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Molecular modeling of 2-chloro-5-nitrotoluene by quantum chemical calculation for pharmaceutical application

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ABSTRACT

In this work, we reported a combined experimental and theoretical study on molecular structure and vibrational analysis of 2-chloro-5-nitrotoluene (2Cl5NT). The Fourier transform infrared and FT-Raman was recorded in the solid phase. The molecular geometry and vibrational frequencies of 2Cl5NT in the ground state have been calculated by using ab initio HF and density functional method (B3LYP) with 6-311++G(d,p) as basis set. Comparison of the observed fundamental vibrational frequencies of 2Cl5NT with calculated results by density functional methods indicates that B3LYP/6-311++G (d,p) is superior to other methods for molecular vibrational problems. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. The thermodynamic functions of the title compound was also performed at B3LYP/6-311++G(d,p) level of theory. A detailed interpretation of the infrared spectra of 2Cl5NT was also reported. The theoretical spectrograms for FTIR and FT-Raman spectra of the title molecule have been constructed. Time depended B3LYP (TD-B3LYP) calculations of electronic absorption spectrum were performed on the optimized structures at the same 6-31G++(d,p) basis set for elaborate usage in pharmaceutical application.

Key words: Geometry and Spectral analysis, Quantum Chemical Calculation, 2-Chloro-5-Nitrotoluene.

INTRODUCTION

Aniline and substituted anilines are widely used as starting materials in a vast amount of pharmaceuticals, electro-optical and many other industrial processes. They have attracted considerable attention over the years [1, 2]. In recent time toluene and substituted toluene have become very important on account of their wide range of applications in medicine and industry. 4-amino-3bromotoluene (C_7H_8BrN) derivatives find use in herbicidal activity [3] and central nervous system activity [4].

The IR and Raman spectra of toluene and m-xylene have been investigated by numerous workers and vibrational assignments have been made by Pitzer and Scott [5]. The IR spectra of the monodeutero toluenes have been investigated from 2 to 16 μ by Turkeivich et al [6] who failed to find a band characteristic of unduetrated toluene. The absorption spectra of some fluorinated toluenes in the vapour phase have been measured in the near ultraviolet. Benzotrifluoride, o-, m- and p-fluorotoluenes have been studied. A vibrational analysis has been made in each case and although this is incomplete, important deductions about the values of molecular vibration frequencies have been made. The latter have been correlated with values obtained from the Raman spectra [7].

Nagabalasubramanian et al [8] studied the vibrational analysis of α,α dichlorotoluene was performed on the basis of DFT calculations at HF/6-31G(d) level of theory. The Raman spectrum of the liquid p-fluorotoluene is also recorded. A complete assignment of fundamental vibrational frequencies is given and the spectra are interpreted in details. Raman and fluorescence spectrum of o-, m-and p- bromotoluene in the solid state at low temperatures are studied by Biswas [9]. Wilmshurst and Bernstein [10] recorded the IR spectra of toluene, toluene-α-d_3, m-xylene and m-xylene-α α'- d_6 in the range 2 to 30μ for the vapours and liquids. The Raman spectra liquids have also been obtained photo electrically together with depolarization ratios. Vibrational assignments have been made for the same molecules.

The characteristic ring vibrations of the o-chloro and bromotoluenes [11], p-chloro- and bromotoluenes [12] and m-chlorotoluene [13] in the 800-1600 cm^{-1} region has been assigned. A comparative study of the gas and liquid IR spectra of $C_6H_5CH_3$, $C_6H_5CD_3$ and $C_6D_5CD_3$ and the liquid Raman spectra of the two former, leads to a vibrational assignment for these molecules inconsistent with the relative bands intensities, vapour bands countours, polarization data and the Redlich–Teller isotope product rule [14]. The Raman and IR spectrum of o-fluorotoluene have been investigated by Deb [15] in liquid and in different aliphatic solvents viz, CCl4, CS_2 and n-hexane solutions.

Scott et al. [16] studied the thermodynamic properties, vibrational assignments and internal rotation of 4-fluorotoluene. The FT-IR spectra (950-650cm^{-1}) of twelve organic liquids: benzene, chlorobenzene, bromobenzene, toluene etc, in the liquid state have been measured. Partial assignments are suggested for eight of these spectra [17]. The IR spectra o-, m- and p-halogentoluenes are studied by Mooney [18]. The low frequency out-of-plane deformation modes of m-halogentoluenes are shown to be essentially mass dependant upon Hammett functions. The X-sensitive vibrations have been assigned in each isomer.

The IR spectrum of o-bromotoluene has been investigated in liquid phase in the region 700-4590 cm^{-1}. Assignments of the observed frequencies have been proposed by assuming C_s symmetry for the molecule [19]. Joshi and Sing [20] recorded IR absorption spectrum of o-fluorotoluene in the region 2- 15μ on a Perkin-Elmer spectrophotometer with NaCl optics. The frequencies observed have been proposed to different modes of vibration, assuming C_s symmetry of the molecule.

The Raman spectrum of 2, 4-dichlorotoluene has been reported Landolt-Bornstein table [21]. The IR spectrum of this compound in the region 700-1600 cm^{-1} was also reported, but they have not given the complete assignments. Thakur et al [22] recorded the IR absorption spectra of 2,4-difluoro- and 2,4-dichlorotoluenes in liquid phase in the region 250- 4000 cm^{-1}. The spectra have been analyzed assuming C_s point group for both compounds and assignments for the different fundamental are given. Utilizing the result of new measurements of the IR spectra(50-3650 cm^{-1}) together with the Raman shifts, wave numbers for all the fundamentals frequencies, and complete interpretations of the observed spectra are presented for the fifteen compounds p-XC_6H_4Y; X,Y= CH_3, F,Cl, Br or I [23].

Literature survey reveals that to the best of our knowledge, the quantum chemical calculations for 2Cl5NT have not been reported so far. Therefore the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wavenumber accuracy. Density functional theory (DFT/B3LYP) calculations have been performed to support our wavenumber assignment.

Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity.

EXPERIMENTAL SECTION

The compound 2-chloro-5-nitrotoluene (2Cl5NT) was obtained from Sigma-Aldrich Chemical Company, USA with a stated purity of greater than 99% and it was used as such without further purification. The FT-Raman spectrum of 2Cl5NT has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 50-3500 cm^{-1} on a Brucker model IFS 66 V spectrophotometer. The FT-IR spectrum of this compound was recorded in the region 400-4000 cm^{-1} on IFS 66 V spectrophotometer using KBr pellet technique. The spectra were recorded at room temperature, with scanning speed of 30 cm^{-1}min^{-1} and the spectral resolution of 2.0 cm^{-1}. The observed experimental FT-IR and FT-Raman spectra of the title compound is shown in Figure 1 and 2 and scaled FT-IR all the methods are also shown in Figure 3. The theoretical FT-Raman by B3LYP/6-311++G(d,p) (best-level) for the title molecule is shown in Figure 4. The spectral measurements were carried out at Central Electro Chemical Research Institute (CECRI), Karaikudi, Tamilnadu.

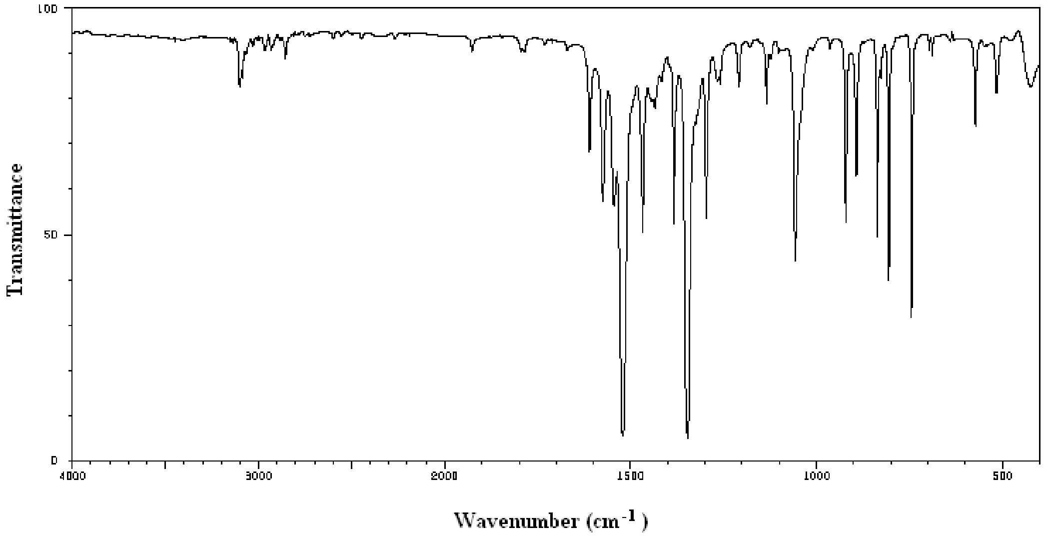


Fig. 1. FT-IR Spectrum of 2-chloro-5-nitrotoluene

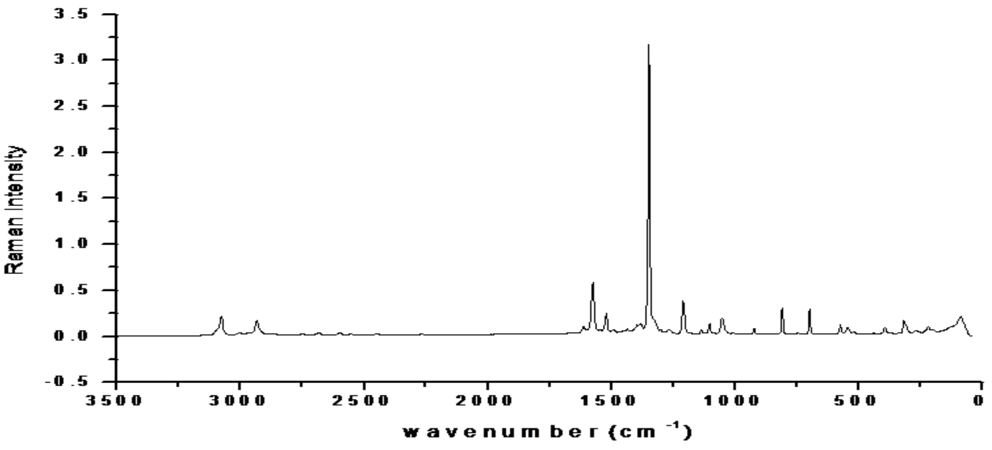


Fig. 2 FT-Raman spectrum of 2-chloro-5-nitrotoluene

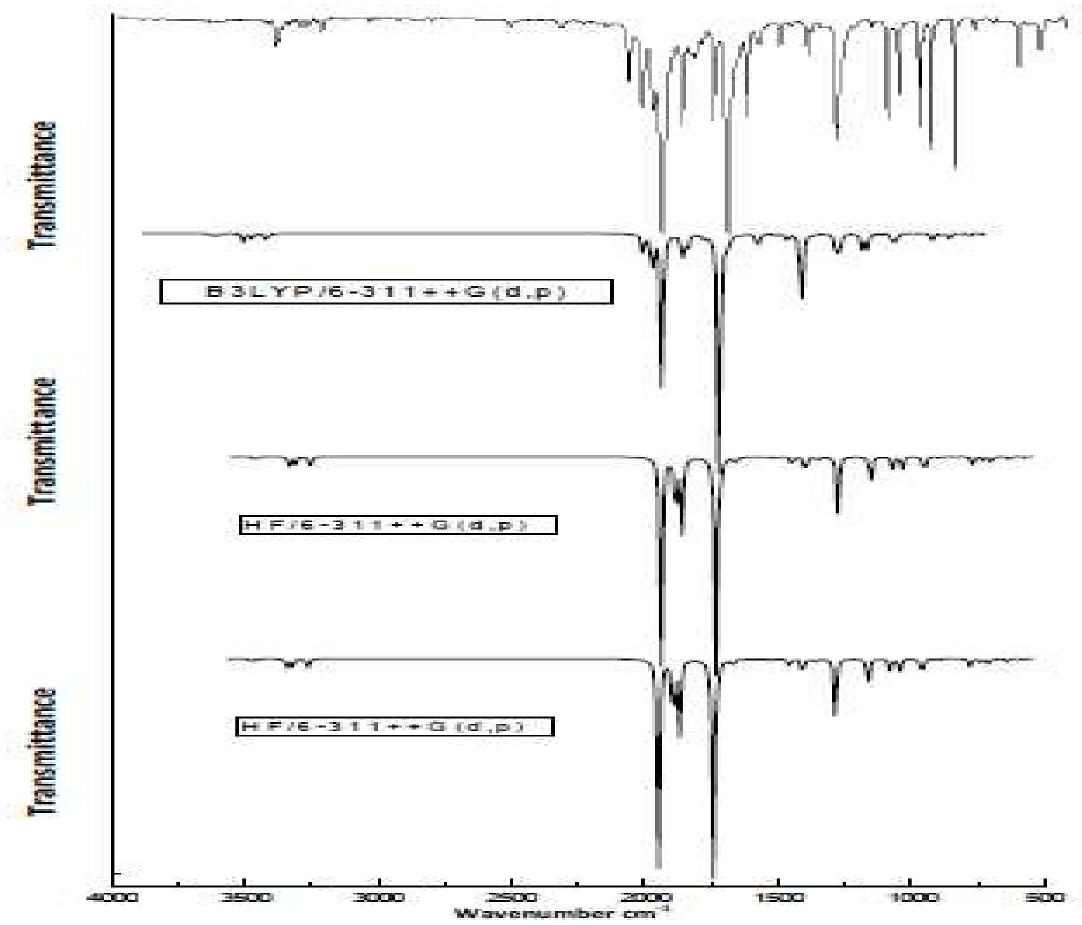


Fig. 3. Comparison of Experimental and theoretical FT-IR spectrum of 2-chloro-5-nitrotoluene

3. Computational Details

DFT calculations were performed using GAUSSIAN 03 [24] program package on core 2 due quad personal computer without any constraint on the geometry[13]. Geometries of the model 2Cl5NT, have been first optimized with full relaxation on the potential energy surfaces at HF /6-311++G(d,p) level and the resultant geometries have been used as inputs for further calculations at DFT level. Polarization functions have been added for the better treatment of the chloro, and nitro groups. The optimized structural parameters were used in the vibrational frequency calculations at DFT levels to characterize all stationary points as minima.

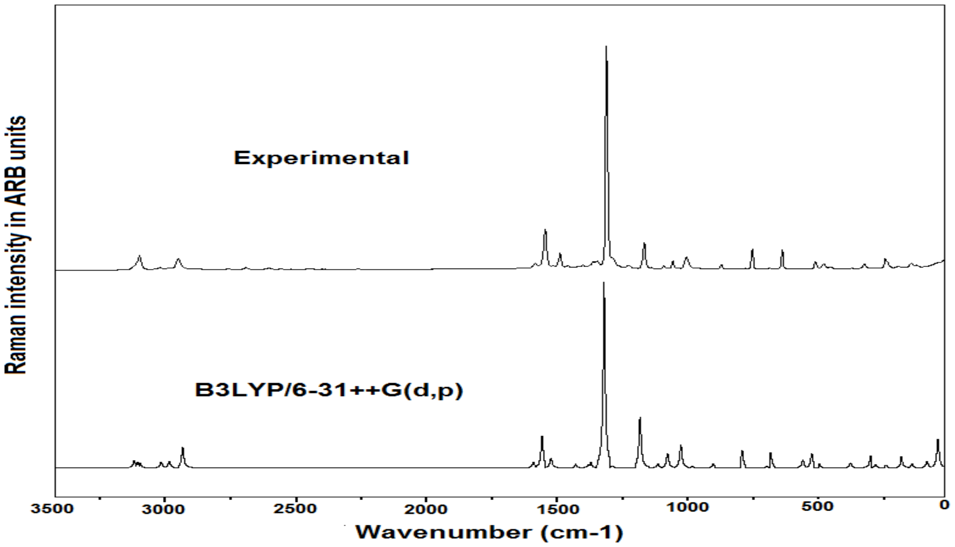


Fig. 4. Comparison of Experimental and Theoretical FT-Raman Spectrum of 2-chloro-5-nitrotoluene

We have utilized ab initio HF and DFT/B3LYP/6-311++G(d,p) approach for the computation of molecular structure, vibrational frequencies and energies of optimized structures, in the present work. By the use of GAUSSVIEW program [25] with symmetry considerations along with available related molecules vibrational frequency assignments were made with a high degree of accuracy. Time depended B3LYP (TD-B3LYP) calculations of electronic absorption spectrum were performed on the optimized structures at the same 6-31G++(d,p) basis set.

3.1 Prediction of Raman Intensities

The Raman activities (S_i) calculated with Gaussian 03 program converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [26, 27].

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i[1-\exp(-hc\nu_i/kt)]}$$

Where ν_o is the exciting frequency in cm^{-1}, ν_i the vibrational wave number of the ith normal mode, h, c and k fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities. For simulation of calculated FT-Raman spectra have been plotted using pure Lorentizian band shape with a bandwidth of (FWHM) of 10 cm^{-1} as shown in Figure 4.

RESULTS AND DISCUSSION

4.1. Geometric Structure

The optimized structure parameters of 2Cl5NT calculated by ab initio HF and DFT (B3LYP) level with the 6-311++G(d,p) basis set are listed in Table 1. In accordance with the atom numbering scheme has been given in Figure 5. Since the crystal structure of the exact title compound is not available till now, the optimized structure can be only be compared with other similar systems for which the crystal structures have been solved. From the theoretical values we can find that most of the optimized bond lengths are slightly larger than the experimental values. Comparing bond angles and lengths of B3LYP/6-311++G (d,p) method with other basis sets leads to geometric parameters which are much closer to experimental values.

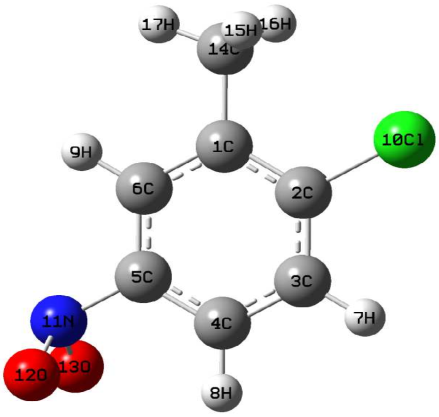


Fig. 5. Atom numbering system adopted in this study for 2-chloro-5-nitrotoluene

Table 1. Geometrical parameters optimized in 2-Chloro-5-nitrotoluene (2Cl5NT), bond length (A°), bond angle (°) and dihedral angle (^{o})

Parameters	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
Bond length(Å)		
C1-C2	1.392	1.404
C1-C6	1.388	1.396
C1-C14	1.508	1.505
C2-C3	1.384	1.394
C2-Cl10	1.742	1.754
C3-C4	1.381	1.388
C3-H7	1.073	1.082
C4-C5	1.379	1.390
C4-H8	1.071	1.081
C5-C6	1.381	1.390
C5-N11	1.466	1.478
C6-H9	1.072	1.082
N11-O12	1.187	1.225
N11-O13	1.187	1.225
C14-H15	1.085	1.093
C14-H16	1.085	1.093
C14-H17	1.083	1.090
Bond Angle(°)		
C2-C1-C6	117.00	116.90
C2-C1-C14	122.48	122.31
C6-C1-C14	120.52	120.79
C1-C2-C3	122.46	122.50
C1-C2-Cl10	119.76	119.54
C3-C2-Cl10	117.78	117.96
C2-C3-C4	119.84	119.76
C2-C3-H7	119.79	119.74
C4-C3-H7	120.36	120.49
C3-C4-C5	118.08	118.25
C3-C4-H8	121.26	121.57
C5-C4-CH8	120.66	120.18
C4-C5-C6	122.24	122.07

The optimized bond lengths of C-C in 2Cl5NT fall in the range: 1.404-1.39 Å at B3LYP/6-311++G(d,p). While the introduction of the substituent group causes slight difference between them. The breakdown of hexagonal symmetry of the benzene ring is obvious from the elongation of C1-C2 (~1.404 Å) from the remaining C-C bond lengths are (~1.39Å). The asymmetry of the benzene ring is also evident from the negative deviation of C2-C1-C6 (116°), C3-C4-C5 (118°) and positive deviation of C1-C2-C3 (122°) from the normal value of 120° this may be due to electron donating nature of CH_3 group. The small discrepancy found between the experimental and theoretically calculated values, this is due to that the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecule in solid state.

4.2 Vibrational assignments

The molecule under consideration would belongs to the C_s point group. It has 17 atoms, so 45 normal modes of fundamental vibrations which span the irreducible representations: $31A^{'}+14A^{''}$. All 45 fundamental vibrations are active in both IR and Raman.

The harmonic-vibrational frequencies calculated for 2Cl5NT at ab initio HF and B3LYP level using 6-311++G(d,p) basis set is given in Table 2. The observed FT-IR and FT-Raman frequencies for various modes of vibrations are also presented in Table 2. Comparison of the frequencies calculated by B3LYP with experimental values reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with experimental values. Any way not withstanding the level of calculations it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experiment. In our study we have followed two different scaling factors B3LYP/6-311++1G(d,p): 0.9668 and HF/6-311++G(d,p): 0.9050 [28].

(i) C-H Vibrations: The 2 chloro-5-nitrotoluene molecule give rise to three C-H stretching, three C-H in-plane bending vibrations and three C-H out-of-plane bending vibrations. Since 2Cl5NT is a trisubstituted aromatic system it has two adjacent and one isolated C-H moieties. The aromatic structure shows the presence of C-H stretching vibrations in the region 3000–3100 cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibration [29]. The expected three C-H stretching vibrations correspond to (mode nos. 45-43) stretching modes of C3-H, C4-H and C6-H units. The vibrational mode nos: 45-43 assigned to aromatic C-H stretching computed by B3LYP/6-311++G(d,p) method at 3120, 3107 and 3098 cm^{-1} shows good agreement with recorded FT-IR spectrum at 3101-3064 cm^{-1} but the FT-Raman spectrum shows only one peak at 3077 cm^{-1} is assigned to C-H stretching vibration. The same C-H vibrations stretching vibrations computed by HF/6-311++G (d,p) method in the region 3076-3047 cm^{-1} are assigned to C-H stretching vibration.

The aromatic C-H in- plane bending modes of benzene and its derivatives are observed in the region 1300-1000cm^{-1}. The bands are sharp but are weak to medium intensity. The C-H in-plane bending vibrations computed in the range at 1291-985 cm^{-1} (mode nos: 30-23) by B3LYP/6-311++G(d,p) method shows good agreement with FT-IR spectral region at 1267-1068 cm^{-1} and 1267-1102 in FT-Raman spectral region respectively.

The C-H out-of-plane bending vibration falls in the FT-IR spectrum as a medium bands at 921, 837, 745 cm^{-1} shows good agreement with theoretically computed B3LYP/6-311++G(d,p) method at 945, 888, 811 701 cm^{-1} (mode nos: 22, 20, 19 and 17). The same vibrations computed by HF/6-311++G (d,p) also shows good agreement with experimental data. In general the aromatic C-H vibrations (viz stretching, in-plane and out of plane vibrations) calculated theoretically are in good agreement with experimental and literature value [29].

Table 2. Comparison of the observed (FT-IR and FT-Raman) and calculated vibrational frequencies of 2-chloro-5-nitrotoluene

Vibrational mode nos.	**Species**	**Experimental (cm^{-1})**		**Scaled wavenumbers (cm^{-1})**		**Vibrational assignments**	**Ir**	**Raman**	**PED (%)**
		FT-IR	**FT-Raman**	**HF/6-311++G(d,p)**	**B3LYP/6-311++G(d,p)**				
1	A’’			39	44	τ NO_2	0.2375	0.0223	τ NO_2 (79)
2	A’’		67br	91	86	γ C-C1	0.4163	4.3572	γ C-C1(69)
3	A’’			153	144	τ CH_3	0.08	0.2363	τ CH_3 (84)
4	A’’			191	186	γ C-CH_3	2.1478	0.033	γ C-CH_3 (94)
5	A’			193	188	β C-NO_2	1.0496	4.4804	β C-NO_2(86)
6	A’		219w	247	244	β C-CH_3 + β C-Cl	0.2517	0.6616	β C-CH_3 (74)+ β C-Cl (20)
7	A’’			295	284	γ C-C-C	1.7829	4.9109	γ C-C-C (91)
8	A’		315	307	303	β C-C-C	4.4734	0.0049	β C-C-C (72)
9	A’		394w	385	380	β C-C-C	1.3791	2.0356	β C-C-C (88)
10	A’	425br		441	430	β C-C-C	0.1797	3.7815	β C-C-C (90)
11	A’			505	500	β C-CH_3	3.141	11.0816	β C-CH_3 (79)
12	A’’	516m		515	505	γ C-C-C	0.0889	0.0125	γ C-C-C(95)
13	A’		543w	533	528	β C-NO_2	5.1839	5.9939	β C-NO2(86)
14	A		574w	569	562	β C-C-C	3.5773	15.7398	β C-C-C(87)
15	A’’	673m		673	655	γ C-C-C	13.4649	1.4197	γ C-C-C(90)
16	A’	690w	698m	688	685	υ C-Cl	0.0735	0.7114	υ C-Cl(74)
17	A’’	745s		738	701	γ C-NO_2 + γ C-H	3.043	48.5332	γ C-NO_2(63) + γ C-H(24)
18	A’	827ms		816	794	υ C-CH_3+ **δ** NO_2	5.1636	31.4545	υ C-CH_3(71)+ **δ** NO_2(22)

Table cont’d

Vibrational mode nos.	Species	Experimental (cm^{-1})		Scaled wavenumbers (cm^{-1})		Vibrational assignments	Ir	Raman	PED(%)
		FT-IR	FT-Raman	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)				
19	A’	837m		849	811	γ C-H	1.5676	15.0296	γ C-H(92)
20	A’’			926	888	γ C-H	2.7772	34.6914	γ C-H(93)
21	A’	893ms		926	904	Ring breathing	1.7236	12.0009	
22	A’’	921ms	923w	987	945	γ C-H	1.5863	0.1351	γ C-H(94)
23	A’			989	985	CH$_3$ Rocking + β C-H	1.4652	0.2231	CH$_3$ Rocking (69)+ β C-H(18)
24	A’			1040	1027	CH$_3$ Rocking	12.6159	93.9149	CH$_3$ Rocking(54)
25	A’		1062m	1053	1028	υ C-Cl + β C-CH$_3$	0.7072	2.49	υ C-Cl (71)+ β C-CH$_3$(12)
26	A’	1068s		1104	1079	β C-H	9.0732	2.9205	β C-H(97)
27	A’	1124m	1102m	1116	1116	β C-H	1.6461	2.9327	β C-H(98)
28	A’	1208w		1154	1184	υ C-CH$_3$+ β C-H	9.7951	30.2156	υ C-CH$_3$(56)+ β C-H(27)
29	A’			1200	1240	β C-H	22.3307	17.0717	β C-H(61)
30	A’	1267w	1267m	1264	1291	υ C-C + β C-H	0.4027	3.412	υ C-C(65) + β C-H(30)
31	A’	1298ms		1393	1322	υ sym NO$_2$	2.0222	11.1839	υ sym NO$_2$(83)
32	A’	1347m	1348vs	1403	1374	CH$_3$ sym deform	9.6533	2.4877	CH$_3$ sym deform(59)
33	A’	1384vs	1380w	1451	1381	υ C-C + β C-H	16.437	104.4055	υ C-C(65) + β C-H(23)
34	A’	1436w	1435w	1453	1433	CH$_3$ asy deform	17.2582	6.6991	CH$_3$ asy deform(77)
35	A’	1444w		1466	1436	CH$_3$ asy deform	106.1105	307.4376	CH$_3$ asy deform

Table cont’d

Vibrational mode nos.	**Species**	**Experimental (cm^{-1})**		**Scaled wavenumbers (cm^{-1})**		**Vibrational assignments**	**Ir**	**Raman**	**PED(%)**
		FT-IR	**FT-Raman**	**HF/6-311++G(d,p)**	**B3LYP/6-311++G(d,p)**				
36	A’	1468m		1484	1453	υ C-C	30.9752	6.531	υ C-C(96)
37	A’	1522vs	1520w	1582	1526	υ_{asy} NO_2 + υ C-C	35.6892	64.5419	υ_{asy} NO_2 (55)+ υ C-C(32)
38	A’	1575m	1576s	1606	1560	υ C-C	67.6243	78.9046	υ C-C(73)
39	A’	1611m	1612w	1656	1593	υ C-C	0.9062	383.178	υ C-C(99)
			2684vw			overtone/ combination			
		2866vw				overtone/ combination			
40	A’		2934w	2880	2935	υ sym C-H in CH_3	128.4549	18.7087	υ sym C-H in CH_3(88)
41	A’			2933	2986	υ asym C-H in CH_3	73.1423	14.8486	υ asym C-H in CH_3(81)
42	A’			2952	3017	υ asym C-H in CH_3	56.6739	18.0986	υ asym C-H in CH_3(89)
43	A’	3067w	3077m	3047	3098	υ C-H	65.6861	1.2911	υ C-H(99)
44	A’	3086w		3068	3107	υ C-H	52.9647	1.4248	υ C-H(99)
45	A’	3101m		3076	3120	υ C-H	78.3683	1.9974	υ C-H(99)

w-weak ; vw- very weak ; s-strong ; vs-very strong ; m-medium; br, sh- broad, shoulder ; υ - stretching; υsym – symmetric stretching ; υ_{asy}- asymmetric stretching ; β- in plane bending ; γ- out-of –plane bending ; ω – wagging ; t- twisting ; δ –scissoring ; τ- torsion.

(ii) C-Cl vibrations: The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule [30]. The assignments of C-Cl stretching and deformation vibration have been made by comparison with halogen substituted benzene derivatives [31]. Mooney [32, 33] assigned vibrations of the C-X group (X= Cl, Br, I) in the frequency range of 1129-480 cm^{-1}. Based on the above literature data, the theoretically computed by B3LYP/ HF 6-311++G (d,p) method at 685/688 cm^{-1}(mode no: 16) are assigned to C-Cl stretching vibration shows good agreement with experimental FT-IR and FT-Raman bands at 690 and 698 cm^{-1}. The C-Cl in-plane bending vibration computed by B3LYP/6-311++G(d,p) method at 244 cm^{-1} (mode no:6) correlate well with FT-Raman band at 219 cm^{-1}. The C-Cl out-of- plane bending vibration computed by B3LYP/6-311++G(d,p) method at 86 cm^{-1} (mode no:2) shows good agreement with HF method, but the recorded spectrum does not show the good correlation and also show a negative deviation of about 23 cm^{-1}.

(iii) Phenyl ring vibrations: There are six equivalent C-C bonds in benzene and consequently there will be six C-C stretching vibrations. In addition, there are several C-C-C in-plane and out-of – plane bending vibrations of the ring carbons. However, due to high symmetry of benzene, many modes of vibrations are infrared inactive. In general the bands around 1400 to 1650 cm^{-1} in benzene derivatives are assigned to skeletal stretching C-C bands. The FT-IR band observed at 1611, 1575, 1522, 1468 1384 and 1267 cm^{-1} and 1612, 1576, 1520, 1435, 1380 and 1267 cm^{-1} in FT-Raman spectrum are assigned to C-C stretching vibration shows good agreement with theoretically computed B3LYP/ 6-311++G (d,p) method in the region at 1593- 1291 cm^{-1} (mode nos: 39-30). The same vibration computed by HF method also shows the same kind of result. The ring breathing mode observed as medium strong band at 839 cm^{-1} in FT-IR spectrum show good agreement with theoretically computed B3LYP/6-311++G(d) method at 904 cm^{-1} (mode no:21). For the in-plane deformation vibration Shimanouchi et al. [34] gave the frequency data for different benzene derivatives as a result of normal coordinate analysis.

The theoretically calculated C-C-C in plane bending vibration i.e. on viewing the vibration we found that C6-C1-C2 and C3-C4-C5 angle vary in the opposite direction, coupled with C1-CH_3 and C5-NO_2 stretching modes. The pairs C2-C5 and C3-C6 of the phenyl ring move radially such that when C2 and C5 come closer, C3 and C6 move away. In general, the C-C-C out- of-plane and in- plane - bending vibrational wavenumber observed in FT-IR spectrum and FT-Raman spectrum shows good agreement with theoretically computed wavenumber.

(iv) CH_3 vibrations: The title molecule 2Cl5NT under consideration possesses one CH_3 groups in the para position of the ring. For the assignments of CH_3 group frequencies one can expect that nine fundamentals can be associated to each CH_3 group, namely the symmetrical stretching in CH_3 (CH_3 sym.stretch) and asymmetrical stretching (CH_3 asy, stretch), in- plane stretching modes (i.e. in plane hydrogen stretching mode); the symmetrical (CH_3 sym. deform) and asymmetrical (CH_3 asy deform) deformation modes; the in-plane rocking (CH_3 ipr) out- of - plane rocking (CH_3 opr) and twisting (t CH_3) bending modes. For the O-CH_3 group compounds, the stretching mode appear in the range 2825-2870 cm^{-1}, lower in magnitude compared to its value in CH_3 compounds(2860-2953 cm^{-1}), whereas two asymmetric modes for both the type of the compounds lie in the same region 2925-2985 cm^{-1}.

In the case of 2Cl5NT, the asymmetric stretching vibrations have been identified at 3017, 2986 cm^{-1} by B3LYP method and symmetric stretching vibrations has been identified at 2935 cm^{-1}. The recorded FT-Raman spectrum show only one peak observed at 2934 cm^{-1} is assigned to C-H symmetric stretching vibration of CH_3. The same vibration computed by HF /6-311++G (d,p) method at 2952-2880 cm^{-1} (mode no: 42-40) are assigned to asymmetric and symmetric bending vibrations. The rocking vibration for CH_3 has been calculated at 1027-985 cm^{-1} by B3LYP/6-311++G(d) method.

The asymmetric and symmetric CH_3 deformation vibrations computed by B3LYP/6-311++G(d,p) method at 1436, 1433 and 1374 cm^{-1} shows good agreement with FT-IR bands at 1444, 1436 and 1347 cm^{-1}. The CH_3 torsional mode computed by B3LYP/6-311++G(d,p) method at 144 cm^{-1} (mode no.3) also shows good agreement with HF method at 153 cm^{-1}.

(v) C-CH_3 vibrations: It is noted from literature that strong band around 1200 cm^{-1} appears due to valence oscillations in toluene and substituted toluenes. The C-CH_3 stretching computed at 1184 cm^{-1} (mode no. 28) by B3LYP/6-311++G(d,p) method shows good agreement with FT-IR recorded band at 1208 cm^{-1}. The C-CH_3 in plane bending and out of plane bending vibration computed by B3LYP/6-311++G(d,p) and HF method also shows good agreement with recorded spectrum.

(vi) NO_2 Vibration: The deformation vibration of NO_2 group (rocking) contributes to several modes in the low frequency range. The frequency computed theoretically by B3LYP/6-311++G(d,p) method at 44 cm^{-1} (mode no 1) is assigned to torsion mode of NO_2 group. In all nitro substituted benzene, two strong bands are observed near 1530 and 1340 cm^{-1} which are the asymmetric and symmetric stretching vibrations of NO_2 groups and provide an unmistakable identity for the existence of NO_2 group in the molecule [35, 36].

Based on the above literature data the very strong band observed at 1298 cm^{-1} in FT-IR spectrum are assigned to NO_2 symmetric stretching vibration. The theoretically computed B3LYP/6-311++G (d,p) 1322 cm^{-1}(mode no: 31) is assigned to NO_2 symmetric stretching vibration. The NO_2 asymmetric stretching vibration computed by B3LYP/6-311++G(d,p) method 1526 cm^{-1} also coincides exactly with very strong FT-IR band at 1522 cm^{-1}.

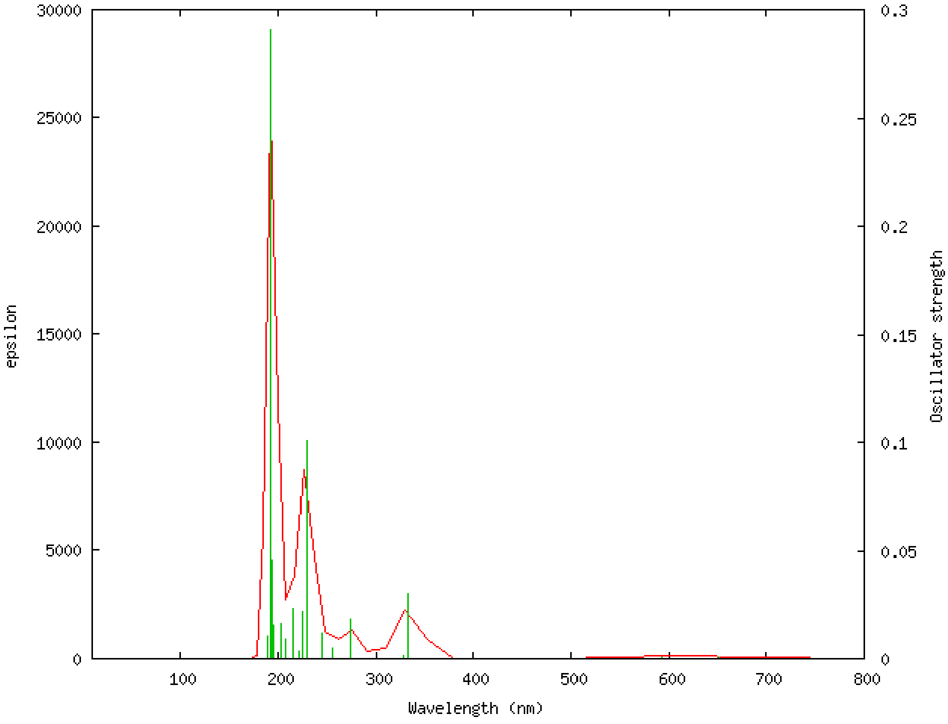


Fig. 6. Calculated electronic absorption spectra of 2-chloro-5-nitrotoluene

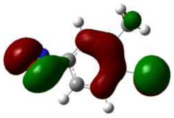
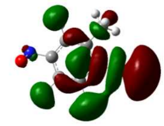
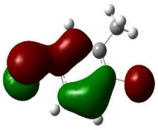
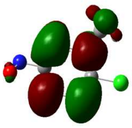
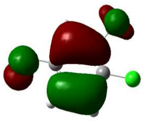
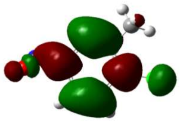
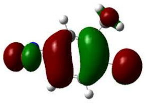
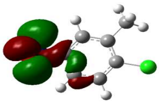
MO	Occupied	MO	Unoccupied
(HOMO-3)	 -8.657914772	(LUMO+3)	 -0.021225048
(HOMO-2)	 -8.099804856	(LUMO+2)	 -1.24629128
(HOMO)-1	 -7.835308104	(LUMO+1)	 -1.4354119
(HOMO)	 -7.277470304	(LUMO)	 -4.874413908

Fig.7. Isodensity plots (isodensity contour = 0.02 a.u.) of the frontier orbitals of 2-chloro-5-nitrotoluene

4.3 Electronic absorption spectra

From a theoretical point of view, we have characterized the orbital nature of the electronic transition energies and the net charge transfer in excited electronic states. Time depended B3LYP (TD-B3LYP) calculations of electronic absorption spectrum were performed on the optimized structures at the same 6-31G++(d,p) basis set. Our present study has permitted us to determine the three main electronic transitions localized under the broad absorption spectral band in the spectral region between 250 and 450 nm. The HOMO–LUMO gap of 2 chloro-5-nitrotoluene is 2.403eV, TDDFT calculations on electronic absorption spectra in vacuum were performed, and the results are shown in Fig.6. It is seen that, the absorption in the visible region is much weaker than that in the UV region. In order to obtain the icroscopic information about the electronic transitions, we check the corresponding MO properties. The absorption band in visible and near-UV region for 2 chloro-5-nitrotoluene are listed in Table 3. The data of Table 3 and Fig.7 are based on the B3LYP/6-311++G(d,p) results.

Table 3 Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions of the absorption bands in visible and near- UV region for the 2-chloro-5-nitrotoluene

State	Configurations composition (corresponding transition orbitals)	Excitation energy (eV/nm)	oscillator strength (f)
1	-0.29797 (42 → 45) 0.20333(43 → 45) 0.49920(44 → 45)	0.9482 /1307.55	0.0000
2	-0.10573(38 → 45) -0.20916(41 → 45) 0.31864(42 → 45) -0.34431(43 → 45) 0.42888(44 → 45)	1.9042 / 651.11	0.0010
3	0.64970(40 → 45)	2.0898 / 593.28	0.0008
4	0.43945(42 → 45) 0.54420(43 → 45)	2.1851/ 567.41	0.0001
5	-0.21163(38 → 45) -0.12938(39 → 45) 0.11348(40 → 46) 0.52001(41 → 45)	3.7271 / 332.66	0.0303
6	0.68851(39 → 45)	3.7771 / 328.25	0.0014
7	0.64048(38 → 45) 0.10078(40 → 46) 0.10134(42 → 45)	4.5188 / 274.38	0.0184
8	0.68405(37 → 45) -0.10193(44 → 46)	4.8507 / 255.60	0.0047
9	-0.11578(42 → 46) -0.37354(43 → 46) 0.13478(43 → 47) 0.21714(44 → 46) 0.52992(44 → 47)	5.0582 / 245.12	0.0119
10	-0.21473(36 → 45) -0.16850(42 → 46) 0.18841(43 → 46) 0.12467(43 → 47) 0.52737 (44 → 46) -0.18381(44 → 47)	5.4094 / 229.20	0.1007
11	0.65487(36 → 45) 0.15658(44 → 46)	5.5177 / 224.70	0.0215
12	0.68636 (35 → 45) 0.11726 (38 → 45)	5.5953 / 221.59	0.0036
13	0.10533(41 → 46) 0.56039(42 → 46) -0.28598(43 → 46) 0.13380(43 → 47) 0.13708(44 → 46) -0.17562(44 → 47)	5.7567 / 215.38	0.0230
14	0.54291(42 → 47) -0.17495(43 → 46) -0.35545(43 → 47) -0.13480(44 → 47)	5.9516 / 208.32	0.0093
15	0.66878(34 → 45) -0.11924(41 → 46) 0.11797(42 → 47)	6.0911 / 203.55	0.0158
16	0.68135(44 → 48)	6.2025 / 199.89	0.0001
17	0.13242(34 → 45) 0.54903(41 → 46) -0.17123(41 → 47) -0.14099(42 → 46) -0.21574(42 → 47) -0.13333(43 → 46) -0.16257(43 → 47)	6.3410 / 195.53	0.0153
18	0.68039(33 → 45)	6.3905 / 194.01	0.0452
19	0.13488(33 → 45) 0.12222 (38 → 47) 0.23651(41 → 46) 0.29929(41 → 47) 0.23716(42 → 46) 0.27026(43 → 46) -0.22286(43 → 47) 0.24282(44 → 47)	6.4302 / 192.81	0.2908
20	0.10703(29 → 45) 0.19517(39 → 46) 0.64269(40 → 46)	6.5550 / 189.14	0.0106

5. Other molecular properties

Several calculated thermodynamic parameters are presented in Table 4. Scale factors have been recommended [37] for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy, Svib (T). The variations in the ZPVE's seem to be insignificant. The total energies and the change in the total entropy of 2Cl5NT at room temperature at different methods are also presented.

Table 4. Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol^{-1} K^{-1}) and dipole moment (D) for 2-chloro-5-nitrotoluene

Parameters	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
Total energy	-932.253	-935.825
Zero-point energy	81.2533	75.4973
Rotational constants		
	2.37605	2.33556
	0.54821	0.53837
	0.44666	0.4387
Entropy		
Total	96.179	98.549
Translational	41.317	41.317
Rotational	30.692	30.745
Vibrational	24.17	26.487
Dipole moment	3.7197	3.8199

CONCLUSION

We have carried out ab initio HF and DFT calculations on the structure and vibrational spectra of 2Cl5NT. Vibrational frequencies, molecular geometry also calculated by above methods. When compared to HF method B3LYP/6-311++G (d,p) method agree very well with experimental result. Any discrepancy noted between the observed and calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. On the basis of the agreement between the calculated and observed results, assignments of fundamental vibrational modes of 2Cl5NT were examined and all the assignments are proposed. This study demonstrates that scaled DFT/B3LYP calculations are powerful approach for understanding the vibrational spectra of medium sized organic compounds used in pharmaceutical application. The electronic absorption spectral features in visible and near-UV region were assigned based on the qualitative agreement to TDDFT calculations. The absorptions are all ascribed to π→π* transition.

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