Spectroscopic Studies and Normal Coordinate Analysis of 2,5-Dichloro Phenyl Isocyanate

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ABSTRACT

The FTIR and FT-Raman spectra of 2,5-Dichloro Phenyl Isocyanate (DCPIC) have been recorded in the region 4000–400 and 4000–100 cm^{-1}, respectively. The structural analysis, optimized geometry, frequency and intensity of the vibrational bands of DCPIC were obtained by the density functional theory (DFT) with complete relaxation in the potential energy surface using ab initio (HF/3-21+G) and DFT (B3LYP/3-21+G) methods. The harmonic vibrational frequencies were calculated and the scaled values have been compared with experimental FTIR and FT-Raman spectra. The observed and the calculated frequencies are found to be in good agreement. Calculations of molecular orbital geometry show that the visible absorption maxima of these molecules correspond to the electron transition between frontier orbitals such as translation from HOMO to LUMO. As can be seen from theoretical UV–Vis spectra, the energies of important MO's and the λ_{max} of the compound were also determined from TD-DFT method. The strong band system falling on the higher wavelength side with maximum at 203.53 for 2,5-Dichloro Phenyl Isocyanate and it is attributed to the most prominent π-π* transitions.

KEYWORDS

FTIR, FT-Raman, Dichloro Phenyl Isocyanate, ab initio, DFT and UV–Vis spectra.

1. INTRODUCTION

The importance of organocyanates in synthetic and drug industries has made them to the subject of many studies [1]. The combined roles of isocyanate and substituents in the vibration structure of aromatic phenyl isocyanate molecules are of spectroscopic interest. After extensive studies on the phenyl isocyanate by many workers [2–13], recently, structures and vibrational assignments for three isomeric compounds namely, 3-chloro, 4-chloro and 5-chloro-2-methylphenyl isocyanates [14] and 2-methyl-3-nitrophenyl isocyanate [15] have been reported. Also Vibration and DFT analysis of two compounds 2-methyl-3-nitrophenyl isocyanate and 4-methyl-2-nitrophenyl isocyanate have been reported by J. Tonannavar et. al., [16]. 2-Methoxyphenyl isocyanate and 2-Methoxyphenyl isothiocyanate have been reported by Jayashree Yenagi, et. al., [17].

The combination of vibrational spectroscopy coupled with quantum mechanical calculations can be a powerful method for understanding the structural, conformational, vibrational and electronic behaviour of molecules. Electronic correlation to the calculations is necessary to get more reliable results on the structural parameters, physio-chemical properties and vibrational properties[18].

Thus, in the present investigation, owing to the industrial and biological importance of 2,5-Dichloro Phenyl Isocyanate (DCPIC) the vibrational frequencies are determined using quantum chemical calculations. The structural parameters and thermodynamic properties of the compounds were also determined from ab initio/HF and DFT/ B3LYP methods with the standard 3-21+G basis set and are discussed in detailed manner.

2. EXPERIMENTAL ANALYSIS

2.1. Measurement of the vibrational spectra

DCPIC was obtained from Lancaster chemical company, UK and used as such for the spectral measurements without further purification.

2.1.1. Infrared spectra

The infrared spectra were recorded with a BRUKER IFS 66V model FT-IR spectrometer equipped with a room temperature MCT detector. The spectra of the DCPIC molecules were recorded by using KBr pellets in the 4000–400 cm^{-1} spectral region.

2.1.2. Raman spectra

The Raman spectra (3500–50 cm^{-1}) were measured with a BRUKER IFS 66V model interferometer equipped with FRA-106 FT-Raman spectrometer. 1064 nm of an Nd:YAG laser was used for excitation at 200 mW output power. The reported wavenumbers are expected to be accurate within ± 1 cm^{-1}.

3. METHOD OF CALCULATIONS

The initial geometry of DCPIC was optimized using the ab initio/HF and DFT/B3LYP of GAUSSIAN 09W program package [78]. The vibrational frequency analysis was computed using ab initio (HF/3-21+G) and DFT (B3LYP/3-21+G) methods to determine the nature of a stationary point found by geometry optimization. The most of the observed frequencies are generally lower than the calculated frequencies due to anharmonic nature of molecular vibrations. In principle, we should compare the calculated frequencies with experimental harmonic frequencies. However, as all the vibrations are more or less anharmonic, harmonic frequencies are not directly observable. Despite they can be deduced theoretically, it requires detailed knowledge of both quadratic and anharmonic force constants and is only feasible for every molecule. It should be pointed out that reproduction of observed fundamental frequencies is more desirable practically because they are directly observable in a vibrational spectrum. Therefore, comparison between the calculated and the observed vibrational spectra helps us to understand the observed spectral features. In order to improve the agreement of theoretically calculated frequencies with experimentally calculated frequencies, it is necessary to scale down the calculated frequencies by using the scale factors 0.914, 0.87, 0.99 and 1.07 for HF/3-21+G and 0.955, 0.93, 1.01, 0.99, and 1.07 for B3LYP/3-21+G. Hence, the vibrational frequencies theoretically calculated at HF/3-21+G and B3LYP/3-21+G are scaled down by using MOLVIB 7.0 version written by Tom Sundius [20-22].

4. RESULTS AND DISCUSSION

4.1. Molecular geometry

The molecular structures of DCPIC along with numbering of atoms are shown in Fig.1. From the structural point of view, the molecules belong to have C1 point group symmetry and hence, all the calculated frequency transforming to the same symmetry species. The optimized geometrical parameters (bond lengths, bond angles and diheadral angles) obtained by HF and B3LYP methods with 3-21+G basis set for DCPIC is presented along with the experimental data of Isocyanate [23-25] in Table 1.

4.2. ANALYSIS OF VIBRATIONAL SPECTRA

The molecule DCPIC consists of 14 atoms, has C1 symmetry and it has 36 normal modes of vibrations. The FT-IR and FT-Raman spectra of the DCPIC are shown in Figs. 2 and 3, respectively. The observed FT-IR and FT-Raman frequencies for various modes of vibrations are also presented in Table 2 for the DCPIC. Comparison of the frequencies calculated by ab initio HF B3LYP with experimental values reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Anyway, 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 the present investigation, the scale factors for HF and B3LYP methods are 0.9752 and 0.9713.

C–H Vibrations

The wavenumbers in the high wavenumber region of the vibrational spectra are systematically higher than their corresponding counterparts. Such differences are usually observed for X–H vibrations (X=C, N). Moreover, the substitition group does not appear to affect the position of characteristic C–H bands and these bands occur in the range 3100–3000 cm^{-1}. In the present investigation, the C–H vibrations are observed at 3294 cm^{-1} in FT-IR spectrum and at 3113, 3078 cm^{-1} in FT-Raman spectrum, respectively for DCPIC. The assigned values of C–H showed good agreement with the available literature data [26].

The in-plane C–H bending vibrations appear in the range 1300–1000 cm^{-1} in the substituted benzenes and the out-of-plane bending vibrations in the range 1000–750 cm^{-1} [27,28].The C-H in-plane bending vibrations have been observed at 1184, 1133, 1096 cm^{-1} in FT-IR spectrum with a support at 1137, 1096 cm^{-1} in FT-Raman spectrum for DCPIC, respectively.

For DCPIC, the C–H out-of-plane bending vibrations fall at 873, 826, 814 cm–1 in FT-IR spectrum and 918 cm–1 in FT-Raman, 795, 775 cm–1 in FT-IR spectra, respectively. These in-plane and out-of-plane vibrational frequencies are found to be well within their characteristics region.

C–C Vibrations

The bands between 1430–1650 cm^{-1} in the aromatic and heteroaromatic compounds are assigned to C=C stretching vibrations [29]. Accordingly, in the present investigation, the C–C stretching vibrations of DCPIC are observed at 1649, 1594, 1585, 1519, 1469, 1461 cm^{-1} in FT-IR spectrum. As predicted in the earlier reference [30], for DCPIC, the prominent peaks in FT-IR and FT-Raman spectra, due to C–C skeletal vibrations are presented in Table 2.

C–N Vibrations

The identification of C–N vibrations is a difficult task, since the mixing of vibrations [31,32] is possible in this region 1600–1500 cm^{-1}. However, with the help of the force field calculations, the C–N vibrations are identified and assigned in this investigation. The bands appearing at 1287 cm^{-1} in FT-IR and 1286 in FT-Raman spectra are assigned to C–N stretching vibrations for DCPIC. The C–N in-plane bending and out-of-plane bending vibrations of DCPIC are presented in Table 2 shows good agreement with calculated values.

C–Cl vibrations

The vibrations belong 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. Generally, the C–Cl absorption is obtained in the broad region between 850–550 cm^{-1}. Therefore, the strong band found at 742 and 723 cm^{-1} in the FT-IR and FT-Raman spectra have been designated to C–Cl stretching mode of vibration for DCPIC. These are in good agreement with the literature data [33].

NCO Vibrations

There are six vibrations for NCO moiety: asymmetric stretching, symmetric stretching, in-plane bending, in-plane wagging, out-of-plane bending and out-of-plane wagging vibrations [36]. The asymmetric stretching vibration appears always as the strongest and broad band near at 2274 cm^{-1} in the FT-IR spectrum; conversely, the band is an unfailing evidence for the presence of the isocyanate moiety [6-8].

In DCPIC, the FT-IR band is observed at 2281 cm^{-1} as a weak band due to asymmetric stretching vibration. The symmetric stretching vibration is generally observed to be FT-IR weak but FT-Raman strong in the range 1460–1340 cm^{-1} [35,138]. However, in some substituted phenyl isocyanates, the band has been observed to be strong in the FT-IR spectrum [3,6,37]. In the present study, the FT-IR and FT-Raman spectra of the compound show a very strong and medium band at 1409 and 1413 cm^{-1} and assigned to symmetric

stretching vibration. The weak FT-Raman bands at 661 and 415 cm^{-1} in DCPIC have been assigned to in-plane bending and wagging, respectively. The medium FT-Raman bands at 132 and 119 cm^{-1} are assigned to out-of- bending and wagging modes of vibration, respectively.

5. UV–VIS SPECTRAL ANALYSIS

Ultraviolet spectral analysis of DCIPC has been investigated by TD-DFT/B3LYP/3-21+G method. Calculations of molecular orbital geometry show that the visible absorption maxima of these molecules correspond to the electron transition between frontier orbitals such as translation from HOMO to LUMO. As can be seen from theoretical UV–Vis spectra in Fig.4, absorption maxima values have been found to be 203.53, 202.99 and 184.89 nm for DCPIC. The λ_{max} is a function of substitution, the stronger the donor character of the substitution, the more electrons pushed into the molecule, the larger λ_{max}. The calculated results involving the vertical excitation energies, oscillator strength (f) and wavelength are carried out and presented as in Table 3

8.6. CONCLUSION

Based on the ab initio HF and density functional theory calculations with 3-21+G level, complete vibrational properties of 2,5-Dichloro Phenyl Isocyanate has been investigated by FT-IR and FT-Raman spectroscopy. A good correlation is found between the computed and experimental wavenumbers. The computed geometrical parameters are in good agreement with the observed X-ray diffraction data of similar compound. The energies of important MO's and the ——————————————max of the compound were also determined from TD-DFT method. The strong band system falling on the higher wavelength side with maximum at 203.53 for 2,5-Dichloro Phenyl Isocyanate are attributed to the most prominent π-π* transitions. Thus the present investigation provides complete vibrational assignments, structural information and electronic properties of the title compound.

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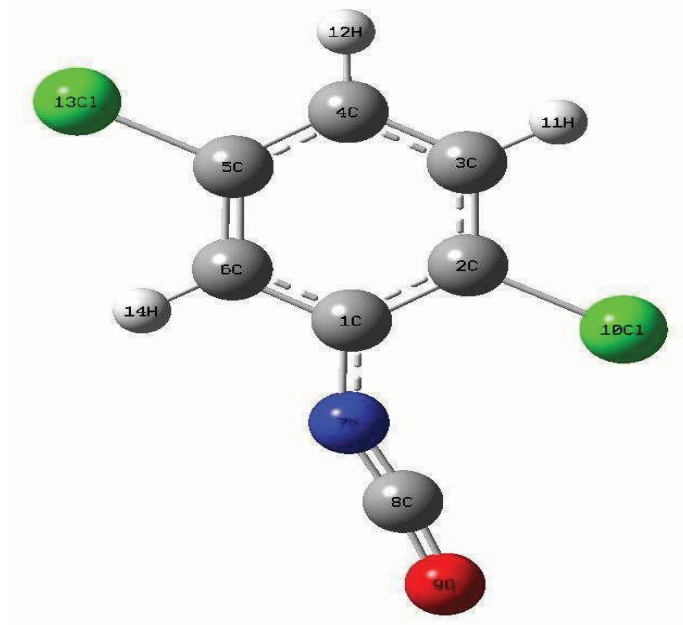
Fig. 1: Molecular structure of 2,5-dichloro phenyl isocyanate
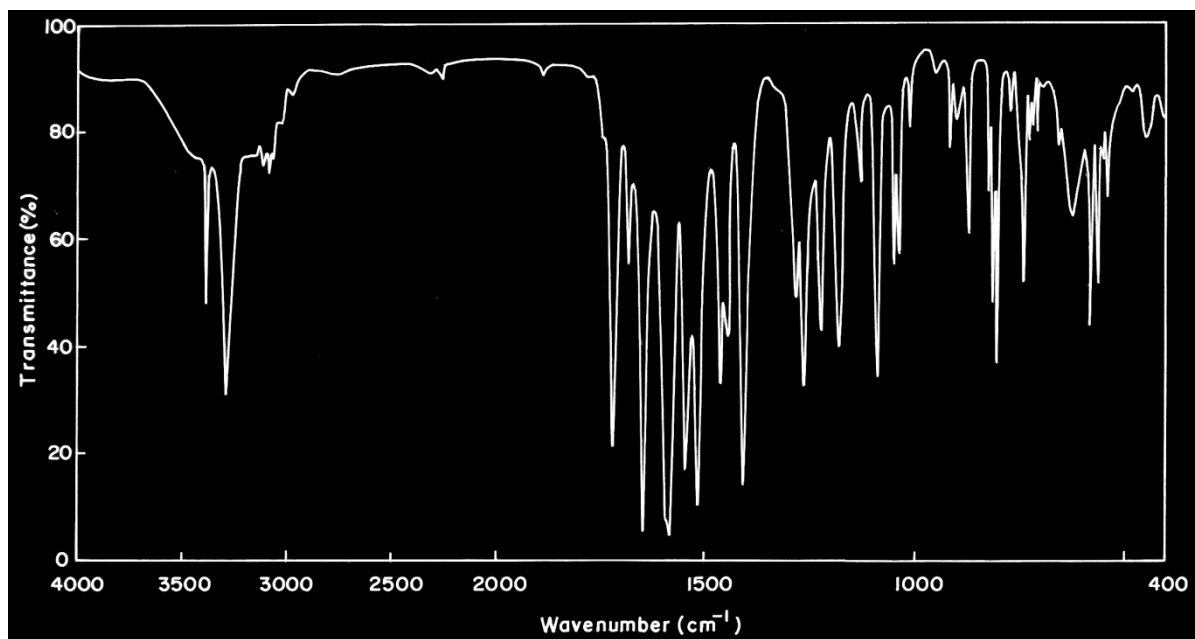

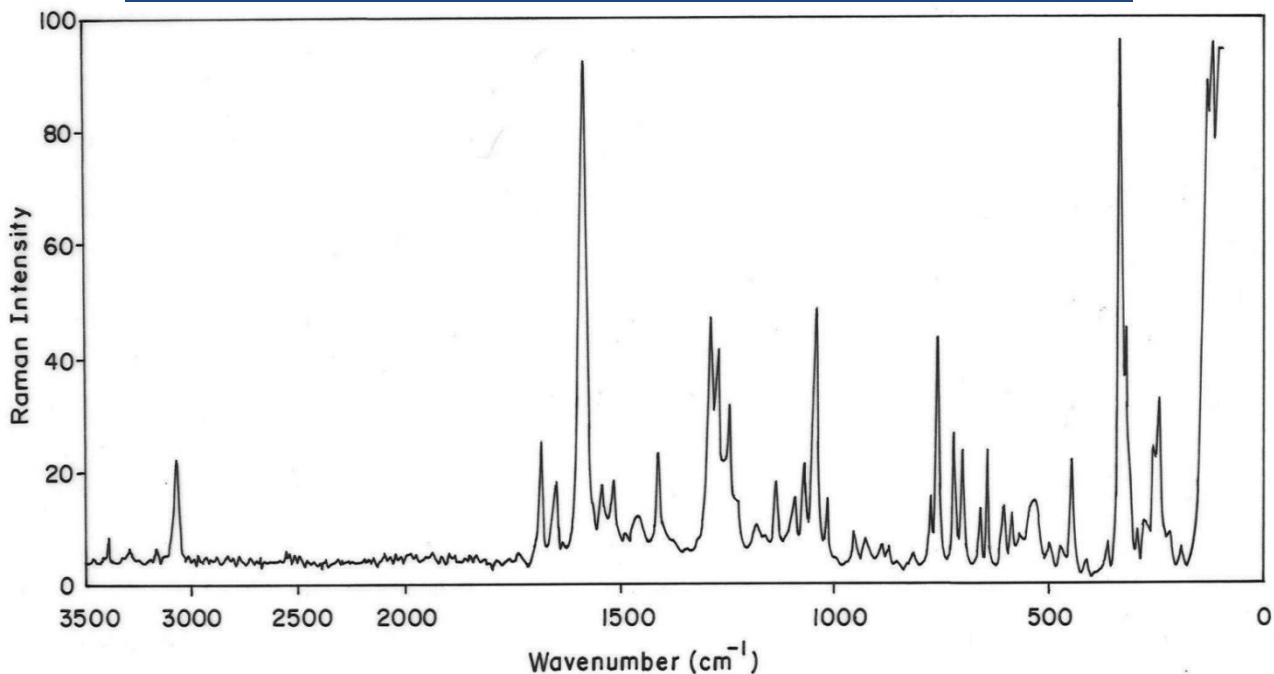**Fig. 2: The FT-IR spectrum of 2,5-dichloro phenyl isocyanate**

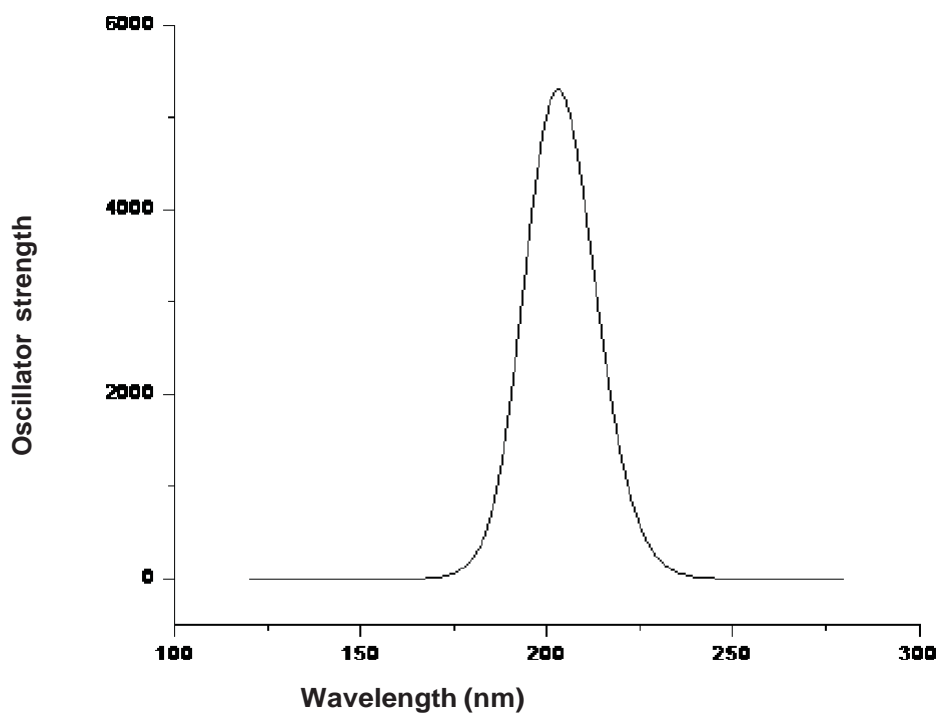**Fig. 3: The FT-Raman spectrum of 2,5-dichloro phenyl   isocyanate**

Fig.4 : The theoretical UV-VIS spectrum for 2,5-dichloro phenyl isocyanate

Table 1: Optimized geometrical parameters of 2,5-dichloro phenyl isocyanate by HF/3-21+G and B3LYP/3-21+G methods.

Bond length	Value(Å)		Exptᵃ	Bond Angle	Value(°)		Exptᵃ	Dihedral Angle	Value(°)	
	B3LYP/ 3-21+G	B3LYP/ 3-21+G			B3LYP/ 3-21+G	B3LYP/ 3-21+G			B3LYP/ 3-21+G	B3LYP/ 3-21+G
C1-C2	1.3852	1.4045	1.394	C2-C1-C6	118.8352	118.345	120.6	C6-C1-C2-C3	-0.0068	0.0
C1-C6	1.3913	1.406	1.396	C2-C1-N7	121.767	123.0668	120.2	C6-C1-C2-Cl10	179.9769	180.0
C1-N7	1.37	1.3818	1.394	C6-C1-N7	119.3978	118.5881	120.1	N7-C1-C2-C3	180.0079	180.0
C2-C3	1.3766	1.3882	1.399	C1-C2-C3	121.1751	121.604	120.1	N7-C1-C2-Cl10	-0.0083	0.0
C2-Cl10	1.8028	1.8205	1.766	C1-C2-Cl10	119.7914	119.3811	119.6	C2-C1-C6-C5	0.0073	0.0
C3-C4	1.3843	1.3984	1.414	C3-C2-Cl10	119.0335	119.0148	120.2	C2-C1-C6-H14	-179.9842	180.0
C3-H11	1.0709	1.0835	1.083	C2-C3-C4	119.9639	119.8444	120.3	N7-C1-C6-C5	-180.0068	180.0
C4-C5	1.3767	1.3905	1.396	C2-C3-H11	119.6102	119.7555	120.05	N7-C1-C6-14	0.0017	0.0
C4-H12	1.0703	1.0827	1.083	C4-C3-H11	120.4258	120.4	120.05	C2-C1-N7-C8	-0.2041	0.0
C5-C6	1.3719	1.3849	1.388	C3-C4-C5	118.6112	118.4309	119.6	C6-C1-N7-C8	179.8107	180.0
C5-Cl13	1.8094	1.8262	1.766	C3-C4-H12	120.7432	120.738	120.7	C1-C2-C3-C4	-0.0001	0.0
C6-H14	1.0693	1.0819	1.084	C5-C4-H12	120.6456	120.8312	120.7	C1-C2-C3-H11	-180.002	180.0
N7-C8	1.1674	1.2022	1.201	C4-C5-C6	122.0971	122.4499	120.1	Cl10-C2-C3-C4	180.0161	180.0

C8-O9	1.1804	1.1982	1.171	C4-C5-Cl13	119.1852	118.9913	120.2	Cl10-C2-C3-H11	0.0142	0.0
				C6-C5-Cl13	118.7177	118.5588	120.2	C2-C3-C4-C5	0.0065	0.0
				C1-C6-C5	119.3175	119.3258	119.2	C2-C3-C4-H12	-179.9887	180.0
				C1-C6-H14	119.4927	119.2005	119.9	H11-C3-C4-C5	-179.9916	180.0
				C5-C6-H14	121.1898	121.4737	119.9	H11-C3-C4-H12	0.0132	0.0
				C1-N7-C8	170.6757	151.4908	140.3	C3-C4-C5-C6	-0.0061	0.0
								3-4-C5-Cl13	179.9953	180.0
								H12-C4-C5-C6	-180.0109	180.0
								H12-C4-C5-Cl13	-0.0095	0.0
								C4-C5-C6-C1	-0.0009	0.0
								C4-C5-C6-H14	179.9903	180.0
								Cl13-C5-C6-C1	179.9977	180.0
								Cl13-C5-C6-H14	-0.011	0.0

[a] Ref. [23-25].

Table 2: Vibrational assignments of fundamental modes of 2,5-dichloro phenyl isocyanate along with calculated frequencies and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using HF and B3LYP methods.

Modes	Symmetry Species	Observed fundamentals (cm^{-1})		Calculated fundamentals(cm^{-1})				Assignments with TED %
				HF/3-21+G		B3LYP/3-21+G		
		FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled	
1	A	3294	---	3791	3293	3242	3291	γC-H(100)
2	A	---	3113	3285	3124	3237	3121	γC-H(99)
3	A	---	3078	3268	3089	3220	3086	γC-H(100)
4	A	2281	---	2252	2274	2340	2291	γ_{as}NCO(92)
5	A	1649	---	1708	1658	1614	1637	γC=C(78)
6	A	1594	1594	1672	1608	1574	1584	γC=C(82)
7	A	1585	---	1619	1594	1538	1572	γC=C(81)
8	A	1519	---	1558	1528	1486	1507	γC-C(76)
9	A	1469	---	1482	1477	1394	1456	γC-C(79)
10	A	1461	---	1401	1456	1315	1449	γC-C(81)
11	A	1409	1413	1308	1395	1295	1398	γ_{ss}NCO(78)
12	A	1287	---	1267	1281	1184	1274	γC-N(81)
13	A	1184	---	1202	1197	1182	1183	βC-H(72)
14	A	1133	1137	1188	1148	1153	1135	βC-H(74)
15	A	1096	1096	1177	1109	1111	1106	βC-H(69)
16	A	873	---	1151	889	1065	882	ωC-H(68)
17	A	826	---	1129	839	1013	834	ωC-H(73)
18	A	814	---	1064	825	913	823	ωC-H(69)
19	A	807	---	1023	819	862	819	βring(82)

20	A	---	776	873	786	831	788	βring(81)
21	A	---	760	804	771	714	749	βring(79)
22	A	742	---	755	749	708	731	yC-Cl(82)
23	A	---	723	723	723	598	712	yC-Cl(84)
24	A	---	661	716	673	594	649	βNCO(74)
25	A	584	586	601	596	556	571	tring(75)
26	A	564	---	588	576	522	552	tring(71)
27	A	542	---	545	543	509	531	tring(69)
28	A	---	447	429	437	401	432	βC-N(65)
29	A	---	410	406	408	352	399	β_{ipw}NCO(88)
30	A	---	338	337	338	320	331	ωC-N(73)
31	A	---	322	326	324	267	329	βC-Cl(69)
32	A	---	276	299	287	260	283	βC-Cl(68)
33	A	---	268	211	257	195	258	ωC-Cl(72)
34	A	---	242	184	231	106	231	ωC-Cl (71)
35	A	---	132	137	135	89	121	ωNCO (84)
36	A	---	119	128	124	62	106	ω_{opw}NCO (86)

Abbreviation: ν - stretching; as - asymmetric stretching; ss - symmetric stretching; β - in-plane-bending; t - out-of-plane bending; ipw - in- plane wagging; opw - out-of-plane wagging.

Table 3: UV–VIS excitation energy (ΔE), wave length (λ) and oscillator strength (f) for 2,5-dichloro phenyl isocyanate calculated by TD-DFT/B3LYP method.

States	Wavelength (nm)	Excitation Energy (eV)	Oscillator Strength (f)
State 1	203.53	6.0918	0.0047
State 2	202.99	6.108	0.126
State 3	184.89	6.706	0.003