105	3028	10.17	ν asy C-H of CH3
9	2978	m	2987	vw	3210	2986	48.67	3054	2978	39.23	ν sy C-H of CH3
10	2958	m	2960	vw	3198	2974	26.33	3047	2971	19.73	ν sy C-H of CH3
	2773		2946								Overtone+combination
	2663		2850								Overtone+combination
	2160		2738								Overtone+combination
	1891										Overtone+combination
11	1639	vs			1870	1655	605.37	1683	1641	480.41	ν C=O + ν C-C
12			1636	w	1791	1639	470.27	1655	1639	276.13	ν C=C + R.asy.def
13	1615	vs			1759	1609	197.96	1621	1605	138.62	ν C=C
14	1582	vs	1584	vw	1647	1531	53.47	1570	1570	88.42	ν C=C
15			1507	vw	1623	1510	17.81	1501	1501	13.86	β C-H of CH3
16	1502	s			1618	1505	27.70	1497	1497	5.94	β C-H of CH3
17			1469	vw	1611	1474	5.00	1484	1469	4.64	δ C-H of CH3
18	1446	vs			1608	1423	9.73	1482	1445	12.83	ν C-C +δ C-H of CH3
19			1444	vw	1606	1422	77.01	1474	1459	101.23	ν C-C-C +γC-H of CH3
20	1391	m	1391	vw	1597	1413	75.95	1472	1376	53.73	ν O-H def.
21	1379	s	1379	vw	1546	1369	3.92	1422	1387	64.86	ν C-C+ δ C-H of CH3
22	1325	vs			1528	1352	104.82	1421	1328	8.65	ν C-C+ β C-CH3
23			1318	s	1455	1331	334.94	1353	1319	42.53	ν C-C-C+ R. asy. def
24	1313	vs			1428	1328	554.80	1341	1308	235.17	β O-H + ν C -O
25	1267	vs	1277	vw	1361	1266	90.06	1287	1274	396.84	β C-H + R.tri.def
26	1243	vs	1253	vw	1341	1248	157.04	1249	1237	107.28	γ C-H of CH3
27	1216	s			1332	1219	82.87	1212	1200	124.33	ν C-O -C+ ν C-C
28	1200	vs	1197	vw	1301	1210	180.80	1197	1185	319.09	β C-H of ring
29	1169	vs			1285	1195	3.10	1191	1162	56.44	γ C-H of CH3
30	1160	vs	1164	vw	1252	1164	195.49	1169	1157	0.89	ν C-C + ν C-O -C
31	1112	s	1123	vw	1231	1126	5.32	1127	1116	79.81	β C-H of CH3
32	1061	m	1060	vw	1158	1060	24.44	1084	1057	7.06	β C-H of CH3
33	1033	w			1157	1058	2.41	1058	1032	2.52	ρ C-H of CH3
34	1000	w	1001	vw	1095	1002	10.01	1014	1004	19.74	ρ C-CH3+ Ring breathing
35	994	w			1087	995	24.74	1010	1000	11.90	β O-C + ν C -C
36	952	m	948	vw	1057	968	10.51	971	946	18.93	ρ C-H of CH3
37	853	m			930	851	14.99	847	847	13.28	ν C-C + ν C-CH3
38	837	m			913	835	3.06	833	824	1.06	γ C-H of ring
39			830	m	909	832	71.84	827	819	1.83	γ O-H
40	800	m			882	807	36.95	812	804	128.02	ρ C-H of CH3
41	753	m			751	743	45.95	778	759	7.47	ρ C-H of CH3
42	702	s	707	vw	752	688	66.63	689	689	12.84	γ C-H of CH3
43	642	vw	651	vw	722	661	2.18	643	636	0.24	β C-C + δ C-O
44	623	w			674	617	32.79	631	624	22.41	β C-C-C + ω C-H
45			619	vw	668	611	4.33	622	619	6.41	β C-C-C + ω C-O
46			578	w	618	566	8.11	581	575	5.57	β C-CH3 + δ C-H
47	576	vw			611	568	1.25	570	570	0.93	β C-C + β C-O
48	542	vw	536	w	568	528	10.31	532	532	10.74	ω C-H + β C-C-O
49			456	vw	468	463	4.87	442	442	2.52	β C-C-O def.
50	434	vw			425	420	8.74	439	435	13.18	ν C-CH3+γ C-C-C
51			380	vw	386	382	108.22	365	365	96.65	β C-CH3 +γ O-H
52			362	vw	372	346	7.01	348	348	5.52	β O-H
53			345	vw	355	330	16.68	330	330	11.33	β O-H+ β C-CH3
54			326	vw	338	314	5.86	319	316	7.36	ν C-OCH3
55			312	w	327	304	10.64	305	305	7.49	β C-OCH3
56			247	vw	279	259	0.52	244	242	0.32	γ C-CH3
57			215	vw	242	225	0.98	220	215	0.69	t C- CH3
58			189	vw	208	194	2.89	191	189	2.91	ω O-H + β C-C
59			176	vw	187	174	1.56	175	176	1.79	ω C-C + t O-H
60			162	vw	184	171	1.83	154	154	2.54	t C- OCH3
61			123	vw	144	134	4.68	132	128	2.65	τ CH3
62			83	w	88	82	0.10	89	83	0.09	τ CH3 + t C-O
63			69	vs	35	33	0.90	49	49	1	τ CH3

[a] **vs** – very strong; **s**-strong; **m**-medium; **w**-weak;

[b] $ν_{asy}$-asymmetric stretching; $ν_{sy}$-symmetric stretching; δ-scissoring; ρ-rocking; τ-torsion; t- twisting; ω-wagging; β-in-plane bending; γ-out-of-plane bending.

Similar line of thought is applicable in the case of bond angles calculated at B3LYP level for C2-C3-O8 (116°) and C4-C3-O8 (123°). All these bond parameters have good compliance with the experimental values and the presence of hydrogen bond within the molecule between O13 and H16 is also supported by IR and NMR spectral studies.

The two phenolic groups of the chosen molecule show variation in their bond length of O-H which are measured as 0.964 Å and 0.988 Å for O7-H15 and O8-H16 respectively at DFT/6-311++G (d, p) level. The difference in the bond length is explained again due to the fact that the bond length increases with hydrogen bonding [12], as expected O8-H16 is involved in the hydrogen bonding thereby the bond length is found to be more than O7-H15.

The bond length and bond angle values listed in the Table-1 at HF and DFT levels for the methyl groups present both in the ester group and in the aromatic methyl group of the chosen molecule are almost equal and satisfactorily agree with the experimental values.

Analysis of Vibrational assignments

The chosen molecule, methyl orsellinate has 23 atoms with 63 normal modes of vibrations and the entire modes of vibrations are categorized in to 43A' (in plane) and 20A" (out of plane). The assignments of the normal modes of the vibration of the molecule along with the observed frequencies, unscaled frequencies and scaled frequencies obtained by HF and DFT computation using 6-311++G (d, p) basis set are reported in Table 2.The experimental FT-IR & FT-Raman spectra and theoretically constructed IR & Raman spectra for the molecule at HF and DFT levels with 6-311++G (d, p) basis set are shown in Fig 2,3.

Scaling Factors

The quantum chemical calculation of IR and Raman wave numbers are usually higher than their experimental values, hence the scaling factor is necessary to match the experimental wave numbers. The linear fitting scaling equation is used to fix the scaling factors and to minimize the root mean square deviation between theoretical and experimental vibrational frequencies.
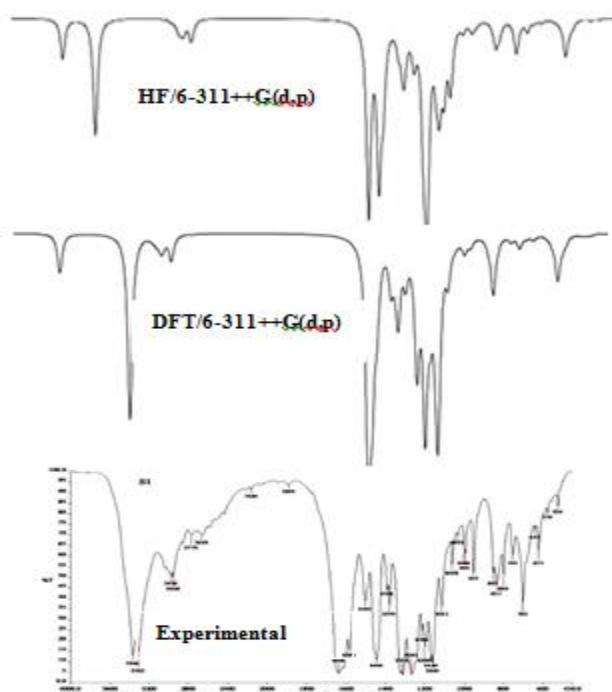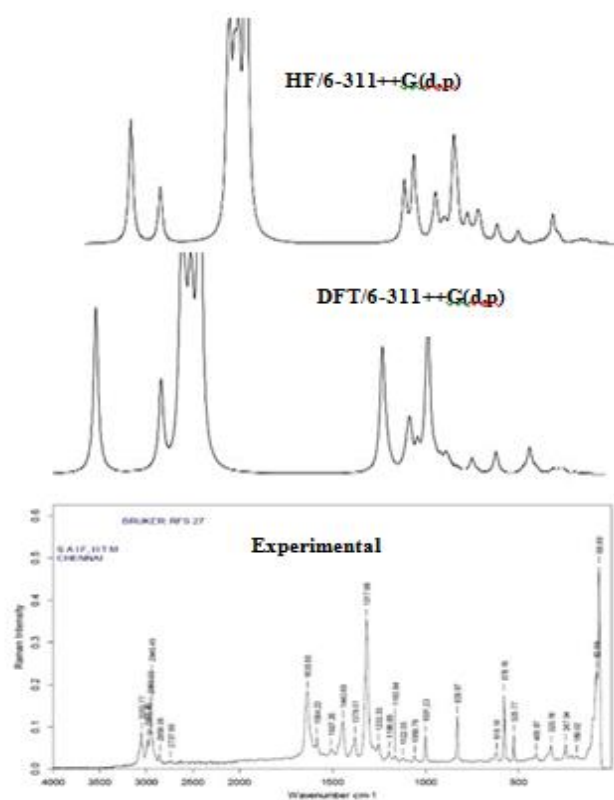

Fig 2. IR-Spectra of methyl orsellinate

Fig 3. Raman spectra of methyl orsellinate.

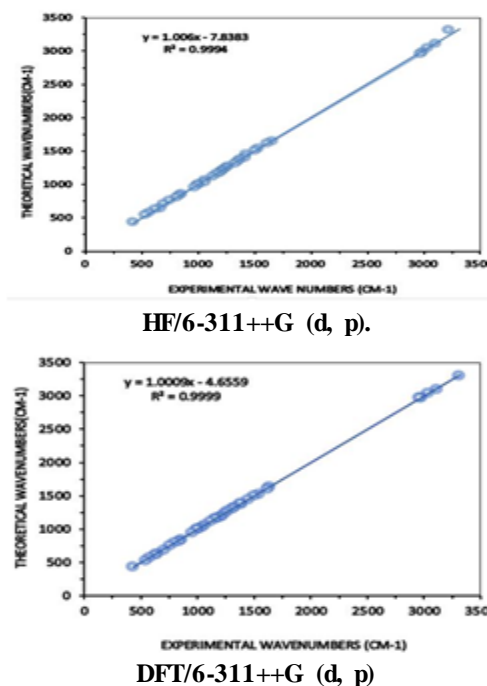**HF/6-311++G (d, p).**

DFT/6-311++G (d, p)

Fig 4. The correlation of experimental and calculated wave numbers of methyl orsellinate.

At HF/6-311++ G (d, p) level, the scaling equation y=1.006x-7.8383 with the regression coefficient (R^2= 0.9994) was used. At DFT/6-311++G (d, p) level, the scaling equation y=1.0009x -4.6559 with regression coefficient, R^2=0.9999 is employed and the correlation graph between theoretical and experimental wavenumbers at both HF and DFT methods are depicted in Fig 4.

OH Vibration

The OH group vibrations in infrared spectroscopy are sensitive to the environment thereby show a shift in the wave numbers of the hydrogen bonded species and generally the OH

group shows three modes of vibrations namely, stretching, in-plane and out-of-plane bending vibrations. In the chosen molecule, out of two phenolic groups, one O7H group is found to be free from hydrogen bond whereas the other O8H group is associated with $COOCH_3$ in the ortho position by hydrogen bonding. Normally in the case of unsubstituted phenols, the OH stretching vibration is observed at 3620 cm^{-1}- 3590 cm^{-1}[13].In our study, the calculated scaled frequency appears at 3731 cm^{-1} by DFT/6-311++G (d, p) level is assigned for the O7H group as stretching vibration and it is very well verified with the animation option of the Gauss View 5.0.8 package.

For both intra and inter molecular association, the frequency increases with the strength of hydrogen bond due to the requirement of large amount of energy to twist the O---H bond [14].In methyl orsellinate the O8H group is getting chelated through carbonyl oxygen with ortho substituted $COOCH_3$ and the expected value of stretching vibration is of the range 3200-2500 cm^{-1}[15], accordingly the frequency with very strong intensity occurs at 3312 cm^{-1} in FTIR spectrum and its counterpart at 3311 cm^{-1}in FT-Raman spectrum is assigned for O8H group and these wavenumbers are in line with the theoretical frequency 3305cm^{-1} calculated by DFT/6-311++G(d, p) method.

Out of plane bending vibration normally appears at 729-600 cm^{-1} for H- bonded OH group and at 300 cm^{-1} for free OH group without H-bonding [13]. In the molecule under study, it is observed that the band at 830 cm^{-1} in FT-Raman is assigned as out-of-plane bending mode for free O7H group and the wave number at 380 cm^{-1} in FT-Raman is assigned for O8 H group which is involved in the H-bonding with carbonyl group in the ortho position of the aromatic ring. The calculated scaled out-of-plane vibrations of O7H and O8H groups at DFT/6-311++G(d, p) are obtained at 819 cm^{-1} and 365 cm^{-1} respectively which coincide with the experimental ones.

Usually the in-plane bending vibration for OH group with hydrogen bonding is observed at 450-375 cm^{-1} and in the absence of hydrogen bond it is shifted by 20-40 cm^{-1}[13].Similarly, in methyl orsellinate, the vibrations occur at 362 cm^{-1} and 345 cm^{-1}in FT-Raman are assigned as in-plane bending vibrations for the O8H and O7H groups respectively and their counterpart of the calculated frequencies appear at 348 cm^{-1} and 330 cm^{-1} respectively at DFT/6-311++G(d, p) level.

COOCH$_3$ vibrations

The characteristic modes of vibrations generally for all ester groups are C=O, C-O-C and CH_3 group stretching and among these vibrations, C=O group vibration is more important in infrared spectroscopy due to its strong intensity of absorption and its high sensitivity with the small changes in the environment. The very strong intensity appears at 1639 cm^{-1}in FTIR is assigned to C=O stretching vibration as the expected value is 1650 cm^{-1} for hydrogen bonded C=O group[13]. The assigned value also agrees well with the theoretically calculated frequency at 1641 cm^{-1} in DFT method. Both scaled and experimental vibrational frequency value of carbonyl group show negative deviation of 9 cm^{-1} and 11 cm^{-1} respectively from the expected value because of the chelated ring formation between the oxygen atom of C=O in $COOCH_3$ group and hydrogen of O8H group of the chosen molecule which drops down the frequency value.

The C-O-C stretching vibrations in aromatic esters are strong and partly associated with C-C vibration appears normally at 1310-1250 cm^{-1} for asymmetric stretching and at 1150-1080 cm^{-1} for symmetric stretching[16]. In our work, the frequencies observed at 1216 cm^{-1} and 1160cm^{-1} in FTIR spectrum are assigned for C-O-C as asymmetric and symmetric stretching respectively. These frequencies also agree well with the calculated scaled values at 1200cm^{-1} and 1157cm^{-1} in DFT level for asymmetric and symmetric stretching respectively.

The other bands such as asymmetric, symmetric stretching, in-plane and out of plane bending vibrations of the CH_3 group in $COOCH_3$ are also identified and tabulated in the Table 2 along with deformation modes of vibrations. The in-plane asymmetric and symmetric bending C-H vibration of CH_3 in esters are expected to be in the range of 1485- 1420 cm^{-1}[16] and for the molecule under investigation, the assigned values are observed at 1507 cm^{-1}, 1502 cm^{-1} and 1469 cm^{-1} in the experimental spectra. These wavenumbers are found to be at little higher end than the expected values as the methyl group is attached in the ester moiety which shifts the wavenumbers to the higher level.

The intra molecular and intermolecular association with -OH group affect the absorption of C=O group due to the inductive, mesomeric and conjugative effects and hence generally the deformation vibration of OH group in combination with C=O is observed at 1410-1310 cm^{-1} [16].Accordingly, in methyl orsellinate, the frequency with very strong intensity appears at 1313 cm^{-1} in FTIR is assigned for O8H group in combination with C=O of $COOCH_3$ and its counterpart of the scaled vibration is found to be at 1308 cm^{-1} computed at B3LYP/6-311++G(d, p) method.

CH$_3$ group vibrations

The methyl group attached with the aromatic ring is associated with fundamental group frequencies such as asymmetric and symmetric stretching, scissoring, rocking, wagging and twisting modes of vibrations [17]. The chosen molecule contains only one methyl group attached to the ring and normally the asymmetric and symmetric stretching vibrations are observed at 3000-2870 cm^{-1}[16].The sharp peaks are identified at 3038 cm^{-1}, 3036 cm^{-1} and 2958 cm^{-1}in experimental spectra are assigned for C-H of CH_3 as asymmetric and symmetric stretching vibrations in the molecule. Some of these vibrations are found to be greater than the expected value this is due to the spatial arrangement of C-H in the CH_3 group and also by the influence of COOCH3 group as ortho substituent. The computed scaled values theoretically reported in this study at 3039 cm^{-1} , 3028 cm^{-1} and 2971 cm^{-1} which are almost in the marginal level with that of the experimental one and these assignments are also supported by the gauss view program.

The asymmetric scissoring mode appears at a fairly constant range from 1400-1460 cm^{-1} for most of the molecules and the symmetric scissoring vibration is very much sensitive to the atoms adjacent to the methyl groups [18].In view of these facts, the vibrations appear at 1469 cm^{-1},1446 cm^{-1} and 1379 cm^{-1} in the experimental spectra are assigned to asymmetric and symmetric deformation modes and the vibrations at 1446 cm^{-1} and 1379 cm^{-1}are analyzed as mixed modes with C-C stretching vibrations. These mode of vibrations have very good agreement with the theoretically computed frequencies of 1469 cm^{-1} , 1445 cm^{-1} and 1379 cm^{-1} at B3LYP/6-311++G(d, p) level.

The rocking mode of vibrations are identified at1033 cm^{-1} and 952 cm^{-1} in the FTIR spectrum and their vibration counter part at 1032 cm^{-1} and 946 cm^{-1} are observed as calculated frequencies at DFT level.

These vibrations are also analyzed and confirmed by the Gauss view 5.0.8 package. The lower frequencies are assigned for CH_3 group as twisting and torsion modes.

Ring C-H and C-C vibrations

For aromatic compounds the C-H symmetric and asymmetric stretching vibrations generally observed in the region 3100-3000 cm^{-1} frequency range[19] which is a characteristic region for ready identification. As methyl orsellinate is a tetra substituted molecule, only two aromatic C-H normal modes of vibration are possible hence the wave numbers appear at 3213 cm^{-1} and 3109 cm^{-1} in the experimental spectra are assigned to these two C-H as stretching vibrational modes and which agree with the theoretically calculated scaled values observed at 3196 cm^{-1} and 3098 cm^{-1} respectively in the B3LYP level.

Generally, the aromatic C-H in-plane bending vibration appears in the range of 1300 -1000 cm^{-1} and the out of plane bending occurs at 1000-750 cm^{-1} in the substituted benzene [20].The experimental FTIR frequencies with very strong intensity at 1267 cm^{-1} and 1200 cm^{-1} are assigned to C-H in-plane bending modes and also the experimental wave numbers obtained at 837 cm^{-1} and 702 cm^{-1}are identified as C-H out of plane deformation vibration modes. These assigned frequencies very well lie in the expected region and has good agreement with the scaled wave numbers at DFT/6-311++G (d, p) level.

Normally, the aromatic C=C stretching vibrations are observed in the region 1650-1400 cm^{-1} for the benzene derivatives [21]. In the molecule under investigation, there are three C=C stretching vibrations observed at 1636 cm^{-1}, 1615 cm^{-1}& 1582 cm^{-1} in the experimental spectra and their theoretical counterparts are found to be at 1639 cm^{-1},1605 cm^{-1} and 1570 cm^{-1} in DFT method with 6-311++G(d,p) level. The actual position of the wavenumbers are estimated not by the nature of the substituents but rather by the form of substitution around the aromatic ring [22]. The in-plane bending vibrations of C-C and C-C-C are also noticed and assigned below the frequency value of 1000 cm^{-1}and they are found to be mixed with other nearby vibrations.

In the experimental FT-IR and FT-Raman spectra of methyl orsellinate, the vibrational bands which are sharp, broad and less intense in the region 2950-1900 cm^{-1} are found to be non-fundamental bands of the benzene ring and assigned as overtone and combination vibrations.

NMR spectral Analysis

NMR spectroscopy is an important technique to get information of the structure of unknown organic molecules. Leaving aside the functional groups, a large part of an organic molecule consists of C-H skeleton and this tool is most useful in the investigation of structural feature of the molecule rather than the complete molecular structure. Chemical shifts in the NMR spectrum are valuable parameter for the interpretation of structure of the molecules and the number of signals in the NMR spectrum which aids to fix the number of sets of equivalent protons in a molecule.

The combination of experimental ^{13}C and ^{1}H NMR spectrum and computational methods of calculating chemical shifts in NMR spectrum attributes the prediction of molecular structure of bulkier molecules [23]. At DFT method, B3LYP/6-311++G (d, p) level, GIAO method is applied to construct the NMR spectrum for the optimized structure of methyl orsellinate in the present work.The experimentally recorded ^{13}C and ^{1}H NMR spectra of methyl orsellinate in DMSO as solvent are shown in the Fig 5,6.

^{13}C NMR spectral analysis

Methyl orsellinate contains totally nine carbon atoms and on the basis of experimental ^{13}C NMR spectrum, as expected, nine signals are obtained using DMSO as solvent .The chemical shift values of experimental and simulated ^{13}C NMR of the chosen molecule are tabulated in the Table 3. Normally the carbonyl (C=O) carbon has partial positive charge and resonates at the downfield and also due to the chelation of C=O with O8H group in the molecule under study, the carbonyl carbon influences deshielding effect. The expected chemical shift of carbonyl carbon of esters usually appears between 150-185 ppm [16] and in the simulated ^{13}C NMR spectrum of the chosen molecule at DFT method , the chemical shift at 179.32 ppm with respect to tetramethylsilane (TMS) is assigned for C=O carbon .
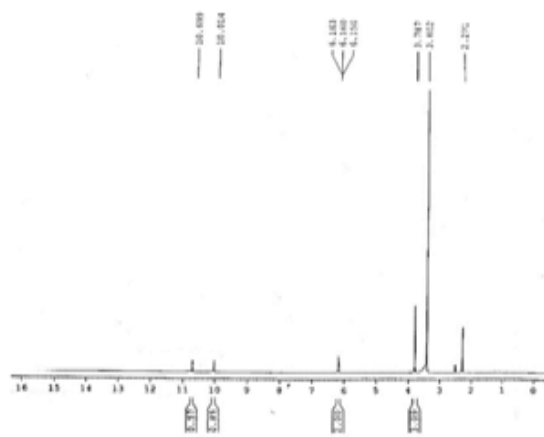

Fig 5. Experimental ^{13}C-NMR spectrum of methyl orsellinate.

Table 3. The Calculated and Experimental ^{13}C & ^{1}H NMR Isotropic chemical shifts (δ_{cal} in ppm) with respect to TMS (in DMSO as solvent) and Isotropic magnetic shielding tensors(σ_{cal}) of methyl orsellinate.

Atom with number	σ_{cal} (^{13}C)	Calculated (δ_{cal})	Experimental (δ_{exp})	Atom with number	σ_{cal} (^{1}H)	Calculated (δ cal)	Experimental (δ_{exp})
C 1	13.83	168.46	140.82	H 11	25.348	6.534	6.16
C 2	79.37	102.79	95.46	H 12	25.332	6.550	6.163
C 3	8.87	173.71	161.11	H 15	25.867	6.015	10.014
C 4	74.51	107.71	100.49	H 16	19.748	12.134	10.699
C 5	28.84	153.72	110.24	H 17	29.192	2.690	2.271
C 6	68.00	114.17	107.62	H 18	29.192	2.690	2.271
C 9	2.95	179.32	170.26	H 19	29.847	2.035	2.5
C 10	156.29	26.27	22.1	H 21	28.023	3.860	3.787
C 20	129.97	51.86	51.83	H 22	28.023	3.860	3.787
				H 23	28.006	3.876	3.787

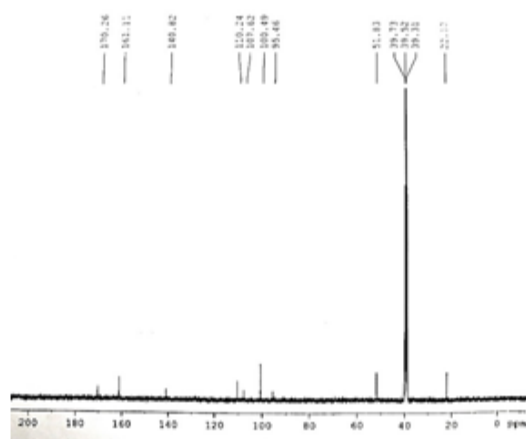**Fig 6. Experimental ^{1}H -NMR spectrum of methyl orsellinate.**

This value lies exactly in the expected range of chemical shift and also good agreement with the experimental value (170.26ppm).

The chemical shift value of carbon atom (C10) of CH$_3$ group is shifted to almost upfield because the electron releasing effect of the methyl group which influences the shielding effect. The δ value at 26.27 ppm with respect to TMS in the simulated ^{13}C NMR spectrum at B3LYP level is assigned for C10 of CH$_3$ in methyl orsellinate and it is in line with the signal at 22.10 ppm in the ^{13}C NMR experimental spectrum.

For C3 and C1 carbon atoms of the molecule on study, the assigned simulated chemical shifts appear at173.71ppm and 168.46ppm respectively at DFT/6-311++G(d, p) method, as these two carbon atoms have the substituents , phenolic OH group which is electron attracting group and also has lone pair of electrons on oxygen atom of the phenolic OH which influence the increase in the charge density at carbon atoms(C1 and C3) and hence have a desheilding influence , so chemical shift values are shifted to downfield.

Similarly C20 in the acetate group with the influence of electron releasing group (CH$_3$) and lone pairs of electrons on the oxygen atom of the COOCH3 group, pushed the chemical shift to upfield and has the simulated chemical shift signals at 51.86ppm with respect to TMS is assigned to C20 of methyl orsellinate. Its experimental counterpart is observed at 51.83ppm which is found to be very good agreement with the expected value of 51.0 ppm [16].

For aromatic ring carbons C1, C2 ,C3 ,C4 ,C5 and C6 the chemical shifts are assigned as 168.46 , 102.79 ,173.71 , 107.71 , 153.72 and 114.17 ppm respectively with respect to TMS at DFT/6-311++G(d, p) level. The experimental ^{13}C-NMR δ $_{exp}$ values also show similar trend in the ring carbons and the variations in the chemical shift values of the carbon atoms are influenced by the delocalization of electrons, position and nature of the substituents.

DEPT (Distortionless Enhancement of Polarization Transfer) is a technique which is proved to be superior to others in providing information on attached protons efficiently with high selectivity and the DEPT-135 shows positive CH$_3$ and CH, and negative CH$_2$ signals[24].As expected, in our study, C2 and C6 carbon atoms of the chosen molecule are appeared as positive signals at 110.11 and 100.36 ppm respectively in Dept 135- NMR spectrum shown in the Fig.7, as these two carbon atoms in the aromatic ring contain free hydrogen atom (CH) and there is no negative signals in Dept -

135 of the chosen molecule which matches with the absence of CH$_2$ part in the molecule. The signals for carbon atoms C1, C3, C4 and C5 in the aromatic ring of the molecule in the present study were not observed as these carbons do not contain any free hydrogen atoms.
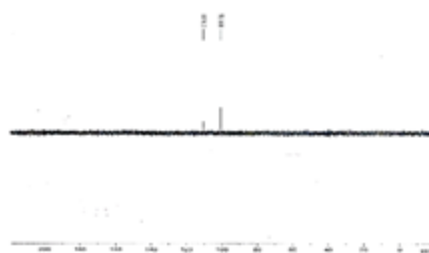

Fig 7. DEPT-135 spectrum of methyl orsellinate.
^{1}H NMR spectral analysis

The molecule under study, methyl orsellinate has ten hydrogen atoms and the corresponding experimental ^{1}H NMR chemical shifts for hydrogen atoms are presented in the Table 3 along with the computed scaled signals at DFT/B3LYP/6-311++G(d,p) level. The chemical shift for phenolic protons is expected at 4-12ppm and the protons of the chelated OH group show the resonance at very high and the chemical shift, δ value at 10-12ppm [25].In methyl orsellinate, the chemical shift of protons H15 and H16 in the phenolic OH group are shifted to the lower field (strong field strength),the assigned signals are appeared at 6.015ppm and 12.134 ppm respectively in the simulated ^{1}H NMR spectrum at DFT/6-311++G(d, p) level. It is also noticed that the H16 of the molecule under study has very high δ value as the H16 proton is involved in the chelation with oxygen atom of ortho C=O group in the aromatic ring.

In methyl orsellinate, the H11 and H12 protons which are directly linked with the aromatic ring, due to delocalisation of π electrons in the ring, get desheilded and hence the computed chemical shift values are assigned for signals appear at 6.534 ppm and 6.550 ppm respectively in DFT/6-311++G(d, p)method and their experimental counterpart are found to be at 6.160ppm and 6.163 ppm respectively. Both the experimental and the calculated chemical shifts show very good agreement with the expected signals of aromatic protons which usually appears at 6-12ppm[25].

In general, the hydrogens in the aromatic methyl group shows the chemical shift δ value at 2.3 ppm [25], accordingly, in the chosen molecule, the computed δ value occurs at 2.689,2.689 and 2.035 ppm are assigned to H17 , H18 and H19 hydrogen atoms of the aromatic CH$_3$ group respectively at DFT/6-311++G(d, p) level and their experimental counterpart are found to be at 2.271, 2.271 and 2.5ppm respectively.

The expected δ value of protons in the methyl group of esters is usually found to be observed at 3.9ppm[25] and in our molecule under investigation, the calculated chemical shifts appear at 3.859 , 3.859 and 3.875ppm in DFT/6-311++G(d, p) method are assigned to H21 ,H22 and H23 protons respectively present in the methyl group of – COOCH$_3$ and these signals show very good agreement with the experimental peaks observed at 3.787ppm for all the protons in the CH$_3$ group of ester part. A very small variation in the chemical shift values are found to be due to the influence of substituents present in the chosen molecule which is a tetra substituted compound.

Analysis of molecular electrostatic potential surface

Molecular electrostatic potential surface (MEPS) is a visual tool to analyse the charge distribution ,dipole moment ,electronegativity and also the reactive sites of a molecule.The total electron density mapped with electrostatic potential surface and the contour map of esp of the methyl orsellinate are constructed at B3LYP/ 6-311 + + G(d, p) level and presented in the Fig.8,9 .In the Fig 8,the areas of negative electrostatic potential surface is of red shade in colour which corresponds to the region with abundance of electrons in the molecule due to the presence of lone pair of electrons on all the four oxygen atoms present in the chosen molecule. The areas with positive electrostatic potential which are of blue shades in colour indicates the relative lesser density of electrons on the methyl groups and hydrogen atoms of the molecule under investigation. The electronegativity nature of the oxygen atoms is clearly identified by MEPS and also the electrophilic attack may take place at the electron rich sites of the molecule. The non-red or blue area in the meps of the molecule represents the region with intermediate potential energy in which the electrostatic potential is almost zero.

Analysis of Mullikan charge

The atomic population and also the Millikan charge distribution in the chosen molecule at HF/6-311++G (d, p) and DFT/6-311++G (d, p) have been reported in the Table 4 and their graphical comparison is shown in the Fig 10. From the table 4, it is observed that the atomic charges of oxygen atoms of methyl orsellinate are found to be negative and in the range of - 0.1513/ -0.2209 to -0.3266/-0.4539 at DFT/ HF levels with 6-311++G (d, p) basis set. The relative variations in the electronegativity nature of carbon and oxygen atoms are also clearly indicated by the charge distribution calculated by these two methods. All the hydrogen atoms present both in the substituents and those attached directly to the aromatic ring have positive charge thereby proving the electro positivity nature and also evidenced by the electro static potential surface map. The calculated atomic charges of C2, C4 and C5 carbon atoms in the present molecule are positive and determined as 0.2813 /0.1940, 1.0677/0.3075 and 0.7322/1.3321 respectively at DFT/HF levels as these atoms are under the vicinity of oxygen atoms and also electron releasing methyl group. The slight variation in the atomic charge distribution of aromatic carbon atoms are due to the delocalisation of electrons in the ring. The distribution of charges also play a vital role in the molecular system based on dipole moment, molecular polarizability, donor-acceptor analysis [26].
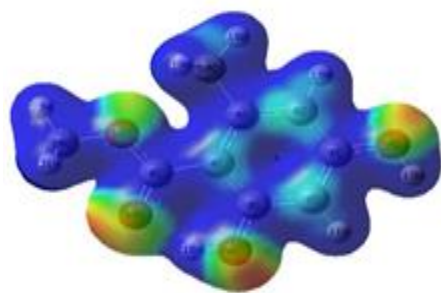

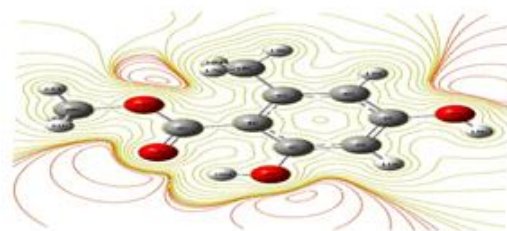**Fig 8. The total electron density surface mapped with electrostatic potential of methyl orsellinate.**

Fig 9. The contour surface of electrostatic potential of methyl orsellinate.

Table 4. Mullikan atomic charges of methyl orsellinate estimated by HF and DFT methods.

Atom with Numbering	HF/6-311++G (d, p)	DFT/6-311++G (d, p)
C1	-0.4168	-0.3957
C2	0.1940	0.2813
C3	-0.6538	-0.8438
C4	0.3075	1.0677
C5	1.3321	0.7322
C6	-0.7412	-0.8678
O7	-0.2863	-0.2148
O8	-0.3932	-0.2957
C9	-0.0283	-0.2222
C10	-0.5560	-0.5264
H11	0.2150	0.1686
H12	0.1891	0.1517
O13	-0.4539	-0.3266
O14	-0.2209	-0.1513
H15	0.2903	0.2723
H16	0.3981	0.3446
H17	0.1789	0.1781
H18	0.1654	0.1780
H19	0.1654	0.1569
C20	-0.2085	-0.2173
H21	0.1798	0.1900
H22	0.1798	0.1900
H23	0.1499	0.1501

## Frontier molecular orbital analysis

The energy between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) has been associated with stability index and hence chemical reactivity of the molecule [27, 28]. The HOMO is the orbital that acts as an electron donor and the LUMO is the orbital which acts as an electron acceptor.

The ionization energy, electron affinity, conjugation and lone pairs can be easily expressed through homo and lumo energies as $I = -E_{HOMO}$ and $A = -E_{LUMO}$ .With the insight of energy gap, the global hardness of the molecule $\eta = 1/2(E_{LUMO} - E_{HOMO})$,electronic potential $\mu = 1/2(E_{HOMO} + E_{LUMO})$ and global electrophilicity index $\omega = \mu^2/2\eta$ are calculated at HF/ B3LYP levels with 6-311g++(d, p) basis set and tabulated in Table-5.

Table 5. The calculated Frontier molecular orbital energy gap (eV) by HF and DFT methods with 6-311++G (d, p) basis set.

Molecular properties	HF/6-311++G (d, p)	DFT/6-311++ G (d, p)
E_{LUMO+1}	0.0410	-0.015
E_{LUMO}	-0.3200	-0.2353
E_{HOMO}	0.0360	-0.0535
E_{HOMO-1}	-0.2500	-0.3380
Homo-lumo energy gap	0.3560	0.1818
Global hardness(η)	-0.1780	-0.0905
Electronic chemical potential(μ)	-0.1420	-0.1444
Global electrophilicity (ω)	-0.0566	-0.1152
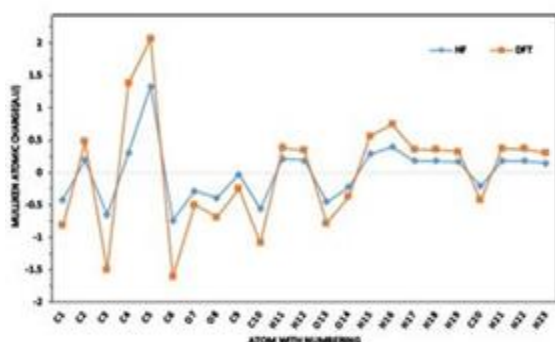
Fig 10. Comparison of calculated atomic charges of methyl orsellinate at HF and DFT methods.

In the molecule under investigation, there are 48 occupied molecular orbital and 49th is the unoccupied molecular orbital which are shown in Fig 11 in which the negative and positive phases are shown in green and red colour respectively. In our molecule the HOMO is located over the aromatic ring and oxygen atoms whereas LUMO is located on the methyl group and acetyl group. A significant degree of an intra molecular charge transfer is expected from HOMO → LUMO energy level and the orbital energy gap is calculated as 0.1818 eV at B3LYP/6-311g++(d, p) level in the molecule. The energies of HOMO, LUMO, HOMO-1 and LUMO+1 of the molecule under study are calculated at HF and DFT methods with 6-311++G (d, p) level and presented in the Table 5. The low HOMO-LUMO energy gap characterizes methyl orsellinate as more polarizable with high chemical reactivity which leads to low kinetic stability and considered as soft molecule with substantial influence on the intramolecular charge transfer within the molecule [29].

Analysis of NLO properties

The non-linear optical properties are significant in current research scenario such as telecommunications, signal processing and also optical switching [30].The mean polarizability(α) and first order hyperpolarizability(β) are calculated at HF and B3LYP levels with 6-311g++(d, p) basis set by using the equations and summarized in the Table-6.

$$\alpha_{Total} = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$
$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$
(or)
$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

The α and β values from Gaussian 09W output are in the atomic unit so the theoretically calculated values of α and β have been converted to electrostatic units(1 a.u = 8. 6393x10^{-33} cm^{-5} esu^{-1}). Urea is a prototypical molecule which

exhibits NLO properties and hence the β value of urea is frequently referred as threshold value (β=0.2991x10^{-30} cm^{-5} esu^{-1}) [31] .The calculated β_{total} value of methyl orsellinate at DFT/6-311++G (d, p) level is reported as 8.592 x10^{-30} cm^{-5} esu^{-1} which is many times greater than that of urea and hence the molecule under study has the potential to act as a good NLO material.

Analysis of Thermodynamic properties

At HF and DFT methods with 6-311++G(d, p) basis set, some of the thermodynamic functions such as specific heat capacity, enthalpy, entropy, total energy, zero point vibrational energy, rotational energy and dipole moment of the chosen molecule are computed at 298.15 K in ground state and presented in Table 7. The dipole moment of the chosen molecule is found to be nearby values 1.716 D and 1.7687 D which are calculated at both HF and DFT levels respectively with the same basis set 6-311++G (d, p).The atomic radius, type of hybridization, delocalization of pi electrons, polarizability of lone pair of electrons and also the position and nature of the substituents in the aromatic ring are the factors which influence the magnitude of the dipole moment of the molecule. As the vibrational intensity increases with temperature, the thermodynamic parameters such as entropy, heat capacity and enthalpy changes also increase with temperature. For methyl orsellinate, these thermodynamic properties are computed from 100 to 700 K at DFT/6-311++G (d, p) framework and listed in Table 8. The correlation graph between the thermodynamic properties (enthalpy, heat capacity and entropy) and temperature are shown in Figs.12-14 and these changes were fitted by the quadratic formulas with the corresponding fitting equations and fitting factors (R^2) are given as follows:

$$H = 112.05 + 0.0108 \ T + 6 \times 10^{-5} \ T^2 \ (R^2 = 0.9998)$$
$$C_p = 2.4431 + 0.1706 \ T - 7 \times 10^{-5} \ T^2 \ (R^2 = 0.9999)$$
$$S = 52.546 + 0.2068 \ T - 6 \times 10^{-5} \ T^2 \ (R^2 = 0.9997)$$

Table 7. Theoretically computed Dipole moment (Debye), energy (a.u), zero point vibrational energy (kcal mol^{-1}), entropy (cal mol^{-1}K^{-1}), thermal energy (k cal mol^{-1}K^{-1}) and Molar capacity at constant volume (cal mol^{-1}K^{-1}) of methyl orsellinate at HF and DFT levels.

Parameters	HF/6-311g++(d, p)	DFT/6-311g++(d, p)
Dipole moment	1.8716	1.7687
Total energy	-646.2829	-650.0884
Zero point vibrational energy	121.1361	112.5879
Entropy	105.905	108.554
Thermal Energy	128.392	120.287
Molar capacity at constant volume	43.616	46.438

Table 6. Calculated polarisibility(a.u) and hyperpolarisibility (a.u) of methylorsellinate at HF and DFT levels.

| Polarizability	HF/6-311++G(d,p)	DFT/6-311++G(d,p)	Hyper-polarizability	HF/6-311++G(d,p)	DFT/6-311++G(d,p)
α_{xx}	126.7712	174.0958	β_{xxx}	-118.0163	804.7619
α_{xy}	12.6923	-0.59798	β_{xxy}	-4.6755	-159.554
α_{yy}	136.7677	132.7672	β_{xyy}	353.2126	198.38689
α_{xz}	-3.7245x10^{-8}	0.0086003	β_{yyy}	262.2666	163.5488
α_{yz}	-9.3175x10^{-9}	0.0022698	β_{xxz}	4.9985x10^{-9}	-0.14885
α_{zz}	67.3493	70.8192	β_{xyz}	-1.5517 x 10^{-7}	-0.023657
α_{total}(a.u)	110.2961	125.894	β_{yyz}	1.3609x10^{-6}	0.08469
			β_{xzz}	7.4530	-8.57898
			β_{yzz}	-2.3039	9.73553
			β_{zzz}	2.2887x10^{-7}	3.4704x10^{-5}
			β_{total} (a.u)	352.2077	994.6646
			β_{total} (e.s.u)	3.0427 x10^{-30}	8.592x10^{-30}
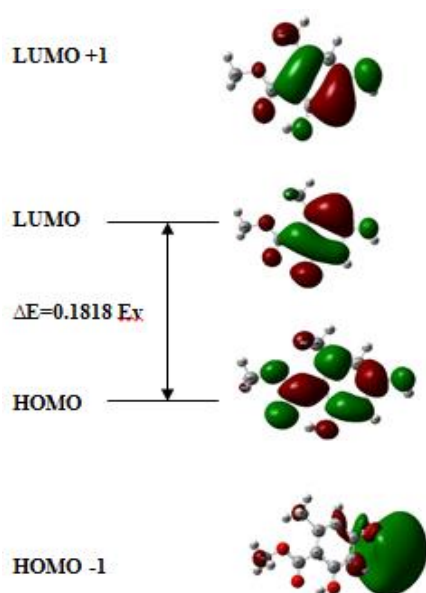
Fig 11. Frontier molecular orbitals (Homo and Lumo) of methyl orsellinate.

From the Table 8 and correlation graphs (Figs. 12-14), it is observed that the thermodynamic parameters (enthalpy, heat capacity and entropy) are increasing with temperature ranging from 100 to 700 K in the title molecule, methyl orsellinate. These thermodynamic data can be utilized to calculate other thermodynamic energies and thereby to determine the direction of chemical reactions for further study on methyl orsellinate.

Table 8. Temperature dependent thermodynamic parameters of methyl orsellinate.

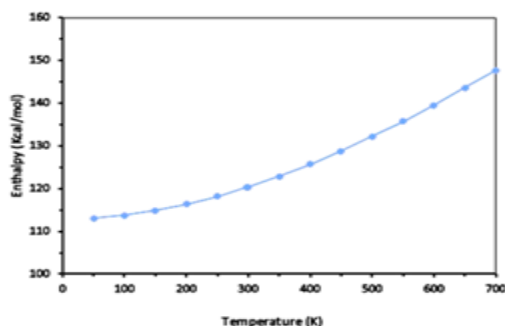| Temperature(K)	Enthalpy (Hm) (kcal mol^{-1})	Heat capacity (Cp,m) (Cal mol^{-1}K^{-1})	Entropy (Sm) (Cal mol^{-1}K^{-1})
50	112.98	10.96	61.502
100	113.73	18.93	72.911
150	114.87	26.44	82.836
200	116.36	33.40	91.975
250	118.2	40.12	100.596
298.15	120.29	46.44	108.554
300	120.37	46.68	108.855
350	122.87	53.00	116.835
400	125.67	58.97	124.578
450	128.76	64.48	132.075
500	132.11	69.50	139.342
550	135.7	74.05	146.373
600	139.5	78.15	153.167
650	143.51	81.85	159.731
700	147.68	85.21	166.069

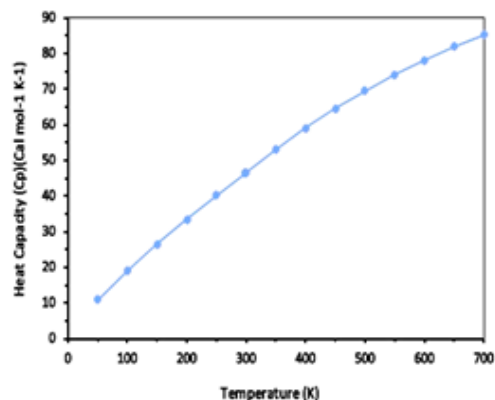**Fig 12. Correlation graphic of enthalpy and temperature of methyl orsellinate**

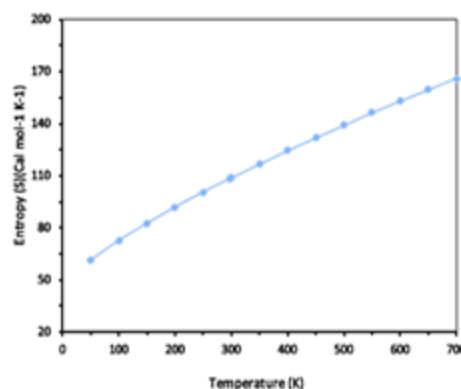**Fig 13. Correlation graphic of heat capacity and temperature of methyl orsellinate.**

Fig 14. Correlation graphic of entropy and temperature of methyl orsellinate

Conclusion

Spectral analysis like FT-IR, FT-Raman,^{13}C-NMR,^{1}H-NMR and DEPT-135 of methyl orsellinate have been made for the first time along with the theoretical combination. A good agreement has been observed between experimental and scaled wavenumbers of methyl orsellinate by DFT level. The reported geometric parameters, IR frequencies , NMR chemical shifts and molecular electro static potential surface analysis by ab-initio calculations of HF/DFT methods stand as the evidences for the presence of intramolecular hydrogen bonding and reactive sites in the chosen molecule. The NLO behavior of methyl orsellinate also identified from the computed values of polarizability and hyperpolarizability in the present study. It has been noticed that the thermodynamic properties such as entropy, heat capacity and enthalpy increase with wide range of temperature from 50K to 700K and the linearity in the increasing trend also proved by the correlation graphic fitted with quadratic formulas with the corresponding fitting equations and fitting factor (R^2).The DFT/B3LYP/ 6-311++G (d, p) framework is considered as an effective tool for the quantum chemical calculation of the molecule, methyl orsellinate.

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