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Awakening to reality

Vibrational Spectroscopy



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Molecular structure and spectroscopic analysis of 2, 6 dichlorophenyl isocyanate; FT-IR, FT -Raman, NMR, NBO, HOMO-LUMO and DFT studies

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ABSTRACT

The Fourier transform infrared (FTIR) and FT - Raman spectra of 2, 6-dichlorophenyl isocyanate have been recorded in the liquid state. The molecular geometry, vibrational frequencies, and atomic charges have been calculated by using density functional theory (DFT) calculation (B3LYP) with 6-311+G(d,p) and 6-311++G(d,p) basis sets. Simulated FTIR and FT - Raman spectra for 2, 6-dichlorophenyl isocyanate showed good agreement with the observed spectra. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. The molecular stability and bond strength were investigated by applying the natural bond orbital (NBO) analysis and electrostatic potential (ESP). The isotropic chemical shift computed by 1H and 13C nuclear magnetic resonance (NMR) chemical shifts of the 2, 6-dichlorophenyl isocyanate calculated using the gauge invariant atomic orbital (GIAO) method also shows good agreement with experimental observations.

Introduction

Cyanic acid (the isomer of fulminic acid) is an unstable (explosive), poisonous, volatile, clear liquid with the structure of H–O–C \equiv N (the oxoacid formed from the pseudohalogen cyanide), which is readily converted to cyamelide and fulminic acid. There is another isomeric cyanic acid with the structure of H–N=C=O, called isocyanic acid. Cyanate group (and isocyanate group) can react with itself. Cyanuric acid (also called pyrolithic acid), white monoclinic crystal with the structure of [HOC(NCOH)₂N], is the trimer of cyanic acid. The trimer of isocyanic acid is called biuret. Cyanic acid hydrolyses to ammonia and carbon dioxide in water. The salts and esters of cyanic acid are not known. The salts and esters of isocyanic acid are isocyanates. The isocyanate group reacts with the hydroxyl functional group to form a urethane linkage.

Diisocyanates (or polyisocyanates) are monomers for polyurethane production. Polyurethane is made from a variety of diisocyanates in conjunction with polyether and polyester polyols as co-reactants by addition polymerization which needs at least -N=C=O groups. Polyurethanes are widely used in the manufacture of flexible and rigid foams, fibres, coatings and elastomers. If isocyanate monomer is polymerized with amide group, polyurea is produced. Cyanates (or Isocyanates) are readily with various forms of amide (including ammonia, primary, secondary-amines, amides and ureas) and hydroxy functional group. They are used in the synthesis for the target molecules such as pharmaceuticals, pesticides, textile softener, lubricants and industrial disinfectants. They can convert to polycyclic compounds such as hydrations and in imidazolons. They are used as plastic additives and as heat treatment salt formulations for metals [1]. 2, 6-dichlorophenyl isocyanate is used as an intermediate in organic synthesis.

The term of tosyl is for p-toluene sulfonyl acid ester functional group, the conjugate base of the strong acid, p-

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Toluenesulfonic acid. The tosyl group, like other sulfonates, has electron-withdrawing properties. It is a highly reactive leaving group due to the stability of resonance structure. It has a distribution negative charge rather than a localized charge. Each oxygen atom bears one-third of the total negative charge. The tosyl group serves as a protecting group which is readily cleaved. Toluene sulfonic acid and their derivatives are used as intermediates for the synthesis of isocyanate compounds used as catalysis for the production of thermosetting resins. p-Toluene sulfonic acid is often used as a catalyst in the formation of acetyl which water must be removed from the reaction mixture to escape reversible reaction. Water is removed azeotropically by distillation (Toluene is a solvent) [1].

The derivatives of phenylisothiocyanate are of spectroscopic interest due to the role of NCO and substituents play in the vibrational structures and spectra. During the past decade, the density functional theory (DFT) has emerged as a powerful tool in studying vibrational spectra of fairly large molecules. The two tops of trifluoromethylsulfonyl isocyanate were investigated by *ab initio* calculations as well as experimental vibrational spectroscopy and electron diffraction method. It was determined that the molecule exist in a single gauche conformation (the isocyanate group nearly eclipses) one of the sulfonyl S=O bonds in the three physical states [2].

The literature search has revealed that density functional theory calculations and vibrational analysis have not been reported so far on 2, 6-dichlorophenyl isocyanate. Therefore, the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with great wavenumber accuracy. The DFT calculations have been performed to support our wavenumber assignment. Prediction of vibrational frequency of polyatomic molecules by quantum chemical computation has become very popular because of its accurate and therefore consistent description of the experimental data. Atomic charges of 2, 6-dichlorophenyl isocyanate molecule was investigated by using B3LYP calculations with 6-311+G(d,p) and 6-311++G(d,p) basis sets. The main objectives of this paper are to measure both FTIR and FT-Raman spectra along with hyperpolarizability, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energies that have been used to elucidate the information regarding charge transfer which occurs within the molecule.

Experimental Detail

The sample 2, 6-dichlorophenyl isocyanate was purchased from Lancaster Chemical Company, U.K with a stated purity of greater than 97%, and it was used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of 2, 6-dichlorophenyl isocyanate was recorded in the region 4000–400 cm⁻¹ at a resolution of ± 1 cm⁻¹, using BRUKER IFS-66V Fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and global source. The FT-Raman spectrum was recorded on the same instrument with FRA-106 Raman accessories in the region 3500–100 cm⁻¹. Nd:YAG laser operating at 200 mw power with 1064 nm excitation was used as source.

Computational Details

The molecular geometry optimization and vibrational frequency calculations were carried out for 2, 6-dichlorophenyl isocyanate, with GAUSSIAN 09W software package [3] the density functional method used is B3LYP i.e. Becke's threeparameter hybrid functional with the Lee-Yang-Parr correlation functional method [4, 5] combined with standard 6-311++G(d,p)basis set. Scaling of the force field was performed according to the SQM procedure [6, 7] using selective scaling in the natural internal coordinate representation [8]. Vibrational frequencies are scaled by 0.9843 and 0.9786 for B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) respectively for the 2, 6-dichlorophenyl isocyanate. Transformation of the force field and subsequent normal coordinate analysis including the least square refinement of the scale factors, calculation of the potential energy distribution [PED] and the prediction of FTIR and FT-Raman intensities were done on a PC with the MOLVIB Program (version 7.0-G77) written by Sundius [9, 10]. For the plots of simulated Raman spectra, pure Lorentizian band shapes were used with a bandwidth of 10 cm^{-1} . Finally the calculated normal mode vibrational frequencies provide atomic charges and thermodynamic properties also through the principle of statistical mechanics.

Result and Discussion *Geometry optimization*

The labeling of atoms of 2, 6-dichlorophenyl isocyanate is given in Fig. 1. The structural parameters obtained by DFT/B3LYP levels with the 6-311+G(d,p) and 6-311++G(d,p) basis sets. The bond lengths, bond angles and dihedral angles

differences between theoretical approaches have been depicted in Table 1 The optimized geometry reveals that NCO group substituted

The optimized geometry reveals that NCO group substituted in para position of benzene ring is laying slightly out-of-plane. The benzene ring appears to be little distorted with (C1–C6) and (C1–C2) bond lengths exactly at the substitution place 1.409Å by B3LYP/6-311+G(d,p) basis set and 1.411Å by B3LYP /6-311++G(d,p) basis set longer than the remaining bonds (C2– C3), (C3–C4), (C4–C5) and (C5–C6).

Several researchers [11-13] have explained the changes in the frequency or bond length of the C–H bond on substitution due to a change in the charge distribution on the carbon atom of the benzene ring. The reverse holds well on substitution with electron donating groups Cl_{10} . The actual charge in the C–H bond length would be influenced by the combined effects of the inductive mesmeric interaction and the electron dipole field of the polar substituent. In this study, the C–H bond lengths were calculated as 1.079, 1.080, 1.079Å by B3LYP /6-311+G(d,p) and 1.083, 1.084, 1.083 Å by B3LYP /6-311++G(d,p) methods. The increase of C–C bond lengths exactly at the substitution place C1–C6 and C1–C2 is accompanied by slightly irregular hexagonal structure of the angle C1–C2–C3 and C1–C6–C5, 122.214 Å and 122.052 Å by B3LYP /6-311+G(d,p) and 122.051 Å and 122.052 Å by 6-311++G(d,p) basis sets, respectively. The C–N single bond length is 1.360 Å, 1.189Å by B3LYP /6-311++G(d,p) basis sets, respectively.



Fig 1. Geometrical structure of 2, 6-dichlorophenyl isocvanate

Vibrational Analysis

The 2, 6-dichlorophenyl isocyanate contains 14 atoms; thus, assuming C₁ symmetry point group, 25 modes of in plane symmetry and 11 modes of out-of-plane symmetry should appear as bands in the spectra. The harmonic vibrational frequencies calculated for 2, 6-dichlorophenyl isocyanate at by B3LYP/6-311++G (d,p)and 6-311++G(d,p) basis sets have been listed in Table 2. All the assignments were subsequently confirmed in the MOLVIB package [9] using B3LYP calculations. By the help of the calculated potential energy distribution (PED), we assigned the vibrational frequencies of the studied molecule. The detailed vibrational assignment of the experimental wavenumbers is based on normal mode analyses and a comparison with theoretically scaled wavenumbers with PED. The calculated frequencies are usually higher than the corresponding experimental quantities, due to the combination of electron correlation effects and basis set deficiencies. After applying the scaling factors, the theoretical calculations reproduce the experimental data well in agreement.

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Table 1. Optimized structural p	parameters of 2, 6-dichloropheny	yl isocyanate utilizing DFT-B3LYP/6-3	11+G(d,p)
	and 6-311++G(d,p)) density fund	ctional calculation	

Bond	Value(Å)		Bond angle	Value(°)		Dihedral angle	Value(°)	
length	6-311+G(d,p)	6-311++G(d,p)	_	6-311+G(d,p)	6-311++G(d,p)	_	6-311+G(d,p)	6-311++G(d,p)
C1-C2	1.409	1.411	C2-C1-C6	116.565	116.777	C6-C1-C2-C3	0.0	0.0
C1-C6	1.409	1.411	C2-C1-N7	121.716	121.612	C6-C1-C2-Cl10	180.0	180.0
C1-N7	1.360	1.361	C6-C1-N7	121.719	121.611	N7-C1-C2-C3	-180.0	-180.0
C2-C3	1.387	1.390	C1-C2-C3	122.214	122.051	N7-C1-C2-C110	0.0	0.0
C2-Cl10	1.816	1.813	C1-C2-Cl10	118.782	118.842	C2-C1-C6-C5	0.0	0.0
C3-C4	1.396	1.399	C3-C2-Cl10	119.004	119.107	C2-C1-C6-Cl14	-180.0	-180.0
C3-H11	1.079	1.083	C2-C3-C4	119.408	119.466	N7-C1-C6-C5	180.0	180.0
C4-C5	1.396	1.399	C2-C3-H11	119.616	119.577	N7-C1-C6-Cl14	0.0	0.0
C4-H12	1.080	1.084	C4-C3-H11	120.976	120.957	C1-C2-C3-C4	0.0	0.0
C5-C6	1.387	1.390	C3-C4-C5	120.193	120.189	C1-C2-C3-H11	180.0	-180.0
C5-H13	1.079	1.083	C3-C4-H12	119.903	119.906	Cl10-C2-C3-C4	180.0	-180.0
C6-Cl14	1.816	1.813	C5-C4-H12	119.904	119.906	Cl10-C2-C3-H11	0.0	0.0
N7-C8	1.189	1.192	C4-C5-C6	119.412	119.465	C2-C3-C4-C5	0.0	0.0
C8-C9	1.200	1.202	C4-C5-H13	120.975	120.958	C2-C3-C4-H12	180.0	180.0
			C6-C5-H13	119.614	119.577	H11-C3-C4-C5	-180.0	-180.0
			C1-C6-C5	122.208	122.052	H11-C3-C4-H12	0.0	0.0
			C1-C6-Cl14	118.777	118.842	C3-C4-C5-C6	0.0	0.0
			C5-C6-Cl14	119.014	119.107	C3-C4-C5-H13	180.0	180.0
						H12-C4-C5-C6	-180.0	180.0
						H12-C4-C5-H13	0.0	0.0
						C4-C5-C6-C1	0.0	0.0
						C4-C5-C6-Cl14	180.0	180.0
						H13-C5-C6-C1	180.0	-180.0
						H13-C5-C6-Cl14	0.0	0.0

Table 2. Experimental and Calculated DFT-B3LYP/6-311+G (d,p)and 6-311++G (d,p)levels of vibrational frequencies (cm⁻¹), IR intensity (kmmol⁻¹) and Raman activity (Å⁴ amu⁻¹) of 2, 6-dichlorophenyl isocyanate

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	No	Sno	Obser	n	Coloulated	fragmenter -	ing (am ⁻¹) D2		ID Intensity) 01 2 , 0-uicin	Domon int	ity (humal-1)	Vibrational
	INU	ope.	freque (cm ⁻¹)	ncies	6-311+G(d	,p)	6-311++G(0	l,p)	(kmmol ⁻¹)		Kaman mensity (Killilloi)		assignments /PED (≥ 10%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			IR	Raman	Unscaled	Scaled	Unscaled	Scaled	6-	6-	6-	6-	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	4			2001	2252	2007	2252	2007	311+G(d,p)	311++G(d,p)	311+G(d,p)	311++G(d,p)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	1	A		3091	3253	3096	3252	3087	4.926	3.225	14.278	14.341	vCH(100)
3 A 3221 3226 3016 3196 3009 3.285 2.735 4.573 4.833 vCH(96) 5 A 1648 1647 1654 1652 1634 1649 5.621 5.590 100.000 100.000 vCC(76), pCH(21) 6 A 1588 1580 1606 1598 1588 7.754 9.702 19.515 20.451 vCC(71), pCH(18) 7 A 1603 1588 1586 1581 20.733 20.625 0.924 0.941 vCC(70), pCH(21) 8 A 1479 1435 1442 1443 1439 63.265 59.357 1961 2.707 BCH(63), VCC(2) 10 A 1312 1342 1325 1329 1314 1.085 0.959 14.303 13.216 pCH(63), VCC(2) 11 A 1220 1205 1204 1205 1203 10.691 1.411 1.004 VCC(71), PCH(18)	2	A			3246	3045	3237	3021	0.772	0.226	4.997	5.176	vCH(96)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	3	A			3226	3016	3196	3009	3.285	2.735	4.573	4.833	vCH(96)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4	A	2271		2453	2276	2413	2274	1734.301	1619.215	12.125	12.316	vNCO(98)
	5	A	1648	1647	1654	1652	1634	1649	5.621	5.590	100.000	100.000	νCC(76), βCH(21)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	6	Α	1588	1580	1606	1598	1593	1588	7.754	9.702	19.515	20.451	νCC(71), γCH(18)
8 A 1479 1495 1484 1483 1479 51.299 48.247 1.963 2.449 pCH(67),vCC(21) 9 A 1437 1435 1446 1442 1443 1632 59.357 1.961 2.707 pCH(60),vCC(22) 10 A 1312 1324 1329 1314 1.085 0.959 14.303 13.216 pCH(60),vCC(20) 11 A 1202 1205 1205 1204 10.692 9.944 0.761 1.004 vCC(71), pCH(20) 12 A 1106 1110 1110 1109 14.219 8.719 16.922 11.849 vCC(71), pCH(18) 13 A 1005 1004 1082 1079 3.162 4.906 10.972 11.849 vCC(71), pCH(18) 14 A 1000 1017 1016 1005 1002 0.594 1.720 0.056 0.001 vC(16), vCC(18) 16 A 000	7	Α			1603	1588	1586	1581	20.733	20.625	0.924	0.941	vCC(80), βCN(17)
9 A 1435 1446 1442 1439 1439 63.265 59.357 1.961 2.707 βCH(60),vCC(2) 10 A 1312 1322 1329 1314 1.085 0.959 14.30 13.216 βCH(63),vCC(2) 11 A 1205 1251 1247 1250 1246 10.737 9.998 1.431 2.183 vCC(71), gCH(2) 12 A 1205 1204 1250 1246 10.737 9.998 1.431 2.183 vCC(71), gCH(2) 12 A 1166 1159 1190 1189 1175 1171 58.052 52.375 5.064 5.960 vCC(7), gCH(1) 14 A 1006 10181 1100 14.219 8.719 16.522 11.849 vCC(59), vCC(1) 15 A 1075 1080 1083 1082 1079 3.162 4.906 10.972 11.849 vCC(59), vCC(15) 16 A	8	А	1479		1495	1484	1483	1479	51.299	48.247	1.963	2.449	βCH(67),vCC(21)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	9	А	1437	1435	1446	1442	1443	1439	63.265	59.357	1.961	2.707	βCH(60),vCC(22)
11 A 1250 1251 1271 1250 1246 10.737 9.998 1.431 2.183 vCC(71), fCH(20) 12 A 1205 1205 1204 1205 1203 10.692 9.944 0.761 1.004 vCC(73), rCH(18) 13 A 1166 1159 1190 1189 1175 58.052 52.375 5.064 5.960 vCC(71), fCN(17) 14 A 1106 1110 1110 1109 14.219 8.719 16.922 11.849 vCC(59), vCC(18) 16 A 1000 1017 1016 1005 0.094 1.720 0.056 0.001 vCH(68), vCC(15) 17 A 924 921 946 935 932 921 0.000 0.004 0.975 vCH(69), vCC(12) 18 A 809 818 815 810 37.594 25.216 2.460 5.584 0.024 0.0216 5.677 vCH(67), vCC(12	10	А		1312	1342	1325	1329	1314	1.085	0.959	14.303	13.216	βCH(63),vCC(20)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	11	А	1245	1250	1251	1247	1250	1246	10.737	9.998	1.431	2.183	vCC(71), βCH(20)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	12	А	1202	1205	1205	1204	1205	1203	10.692	9.944	0.761	1.004	νCC(73), γCH(18)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	13	Α	1166	1159	1190	1189	1175	1171	58.052	52.375	5.064	5.960	νCC(71), βCN(17)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	14	Α	1106		1110	1110	1110	1109	14.219	8.719	16.922	11.849	vCCl(59), vCC(21)
16 A 1000 1017 1016 1005 1002 0.594 1.720 0.056 0.001 γ CH(68), γ CC(1) 17 A 924 921 946 935 932 921 0.000 0.000 0.004 0.975 γ CH(65), γ CC(15) 18 A 809 819 818 815 810 37.594 25.216 2.460 5.547 γ CH(67), γ CC(12) 20 A 761 771 776 772 775 765 47.555 95.086 3.885 0.002 vCCl(60), vCC(27) 20 A 761 771 770 757 765 47.44 97.269 44.958 0.009 0.580 βCC(71), pCH(12) 22 A 554 561 559 560 558 0.244 0.062 2.082 1.490 βCC(71), pCH(12) 23 A 530 531 552 534 549 530 12.734 6.634 1.900 2.054 γ CC(72), pCH(13) 24 A 522 5	15	А	1075	1080	1084	1083	1082	1079	3.162	4.906	10.972	11.583	vCCl(57), vCC(18)
17 A 924 921 946 935 932 921 0.000 0.000 0.004 0.975 γ CH(65), γ CC(15) 18 A 809 819 818 815 810 37.594 25.216 2.460 5.547 γ CH(65), γ CC(12) 19 A 771 765 777 776 772 771 14.695 14.209 1.623 1.470 vCCl(60), vCC2(27) 20 A 761 771 776 772 776 47.555 95.086 3.885 0.002 vCCl(59), vCC2(5) 21 A 743 707 766 750 756 744 97.269 44.958 0.009 0.580 β CC(73), β CH(11) 22 A 554 561 559 560 558 0.244 0.062 2.082 1.490 β CC(73), β CH(13) 24 A 522 540 538 529 527 0.000 0.000 5.859 2.831 β CC(78), γ CH(13) 25 A 507 524 <t< td=""><td>16</td><td>А</td><td></td><td>1000</td><td>1017</td><td>1016</td><td>1005</td><td>1002</td><td>0.594</td><td>1.720</td><td>0.056</td><td>0.001</td><td>γCH(68), γCC(11)</td></t<>	16	А		1000	1017	1016	1005	1002	0.594	1.720	0.056	0.001	γCH(68), γCC(11)
18 A 809 819 818 815 810 37.594 25.216 2.460 5.547 γ CH(67), γ CC(12) 19 A 771 765 777 776 772 771 14.695 14.209 1.623 1.470 vCCl(60), vCC(27) 20 A 761 771 770 757 765 47.555 95.086 3.885 0.002 vCCl(50), vCC(26) 21 A 743 707 766 750 756 744 97.269 44.958 0.009 0.580 β CC(71), γ CH(12) 22 A 554 561 559 560 558 0.244 0.062 2.082 1.490 β CC(71), γ CH(12) 23 A 530 531 552 534 549 530 12.734 6.634 1.900 2.054 γ CC(72), β CH(13) 24 A 522 540 538 529 527 0.000 0.000 5.859 2.831 β CC(78), β CH(13) 25 A 507 524 <	17	Α	924	921	946	935	932	921	0.000	0.000	0.004	0.975	γCH(65), γCC(15)
19A77176577777677277114.69514.2091.6231.470vCCl(60), vCC(27)20A76177177075776547.55595.0863.8850.002vCCl(59), vCC(26)21A74370776675075674497.26944.9580.0090.580 β CC(73), β CH(11)22A5545515595605580.2440.0622.0821.490 β CC(72), β CH(12)23A53053155253454953012.7346.6341.9002.054 γ CC(72), β CH(13)24A5225405385295270.0000.0005.8592.831 β CC(78), β CH(28)25A50752451252151021.2526.9940.0700.004 γ CC(78), γ CH(13)26A4914994974954926.39226.40257.27056.694 γ CC(78), γ CH(18)27A47048848648747333.46830.4403.2533.408 γ NCO(71), γ CC(12)28A3873983973953915.4443.26021.80420.526 γ NCO(66), γ C(13)29A3253423313373260.6270.01021.41731.745 β NCO(67), β CC(13)31A259269265	18	А	809		819	818	815	810	37.594	25.216	2.460	5.547	γCH(67), γCC(12)
20A76177177075776547.55595.0863.8850.002 $vCCl(59), vCC(26)$ 21A74370776675075674497.26944.9580.0090.580 $\betaCC(73), \betaCH(11)$ 22A5545615595605580.2440.0622.0821.490 $\betaCC(71), \gammaCH(12)$ 23A53053155253454953012.7346.6341.9002.054 $\gamma CC(72), \betaCH(13)$ 24A5225405385295270.0000.0005.8592.831 $\betaCC(73), \gammaCH(13)$ 25A50752451252151021.2526.9940.0700.004 $\gamma CC(78), \gammaCH(13)$ 26A4914994974954926.39226.40257.27056.694 $\gamma CC(68), \betaCH(18)$ 27A47048848648747333.46830.4403.2533.408 $\gamma NCO(66), \gamma CC(13)$ 28A3873983973953915.4443.26021.80420.526 $\gamma NCO(66), \gamma CC(13)$ 29A2592692652682630.4680.47526.16526.277 $\beta NCO(67), \beta CC(13)$ 31A2592692652682630.4980.5510.0320.034 $\beta NCO(67), \gamma CH(12)$ 32A19720920820419	19	А	771	765	777	776	772	771	14.695	14.209	1.623	1.470	vCCl(60), vCC(27)
21A74370776675075674497.26944.9580.0090.580 $\beta CC(73), \beta CH(11)$ 22A5545615595605580.2440.0622.0821.490 $\beta CC(71), \gamma CH(12)$ 23A53053155253454953012.7346.6341.9002.054 $\gamma CC(72), \beta CH(13)$ 24A5225405385295270.0000.0005.8592.831 $\beta CC(68), \beta CH(28)$ 25A50752451252151021.2526.9940.0700.004 $\gamma CC(78), \gamma CH(13)$ 26A4914994974954926.39226.40257.27056.694 $\gamma CC(68), \beta CH(18)$ 27A47048848648747333.46830.4403.2533.408 $\gamma NCO(71), \gamma CC(12)$ 28A3873983973953915.4443.26021.80420.526 $\gamma NCO(66), \gamma CC(13)$ 29A3253423313373260.4680.47526.16526.277 $\beta C-NCO(76), \gamma CC(13)$ 31A2732902892882750.6270.01021.41731.745 $\beta NCO(67), \beta CC(13)$ 32A1972092082041990.0000.0007.02315.272 $\beta CC(65), \gamma CC(25)$ 33A1651881671	20	А		761	771	770	757	765	47.555	95.086	3.885	0.002	vCCl(59), vCC(26)
22 A 554 561 559 560 558 0.244 0.062 2.082 1.490 $\beta CC(71), \gamma CH(12)$ 23 A 530 531 552 534 549 530 12.734 6.634 1.900 2.054 $\gamma CC(72), \beta CH(13)$ 24 A 522 540 538 529 527 0.000 0.000 5.859 2.831 $\beta CC(68), \beta CH(28)$ 25 A 507 524 512 521 510 21.252 6.994 0.070 0.004 $\gamma CC(78), \gamma CH(13)$ 26 A 4491 499 495 492 6.392 26.402 57.270 56.694 $\gamma CC(68), \beta CH(18)$ 27 A 470 488 486 487 473 33.468 30.440 3.253 3.408 $\gamma NCO(61), \gamma CC(12)$ 28 A 387 398 397 395 391 5.444 3.260 21.804 20.526 $\gamma NCO(66), \gamma CC($	21	А	743	707	766	750	756	744	97.269	44.958	0.009	0.580	βCC(73), βCH(11)
23 A 530 531 552 534 549 530 12.734 6.634 1.900 2.054 γ CC(72), β CH(13) 24 A 522 540 538 529 527 0.000 0.000 5.859 2.831 β CC(68), β CH(28) 25 A 507 524 512 521 510 21.252 6.994 0.070 0.004 γ CC(78), γ CH(13) 26 A 491 499 497 495 492 6.392 26.402 57.270 56.694 γ CC(68), β CH(18) 27 A 470 488 486 487 473 33.468 30.440 3.253 3.408 γ NCO(71), γ CC(12) 28 A 387 398 397 395 391 5.444 3.260 21.804 20.526 γ NCO(76), γ CC(13) 29 A 325 342 331 337 326 0.468 0.475 26.165 26.277 β NCO(76), γ CC(13) 30 A 273 290 289 288 </td <td>22</td> <td>А</td> <td>554</td> <td></td> <td>561</td> <td>559</td> <td>560</td> <td>558</td> <td>0.244</td> <td>0.062</td> <td>2.082</td> <td>1.490</td> <td>βCC(71), γCH(12)</td>	22	А	554		561	559	560	558	0.244	0.062	2.082	1.490	βCC(71), γCH(12)
24 A 522 540 538 529 527 0.000 0.000 5.859 2.831 $\beta CC(68), \beta CH(28)$ 25 A 507 524 512 521 510 21.252 6.994 0.070 0.004 $\gamma CC(78), \gamma CH(13)$ 26 A 491 499 497 495 492 6.392 26.402 57.270 56.694 $\gamma CC(68), \beta CH(18)$ 27 A 470 488 486 487 473 33.468 30.440 3.253 3.408 $\gamma NCO(71), \gamma CC(12)$ 28 A 387 398 397 395 391 5.444 3.260 21.804 20.526 $\gamma NCO(66), \gamma CC(13)$ 29 A 325 342 331 337 326 0.468 0.475 26.165 26.277 $\beta C-NCO(76), \gamma CC(16), \gamma CC(13)$ 30 A 273 290 289 288 275 0.627 0.010 21.417 31.745	23	Α	530	531	552	534	549	530	12.734	6.634	1.900	2.054	γ CC(72), βCH(13)
25 A 507 524 512 521 510 21.252 6.994 0.070 0.004 $\gamma CC(78), \gamma CH(13)$ 26 A 491 499 497 495 492 6.392 26.402 57.270 56.694 $\gamma CC(68), \beta CH(18)$ 27 A 470 488 486 487 473 33.468 30.440 3.253 3.408 $\gamma NCO(71), \gamma CC(12)$ 28 A 387 398 397 395 391 5.444 3.260 21.804 20.526 $\gamma NCO(66), \gamma CC(13)$ 29 A 325 342 331 337 326 0.468 0.475 26.165 26.277 $\beta C-NCO(76), \gamma CC(13)$ 30 A 273 290 289 288 275 0.627 0.010 21.417 31.745 $\beta NCO(67), \beta CC(13)$ 31 A 259 269 265 268 263 0.498 0.551 0.032 0.034 $\beta NCOwag(62), \gamma CH(12)$ 32 A 197 209 208 204 <t< td=""><td>24</td><td>А</td><td></td><td>522</td><td>540</td><td>538</td><td>529</td><td>527</td><td>0.000</td><td>0.000</td><td>5.859</td><td>2.831</td><td>βCC(68), βCH(28)</td></t<>	24	А		522	540	538	529	527	0.000	0.000	5.859	2.831	βCC(68), βCH(28)
26 A 491 499 497 495 492 6.392 26.402 57.270 56.694 $\gamma CC(68), \beta CH(18)$ 27 A 470 488 486 487 473 33.468 30.440 3.253 3.408 $\gamma NCO(71), \gamma CC(12)$ 28 A 387 398 397 395 391 5.444 3.260 21.804 20.526 $\gamma NCO(66), \gamma CC(13)$ 29 A 325 342 331 337 326 0.468 0.475 26.165 26.277 $\beta C-NCO(76),$ 20 A 273 290 289 288 275 0.627 0.010 21.417 31.745 $\beta NCO(67), \beta CC(13)$ 31 A 259 269 265 268 263 0.498 0.551 0.032 0.034 $\beta NCOwag(62),$ 32 A 197 209 208 204 199 0.000 0.000 7.023 15.272 $\beta CCl(61), \gamma CC(21)$ 33 A 165 188	25	A		507	524	512	521	510	21.252	6.994	0.070	0.004	γCC(78), γCH(13)
27 A 470 488 486 487 473 33.468 30.440 3.253 3.408 $\gamma NCO(71), \gamma CC(12)$ 28 A 387 398 397 395 391 5.444 3.260 21.804 20.526 $\gamma NCO(66), \gamma CC(13)$ 29 A 325 342 331 337 326 0.468 0.475 26.165 26.277 $\beta C-NCO(76), \gamma CC(13)$ 30 A 273 290 289 288 275 0.627 0.010 21.417 31.745 $\beta NCO(67), \beta CC(13)$ 31 A 259 269 265 268 263 0.498 0.551 0.032 0.034 $\beta NCOwag(62), \gamma CH(12)$ 32 A 197 209 208 204 199 0.000 0.000 7.023 15.272 $\beta CCl(55), \gamma CC(25)$ 33 A 165 188 167 187 163 0.144 0.354 25.133 23.904 $\beta CCl(61), \gamma CC(21)$ 34 A 115 113 115 112 <	26	A		491	499	497	495	492	6.392	26.402	57.270	56.694	γCC(68), βCH(18)
28 A 387 398 397 395 391 5.444 3.260 21.804 20.526 $\gamma NCO(66), \gamma CC(13)$ 29 A 325 342 331 337 326 0.468 0.475 26.165 26.277 $\beta C-NCO(76), \gamma CC(16)$ 30 A 273 290 289 288 275 0.627 0.010 21.417 31.745 $\beta NCO(67), \beta CC(13)$ 31 A 259 269 265 268 263 0.498 0.551 0.032 0.034 $\beta NCOwag(62), \gamma CH(12)$ 32 A 197 209 208 204 199 0.000 0.000 7.023 15.272 $\beta CCl(55), \gamma CC(25)$ 33 A 165 188 167 187 163 0.144 0.354 25.133 23.904 $\beta CCl(61), \gamma CC(21)$ 34 A 115 113 115 112 0.096 0.031 34.550 $\gamma NCO(33), \gamma CC(13)$ 35 A 50 50 48 48 0.955 0.120	27	A		470	488	486	487	473	33.468	30.440	3.253	3.408	$\gamma NCO(71), \gamma CC(12)$
29 A 325 342 331 337 326 0.468 0.475 26.165 26.277 $\beta C-NCO(76), \gamma CCl(16)$ 30 A 273 290 289 288 275 0.627 0.010 21.417 31.745 $\beta NCO(67), \beta CC(13)$ 31 A 259 269 265 268 263 0.498 0.551 0.032 0.034 $\beta NCOwag(62), \gamma CH(12)$ 32 A 197 209 208 204 199 0.000 0.000 7.023 15.272 $\beta CCl(55), \gamma CC(25)$ 33 A 165 188 167 187 163 0.144 0.354 25.133 23.904 $\beta CCl(61), \gamma CC(21)$ 34 A 115 113 115 112 0.096 0.031 34.500 34.355 $\gamma NCO(xag(60))$ 35 A 50 50 48 48 0.955 0.120 13.702 8.604 $\beta NCOwag(60)$ 36 A 46 36 31 30 0.034 1.065 575.177	28	A		387	398	397	395	391	5.444	3.260	21.804	20.526	$\gamma NCO(66), \gamma CC(13)$
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	29	А		325	342	331	337	326	0.468	0.475	26.165	26.277	βC-NCO(76),
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	20	٨		272	200	280	200	275	0.627	0.010	21 417	21 745	$\frac{\gamma \text{CCI(16)}}{\text{PNCO}(67) - \text{PCC}(12)}$
31 A 2.59 2.69 2.63 2.68 2.63 0.498 0.531 0.052 0.054 phecowag(62), $\gamma CH(12)$ 32 A 197 209 208 204 199 0.000 0.000 7.023 15.272 $\beta CCl(55), \gamma CC(25)$ 33 A 165 188 167 187 163 0.144 0.354 25.133 23.904 $\beta CCl(61), \gamma CC(21)$ 34 A 115 113 115 112 0.096 0.031 34.500 34.355 $\gamma NCO(53), \gamma CC(13)$ 35 A 50 50 48 48 0.955 0.120 13.702 8.604 $\beta NCOwag(60)$ 36 A 46 36 31 30 0.034 1.065 575.177 546.139 $\nu NCOwag(60)$	21	A		275	290	269	200	273	0.027	0.010	21.417	0.024	$\frac{\text{pine}(0/7), \text{pee}(13)}{\text{pine}(62)}$
32 A 197 209 208 204 199 0.000 0.000 7.023 15.272 $\beta CCl(55), \gamma CC(25)$ 33 A 165 188 167 187 163 0.144 0.354 25.133 23.904 $\beta CCl(61), \gamma CC(21)$ 34 A 115 113 115 112 0.096 0.031 34.500 34.355 $\gamma NCO(53), \gamma CC(13)$ 35 A 50 50 48 48 0.955 0.120 13.702 8.604 $\beta NCOwag(60)$ 36 A 46 36 31 30 0.034 1.065 575.177 546.139 $\nu NCOwag(60)$	51	А		239	209	203	208	203	0.496	0.551	0.032	0.034	γ
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	32	Δ		107	209	208	204	100	0.000	0.000	7.023	15 272	$\beta CC1(55) \gamma CC(25)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	33	A		165	188	167	187	163	0.144	0.354	25 133	23 904	$\beta CCI(61), \gamma CC(21)$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	34	A		100	115	113	115	112	0.096	0.031	34.500	34.355	$\gamma NCO (53), \gamma CC(13)$
36 A 46 36 31 30 0.034 1.055 57.177 546 (39 vNCOwae(69)	35	A			50	50	48	48	0.955	0.120	13.702	8.604	BNCOwag(60)
100 100 100 100 1000 1000 1000 1000 10	36	А			46	36	31	30	0.034	1.065	575.177	546.139	γNCOwag(69)

 $v\text{-stretching}, v_{sym}\text{-sym stretching}, v_{asym}\text{-asym stretching}, \beta\text{-in-plane bending}, \gamma\text{-out-of-plane bending}, \delta\text{-scissoring}, \delta\text{-scissoring},$

ω-wagging, ρ-rocking, $ρ_{ip}$ -in-plane rocking, $ρ_{op}$ -out-of-plane rocking, t-twisting, sd-symmetric deformation, ad-asymmetric deformation, Rtrigd-Ring trigonal deformation, βRing-in-plane ring, γRing-out-of -plane ring τ-torsion.

The simulated IR and Raman spectra of 2, 6-dichlorophenyl isocyanate are shown in Figs 2 and 3, respectively. **C–H vibrations**

The 2, 6-dichlorophenyl isocyanate molecule gives rise to three C–H stretching vibrations, three C–H in-plane and three C–H out-of-plane bending vibrations. The aromatic structure shows the presence of C–H stretching vibrations in the region $3100-3000 \text{ cm}^{-1}$ which is the characteristic region for the ready identification of C–H stretching vibrations [14 -17]. The expected three C–H stretching vibrations appeared medium at 3240 cm^{-1} in FTIR, 3227 and 3091 cm^{-1} in FT-Raman spectrum. Theoretically computed C–H vibrations by B3LYP/6-311++G(d,p) at 3087, 3021, and 3009 cm^{-1} show good agreement with recorded FT-Raman spectrum at 3091 cm^{-1} for 2, 6-dichlorophenyl isocyanate.



Fig 2. Observed FT-IR and simulated spectrum of 2, 6dichlorophenyl isocyanate (a)Observed (b) B3LYP/6-311+G(d,p) (c) B3LYP/6-311++G(d,p)



Fig 3. Observed FT-Raman and simulated spectrum of 2, 6dichlorophenyl isocyanate (a) Observed (b) B3LYP/6-311+G(d,p) (c) B3LYP/6-311++G(d,p)

The aromatic C–H in-plane and out-of-plane bending modes of benzene and its derivatives are observed in the region $1300-1000 \text{ cm}^{-1}$ [18–20]. The bands are sharp but are weak-to-medium intensity. The three C–H in-plane bending vibrations computed at 1479, 1439, 1314 B3LYP/6-311++G(d,p) method

show good agreement FT–Raman bands observed at 1435 and 1312 cm⁻¹ and FTIR band observed at 1479 and 1437 cm⁻¹. The out-of-plane bending vibrations fall in FTIR spectrum at 924 and 809 cm⁻¹, and FT-Raman bands observed at 1000 and 921 cm⁻¹. These bands show good agreement with theoretically computed B3LYP/6-311++G(d,p) methods at 1002, 921, and 810 cm⁻¹. *C–C vibrations*

There are six equivalent C-C bands in benzene and one band in outside of the ring and consequently there will be six C-C stretching vibrations. In general, the bands around $1650-1300 \text{ cm}^{-1}$ [21 -24] in benzene derivatives are assigned to skeletal stretching C-C bands. The FTIR bands observed at 1648, 1588, 1245, 1202 and 1166 cm⁻¹, the FT-Raman bands observed at 1647, 1580, 1250, 1205 and 1159 cm^{-1} , assigned to C-C stretching vibrations for the title molecule show good agreement with theoretically computed B3LYP/6-311++G(d,p). methods in the region at 1649, 1588, 1581, 1246, 1203, and 1171 cm⁻¹. The C-C in-plane bending vibrations are assigned in the region $550-300 \text{ cm}^{-1}$. On account of the heavy substitution on the ring these vibrations have shifted to lower frequencies from their usual range, making assignment difficult. In 2, 6dichlorophenyl isocyanate, the medium FT-Raman band observed at 491 cm⁻¹ without corresponding FTIR band is assigned to the C-C in-plane bending vibration with more contribution to β (CH) mode. The theoretically computed C–C in-plane bending vibration 558 cm⁻¹ and 527 cm⁻¹ by B3LYP/6-311++G(d,p). The FT-Raman band at 507, 491 cm⁻¹ is assigned to C-C out-of-plane bending vibration without corresponding FTIR band and contribution. The theoretically calculated frequencies at 510 cm⁻¹ and 492 cm⁻¹ by B3LYP/6-311++G(d,p) methods are assigned for C-C out-of-plane vibrations approximately coincides with FT-Raman frequency. The FTIR bands identified at 530 cm⁻¹ and FT_Raman band identified at 531 cm⁻¹ for 2, 6-dichlorophenyl isocyanate have been assigned to the ring in-plane vibrations. The FT-Raman bands observed at 325 cm⁻¹ with mixed contribution assigned. The theoretically computed and B3LYP/6-311++G(d,p), show good agreement with experimental observations.

C–Cl vibrations

The C–Cl stretching vibration give rise to strong absorptions in the range 760–505 cm⁻¹. However, vibrational coupling with other vibrations may shift the upper limit to 840 cm⁻¹ [21]. An intense infrared band absorbed at 771 cm⁻¹ and 765 cm⁻¹ in FT-Raman are assigned to the C–Cl stretching vibration. The theoretically computed stretching vibration at 771 cm⁻¹ by B3LYP/6-311++G(d,p). The C–Cl in-plane bending vibrations are assigned to a computed band at 199 and 163 cm⁻¹ by B3LYP/6-311++G(d,p). The same vibration is assigned to a Raman band at 197 cm⁻¹ and a medium strong band at 165 cm⁻¹. The theoretically computed and B3LYP/6-311++G(d,p) basis set show good agreement with experimental observations

NCO vibrations

There are six vibrations for NCO moiety: asymmetric, symmetric stretching, in-plane bend, in-plane wagging, out-of-plane bend and out-of-plane wagging vibrations. The asymmetric stretching vibration appears always as the strongest and broad band near 2274 cm⁻¹ in the FTIR spectrum; conversely, the band is an unfailing evidence for the presence of the isocyanate moiety [25-27]. In 2, 6-dichlorophenyl isocyanate, the FTIR band is observed at 2271 cm⁻¹ as is

assigned to asymmetric stretching vibration. The symmetric stretching vibration is generally observed to be FTIR weak but FT-Raman strong in the range 1460–1340 cm⁻¹ [28]. However, in some substituted phenyl isocyanates, the band has been observed to be strong in the FTIR spectrum [29, 25, 26]. The two in-plane bending vibrations have been assigned in the range $660-640 \text{ cm}^{-1}$, and two out-of-plane vibrations in the range $560-540 \text{ cm}^{-1}$, while these in-plane and out-of-plane assignments corresponding to high and low frequencies in accordance with the theoretical results, they are not in agreement with the previous assignments by others [27, 28]. Hence, the band at 470, 387 cm⁻¹ and 273, 259 in FT-Raman since have been assigned to in-plane and out-of-plane bending vibrations, respectively. The theoretically computed value of in-plane and out-of-plane vibrations at 473, 391 cm^{-1} and 275, 263 cm^{-1} by B3LYP/6-311++G(d,p) basis set coincide with experimental values. The in-plane and out-of-plane wagging vibrations at 48, 30 cm^{-1} by B3LYP/6-311++G(d,p) basis set.

Potential energy distribution

To check whether the chosen set of vibrational frequencies contribute maximum to the potential energy associated with normal coordinates of the molecule, the PED is calculated. PED of the other couple modes which make up 100% distribution are presented in Table 2. This information supports and confirms the present assignments. PED has been calculated using the relation,

$$PED = \frac{F_{ii}L_{ik}^{2}}{\lambda_{k}}$$

PED is the contribution of the *i*th symmetry coordinate to the potential energy of the vibration, whose frequeny is $_{Vk}$ (F_{ii} = potential constant, $L_{ik} = L$ matrix elements and $\lambda_k = 4\pi^2 C^2 {}_{VK}^2$). ¹³C NMR and ¹H spectral analysis

The molecular structure of 2, 6-dichlorophenyl isocyanate are optimized by using B3LYP method with 6-311++G(d,p). Then, GIAO ¹³C calculations of the title molecule is calculated and compared with experimental [232] data are shown in Table3.



Fig 4. NMR spectra of 2, 6-dichlorophenyl isocyanate (a) ${}^{1}H$ (b) ${}^{13}C$

The ¹H and ¹³C NMR spectra are presented in Fig.4. The approximate chemical shift ranges of some ¹³C resonances i.e., C of aromatic ring have the δ range 110–160 and type of carbon having double bond oxygen is in the δ range 150–220. The aromatic protons are having the chemical shift δ (ppm) in the range 6–8.5 [30]. In our title compound, the two chlorine atoms are different at two different positions. This chlorine atoms show electronegative property (they attract the other atom towards), but the chemical shift for C3, C5 seems to be C3 = 128.13; C5 = 128.13 ppm for 2, 6-dichlorophenyl isocyanate by B3LYP/6-311++G(d,p) method. For the other carbon atoms the values are given in Table 3.

Table 3. Experimental and theoretical chemical shifts of 2, 6dichlorophenyl isocyanate in ¹H and ¹³C NMR spectra (δ

		PPm)	
Atom label	Experimental ^a	6-311++G(d,p)	Chemical shift (δ)
C1	133.20	132.06	1.14
C2	134.03	133.83	0.20
C3	128.13	128.03	0.10
C4	128.20	128.11	0.09
C5	128.13	128.03	0.10
C6	134.08	133.83	0.25
H11	7.478	7.431	0.047
H12	7.276	7.189	0.087
H13	7.478	7.431	0.047

^a Taken from Ref. [28] and δ difference between respective chemical

The atom C_6 is having the higher chemical shift value 134.08 ppm for 2, 6-dichlorophenyl isocyanate molecules. The ¹³C chemical shifts of all the carbon atoms are in good agreement with the theoretical range. In our studies the chemical shift of aromatic protons, H_{11} and H_{13} are well agree with the range of aromatic protons chemical shift. **Other molecular Properties**

HOMO and LUMO analysis

Many organic molecules, containing conjugated π electrons are characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy [31, 32]. In most cases, even in the absence of inversion symmetry, the strongest band in the FT-Raman spectrum is weak in the FTIR spectrum and vice-versa. But the intramolecular charge transfer from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making FTIR and FT-Raman activity strong at the same time. The experimental spectroscopic behaviour described above is well accounted by ab initio calculations is π conjugated systems that predict exceptionally FTIR intensities for the same normal modes [32]. It is also observed in our title molecule the bands in FTIR spectrum have their counterparts in FT-Raman shows that the relative intensities in FTIR and FT-Raman spectra are comparable resulting from the electron cloud movement through π conjugated frame work from electron donor to electron accepter groups.

The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The HOMO of π nature, (i.e., benezene ring) is delocalized over the whole C–C bond. By contrast, LUMO the is located over chlorines and isocyanate groups, consequently the HOMO and LUMO transition implies an electron density transfer to aromatic part and propionic acid of π conjugated system from chlorines. Moreover, these orbital significantly overlap in their position for 2, 6-dichlorophenyl isocyanate. The atomic orbital composition of the frontier molecular orbital is shown in Fig.5 for 2, 6-dichlorophenyl isocyanate.



Fig 5. The atomic orbital composition of the frontier molecular orbital for 2, 6-dichlorophenyl isocyanate

Commonly, the atom occupied by more densities of HOMO should have stronger ability for detaching electrons, whereas the atom with more occupation of LUMO should be easier to gain electron. For 2, 6-dichlorophenyl isocyanate, the highest occupied molecular orbital (HOMO) lying at -0.26991 eV, is a delocalized π orbital. The HOMO-1, lying -0.28053 eV below the HOMO, is a delocalized π orbital over both the entire molecules. While, the HOMO-2 lying _0.30520eV below the HOMO, respectively, are π orbitals that localized in benzene ring. Whereas, the lowest unoccupied molecular orbital (LUMO), lying at -0.06571 eV, is π^* orbital that localised for 2, 6-dichlorophenyl isocyanate. The LUMO+1, lying about -0.05293 eV above the LUMO, is also a π^* that is similar to LUMO. The HOMO-LUMO energy gap of 2, 6-dichlorophenyl isocyanate was calculated at the B3LYP/6-311++G(d,p) level and is -0.20420 eV, reveals that the energy gap reflects the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron. The calculated selfconsistent field (SCF) energy of 2, 6-dichlorophenyl isocyanate is -1318 a.u moreover; the lower in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the 2, 6-dichlorophenyl isocyanate molecule.

Hyperpolarizability calculations

The first hyperpolarizabilities (β_0) of this molecular system, and related properties (β , α_0 and α) of 2, 6-dichlorophenyl isocyanate were calculated using B3LYP/6-311++G(d,p) basis set, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field [33]. They determine not only the strength of molecular interactions (long-range inter induction, dispersion force, etc.) as well as the cross sections of different scattering and collision process. First hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [34]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrixes is a tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + \dots$$

where E_0 is the energy of the unperturbed molecules, $F\alpha$ the field at the origin $\mu\alpha$, $\alpha\alpha\beta$ and $\beta\alpha\beta\gamma$ are the components of dipole moments, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moments μ , the mean polarizabilities α_0 , the anisotropy of the polarizabilities α and the mean first hyperpolarizabilities β_0 , using the x, y and z components they are defined as: [35, 36]

The total static dipole moment is

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

The isotropic polarizability is

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

The polarizability anisotropy invariant is

$$\alpha = 2^{-\frac{1}{2}} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2 \right]^{\frac{1}{2}}$$

and the average hyperpolarizability is
$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{\frac{1}{2}}$$
$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$
$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The total static dipole moment, polarizabilities and first hyperpolarizabilities of 2, 6-dichlorophenyl isocyanate were calculated. Table 4 lists the values of the electric dipole moment (Debye) and dipole moment components, polarizabilities and hyperpolarizabilities of the 2, 6-dichlorophenyl isocyanate. In addition to the isotropic polarizabilities and polarizabilities anisotropy invariant were also calculated. The polarizabilities and first hyperpolarizabilities of 2, 6-dichlorophenyl isocyanate -76.784033, -78.272733 a.u and 4.62293×10^{-30} , are 4.58867×10^{-30} esu, by B3LYP/6-311+G(d,p) and 6-311++G(d,p) basis sets, which are comparable with the reported values of similar derivatives [37, 38]. We conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

Table 4. The B3LYP/6-311+G (d,p) and 6-311++G (d,p) calculated electric dipole moments (Debye), Dipole moments compound, polarizability (in a.u), β components and β_{tot} (10⁻³⁰ esu) value of 2, 6-dichlorophenyl isocyanate

Parameters	B3LYP/6-311+G(d,p)	B3LYP/6-311++G(d,p)	Parameters	B3LYP/6-311+G(d,p)	B3LYP/6-311++G(d,p)
μ _x	0.0174	0.2826	β _{xxx}	0.0082	0.0892
μ_{y}	-4.7531	-4.7548	β_{yyy}	-72.8365	-73.1756
μ _z	0.0000	0.0000	β _{zzz}	0.0000	0.0000
μ	4.7531	4.7632	β_{xyy}	0.2631	4.3515
α_{xx}	-77.3627	-78.9242	β _{xxy}	-0.8609	-0.7933
α_{yy}	-76.5836	-77.6878	β_{xxz}	0.0000	0.0001
α_{zz}	-76.4058	-78.2062	β_{xzz}	-0.0432	-0.7544
α_{xy}	-0.0021	-0.0587	β_{yzz}	11.7838	12.6243
α	-76.784033	-78.272733	β_{YYZ}	-0.0003	-0.0004
$\Delta \alpha(esu)$	7.77147×10^{-25}	11.6689×10^{-25}	βtot(esu)	4.62293×10 ⁻³⁰	4.58867×10^{-30}

Table 5. Significant second-order interaction energy (E (2), kcal/mol) between donor and acceptor Orbitals of 2, 6dichlorophenyl isocyanate calculated at B3LYP/ 6-311+G(d,p)level of theory

$Donor (i) \rightarrow Acceptor (j)$	E(2) ^a kcal/mol	$(\varepsilon_j - \varepsilon_i)$ a.u	F_{ij} a.u				
$n(N_7) \rightarrow \pi^*(C_1 - C_2)$	1.3	1.32	0.038				
$n (Cl_{10}) \rightarrow \sigma^* (C_1 - N_7)$	0.6	1.03	0.023				
$n (Cl_{10}) \rightarrow \sigma^* (C_1 - C_2)$	1.5	1.46	0.043				
$n (Cl_{10}) \rightarrow \sigma^* (C_2 - C_3)$	1.9	1.47	0.047				
$n (Cl_{14}) \rightarrow \sigma^* (C_1 - C_2)$	3.3	1.24	0.057				
$n (Cl_{14}) \rightarrow \sigma^* (C_1 - C_6)$	1.5	1.46	0.043				
$n (Cl_{14}) \rightarrow \sigma^* (C_5 - C_6)$	1.9	1.47	0.047				
$n(O_9) \rightarrow \sigma^*(N_7 - C_8)$	16	1.33	0.13				

^a E(2) means energy of hyperconjugative interactions (stabilization energy).

Table 6. Natural atomic orbital occupancies and energies of most interacting NBO's of 2, 6-dichlorophenyl isocyanate along with their hybrid atomic orbitals and hybrid directionality

Parameters ^a	Occupancies	Energies	Hybrid	AO(%) ^b	Deviation at A(°)	Deviation at B(°)
(A–B)	- · · · · · · · · · · ·	(a.u)	5			
$\sigma * (C_1 - C_2)$	0.04239	0.49078	$sp^{1.63}(C_1)$	s(38.06) + p(61.94)	6.7	6.3
- (-1 -2)			$sp^{1.63}$ (C ₂)	s(38.05) + p(61.95)		
$\sigma * (C_1 - C_6)$	0.04234	0.49122	$sp^{1.63}(C_1)$	s(38.07) + p(61.93)	6.7	6.3
			$sp^{1.63}$ (C ₆)	s(38.06) + p(61.94)		
σ*(C1-N7)	0.03066	0.27994	$Sp^{3.23}_{0.00}(C_1)$	s(23.63) + p(76.37)	-	-
			$Sp^{0.88}(N_7)$	s(53.21) + p(46.79)		
$\sigma * (C_2 - C_3)$	0.02624	0.50251	$sp^{1.56}(C_2)$	s(39.11) + p(60.89)	6.4	-
			$sp^{1.82}(C_3)$	s(35.43) + p(64.57)		
$\sigma * (C_2 - Cl_{10})$	0.02886	0.07013	$Sp^{3.4}(C_2)$	<i>s</i> (22.75) + <i>p</i> (77.25)	-	-
			$Sp^{5.19}(Cl_{10})$	s(16.17) + p(83.83)		
$\sigma * (C_3 - C_4)$	0.01718	0.51674	$sp^{1.78}(C_3)$	s(35.93) + p(64.07)	1.4	1.3
			$sp^{1.82}(C_4)$	s(35.47) + p(64.53)		
$\sigma * (C_4 - C_5)$	0.01716	0.51755	$Sp^{1.82}(C_4)$	s(35.05) + p(64.05)	1.3	1.4
			$sp^{1.78}(C_5)$	s(35.96) + p(64.04)		
$\sigma * (C_5 - C_6)$	0.02628	0.50108	$sp^{1.82}(C_5)$	s(35.41) + p(64.59)	-	6.4
			$sp^{1.56}(C_6)$	s(39.09) + p(60.91)		
$\sigma * (C_6 - Cl_{14})$	0.02884	0.07012	$Sp^{3.39}(C_6)$	s(22.75) + p(77.25)	-	-
			$Sp^{5.19}(Cl_{14})$	s(16.17) + p(83.83)		
$\sigma * (N_7 - C_8)$	0.02498	0.53730	$Sp^{1.14}(N_7)$	s(46.79) + p(53.21)	-	-
			$Sp^{0.95}(C_8)$	s(51.38) + p(48.62)		
$\sigma * (C_8 - O_9)$	0.00527	0.43084	$Sp^{1.06}(C_8)$	s(48.47) + p(51.53)	-	-
			$sp^{2.51}(O_9)$	s(28.48) + p(71.52)		
$n(Cl_{10})$	1.99217	0.06640	$Sp^{0.20}$	s(83.67) + p(16.33)	-	-
$n(Cl_{14})$	1.99217	0.06642	$Sp^{0.20}$	s(83.67) + p(16.33)	-	-

^a For numbering of atoms refer Fig 1

^b Percentage of s-type and p-type subshell of an atomic orbitals are given in their respective brackets

Table 7. Accumulation of natural charges and electron population of atoms in core, valance, Rydberg orbitals of 2, 6dichlorophenyl isocyanate

Atoms ^a	Charge (e)	Natural population (e)		Total (e)	Atoms ^b	Charge	Natural population (e)		Total (e)		
		Core	Valence	Rydberg			(e)	Core	Valence	Rydberg	
C1	0.104	1.998	3.881	0.017	5.896	C2	-0.021	1.998	4.005	0.017	6.021
C8	0.845	1.999	3.140	0.016	5.155	C3	-0.210	1.999	4.196	0.015	6.210
Cl10	0.029	10.000	6.964	0.008	16.971	C4	-0.171	1.999	4.161	0.012	6.171
H11	0.228	0.000	0.770	0.002	0.772	C5	-0.210	1.999	4.196	0.015	6.210
H12	0.218	0.000	0.781	0.001	0.782	C6	-0.021	1.998	4.005	0.017	6.021
H13	0.228	0.000	0.770	0.002	0.772	N7	-0.547	1.999	5.536	0.012	7.547
Cl14	0.029	10.000	6.964	0.008	16.971	09	-0.498	2.000	6.494	0.004	8.498

^a Atoms containing negative charges ^b Atoms containing positive charges

Natural bond orbital analysis

The natural bond orbital (NBO) [39] analysis of 2, 6dichlorophenyl isocyanate are being performed to estimate the delocalization pattern of electron density (ED) between the principle occupied Lewis-type (bond or lone pair) orbitals and unoccupied non-Lewis (antibond or Rydberg) orbitals. Table 5 lists the occupancies and energies of most interacting NBO's along with their percentage of hybrid atomic orbital contribution.

The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy E(2) associated with the delocalization from $i \rightarrow j$ is estimated as

$$E(2) = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{(\varepsilon_i - \varepsilon_i)}$$

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements and F(i,j) is the off diagonal NBO Fock matrix element. The NBO analysis provides an efficient method for studying intra and intermolecular bonding and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [40].

The possibilities of ED delocalization from the lone pair donor atoms to the antibonding acceptor atoms of the title molecule are depicted in Table 6. In other words, the delocalization of ED through donor to the acceptor of this type contributed predominantly to the stabilization of entire molecular system. This is due to the fact that greater the value of E (2), the more intensive is the interaction between electron donors and electron acceptors and the greater the extent of conjugation of the whole system.

The natural charges determined by natural bond orbital (NBO) analysis by B3LYP/6-311++G (d, p) method is presented in the Table 6. The more negative charges on C_2 and C_6 carbon atoms are due to the attachment of chlorine atoms with these carbon atoms. When compared the charges of the aromatic ring carbon atoms, less negative charge is observed in the carbon atoms which has Cl group. This is caused by effect of chlorine atom. The chlorine atoms C_1 and C_1 has less negative charge than the carbon atoms C_2 and C_6 . This is due to the hyper conjugative effect.

The hybrid directionality and bond bending analysis of the benzene ring in the title molecule provide excellent evidence to the substituent effect and steric effect. The angular properties of the natural hybrid orbitals are very much influenced by the type of substituent that causes conjugative effect or steric effect [41]. In Table 6, the bending angles of different bonds are expressed as the angle of deviation from the direction of the line joining two nuclear centers. The $\sigma*(C_1-C_2)$ bond is more bent away from the line of C_1-C_6 centers by 6.7 ° results a strong charge transfer path towards NCO. According to the results, we can say that the degree of pyramidalization has affected by Cl substituents.

Natural population analysis

The natural population analysis [42] performed on the title molecule clearly describes the distribution of charges in the various sub-shells (core, valence, Rydberg) in the molecular orbital. The accumulation of natural charges on individual atom of the title molecule is given in Table 7. It shows that an atom N_7 has the lowest electronegative charge of -0.547e and C_1 has the lowest electropositive charge of 0.104e. Likewise, O_9 , C_3 , and C_5 atoms have considerable electron negativity and they are

tending to donate an electron. Conversely, the C_8 , Cl_{10} , Cl_{14} , H_{11} and H_{12} atoms have considerable electropositive and they are tending to acquire an electron. Further, the natural population analysis showed that 94 electrons in the title molecule are distributed on the sub shell as follows:

Core : 37.99005 (99.9738% of 38)

Valence : 55.86379 (99.7568% of 56)

Rydberg : 0.14615 (0.1555% of 94)

Molecular electrostatic potential (MEP) analysis

The molecular electrostatic potential, V(r), at a given point r (x, y, z) in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r. The molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [43,44]. To predict reactive sites for electrophilic and nucleophilic attack for the title molecule, MEP was calculated at the B3LYP/6-311++G(d,p) optimized geometry. The negative (red) regions of MEP were related to electrophilic reactivity and the positive (white) regions to nucleophilic reactivity shown in Fig.6 The negative regions are mainly localized on the carbonyl oxygen atom, O₉ atom. Also, a negative electrostatic potential region is observed around the nitrogen atom (N_7 atom).

A maximum positive region is localized on the hydrogen atoms indicating a possible site for nucleophilic attack. The MEP map shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can have non covalent interactions.



Fig 6. The molecular electrostatic potential map of 2, 6-dichlorophenyl isocyanate

Mulliken atomic charge

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular systems. The calculated mulliken charge values of 2, 6-dichlorophenyl isocyanate are listed in Table 8. The mulliken charge distribution of the 2, 6-dichlorophenyl isocyanate in B3LYP/6-311++G(d,p) methods are shown in Fig.7. The charge distribution of the titled molecule shows all the hydrogen atoms and C_1 are positively charged whereas the other carbon atoms are negative.

Fable 8. Mulliken population analysis of 2, 6-dichlorophenyl
isocyanate performed at B3LYP/6-311+G (d,p) and 6-
311 + C (d n)

	511110	(u , p)
	Atomic charges	
Atoms	B3LYP/-311+G(d,p)	B3LYP/6-311++G(d,p)
C1	0.445058	0.69219
C2	-0.224033	-0.33142
C3	-0.130355	-0.05325
C4	-0.094745	-0.12202
C5	-0.130362	-0.05324
C6	-0.224017	-0.33207
N7	-0.426306	-0.48371
C8	0.346565	0.326437
09	-0.337955	-0.29667
Cl10	0.139377	0.04388
H11	0.171704	0.195056
H12	0.153991	0.175751
H13	0.171706	0.195011
Cl14	0.139372	0.044049

The influence of electronic effect resulting from the hyperconjugation and induction of chlorines in the aromatic ring causes a positively charged value in in 2, 6-dichlorophenyl isocyanate. The charge distribution of chlorine atom is increasing trend in B3LYP/6-311++G(d,p) methods in 2, 6-dichlorophenyl isocyanate. All hydrogen atoms are positive charges in title compound.



Atomic Number

Fig 7. Correlation graph of Mulliken atomic charges with B3LYP/6-311+G (d,p) and 6-311++G(d,p) levels

Thermodynamic function analysis

On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity $(C_{p,m}^{0})$, entropy (S_{m}^{0}) , Gibb's free energy (G_{m}^{0}) and enthalpy changes (H_{m}^{0}) for the title molecule were obtained from the theoretical harmonic frequencies and listed in Table 9.

Table 9. Statistical thermodynamic parameters of 2, 6dichlorophenyl isocyanate at various temperatures.

Temp.	Thermodynamic parameters (k cal mol ⁻¹)							
(Kelvin)	CP	S	$(H^{o} - E^{o}_{o})/T$	$(G_o - E_o^o)/T$				
100	17.6925	76.63999	12.37516	-64.2648				
200	27.7107	95.62987	20.94753	-74.6823				
300	36.6213	113.8971	31.07623	-82.8209				
400	44.0459	132.1826	42.23190	-89.9507				
500	49.9909	150.5685	54.13482	-96.4337				
600	54.6724	169.0320	66.60817	-102.424				
700	58.3767	187.5360	79.53040	-108.006				
800	61.3484	206.0484	92.81294	-113.235				
900	63.7681	224.5448	106.3888	-118.156				
1000	65.7636	243.0079	120.2064	-122.801				

From the Table 9, it can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy, enthalpy, Gibb's free energy changes and temperatures were fitted by quadratic formulas and the corresponding fitting factors (\mathbb{R}^2) for these thermodynamic properties are 0.996, 1.999, 0.999 and 1.000 respectively. The corresponding fitting equations are as follows and the correlation graphics of those shows in Fig.8

$$C_{p,m}^{0} = 7.771 + 0.110T - 5.0 \times 10^{-5}T^{2}(R^{2} = 0.996)$$

$$H_{m}^{0} = 2.411 + 0.088T - 3.0 \times 10^{-5}T^{2}(R^{2} = 1.999)$$

$$G_{m}^{0} = -50.05 - 0.095T - 3.0 \times 10^{-5}T^{2}(R^{2} = 0.999)$$

$$S_{m}^{0} = 58.47 + 0.184T - 3.0 \times 10^{-7}T^{2}(R^{2} = 1.000)$$



Fig 8. Correlation graph of Gibb's energy, entropy and enthalpy With temperature of 2, 6-dichlorophenyl isocvanate

Conclusion

The infrared and Raman spectral measurements have been made for 2, 6-dichlorophenyl isocyanate The structure of the spectra is considerably different from their parent-phenyl isocyanate. The vibrational structure of 2, 6-dichlorophenyl isocyanate shows features different from the spectra, with regard to the substituent' position, and chlorine, in-plane and out-ofplane vibrations. A complete vibrational assignment has been proposed, aided by electronic structure calculations (at B3LYP/6-311+G(d,p) and 6-311++G(d,p) basis sets), and normal coordinate treatment. Potential energy distributions (PEDs) suggest that several normal modes are coupled in varying degrees. Further, first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis, thermodynamic properties of the title compound was performed on the basis of DFT calculations at the B3LYP/6-311+G(d,p) and 6-311++G(d,p) basis sets.

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