



Analyses of Molecular Structure, Vibrational Spectra, Nbo, Mulliken Charge and Nlo Studies of Penta Chloro Nitro Benzene

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ABSTRACT

Benzene is mainly used as an intermediate to make other chemicals; its mostly widely-produced derivatives include styrene, which is used to make polymers and plastics. Benzene is also used to make some types of rubbers, lubricants, dyes, detergents, drugs and pesticides. Natural sources of benzene include volcanoes and forest fires. At one time, chlorobenzene is the main precursor for the manufacture of phenol. The major use of chlorobenzene is an intermediate in the production of commodities such as herbicides, dyestuffs, and rubber. Chlorobenzene is also used as high-boiling solvent in many industrial applications as well as in the laboratory. As a continuation of the recent studies on structural and theoretical investigations of some substituted benzene derivatives, the main aspects of this investigation are: Structural analysis, molecular geometries and vibrational spectra of penta chloro nitrobenzene (PCNB) are calculated by applying density functional theory (DFT) and *ab initio* (HF) computations and thermodynamical parameters, NBO, NLO and Mulliken Charge analyses have been used to give more information regarding charge transfer within the molecules. Thermo dynamical properties like entropy, heat capacity, zero-point vibrational energy and Mulliken's charge analysis have been calculated for PCNB. The most possible interaction is explained using nature bond orbital (NBO) analysis and the potential compound of non-linear optics (NLO) demands the investigation of its structural and bonding features contributing the hyperpolarizability.

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1. Introduction

Benzene is a clear, colorless, non-corrosive and highly flammable liquid with a sweet odour. It evaporates into the air very quickly and dissolves slightly in water [1]. Benzene is mainly used as an intermediate to make other chemicals; its mostly widely-produced derivatives include styrene, which is used to make polymers and plastics [2]. Benzene is also used to make some types of rubbers, lubricants, dyes, detergents, drugs and pesticides. Natural sources of benzene include volcanoes and forest fires. Benzene is also a natural part of crude oil, gasoline and cigarette smoke [3-5]. At one time, chlorobenzene is the main precursor for the manufacture of phenol. The major use of chlorobenzene is an intermediate in the production of commodities such as herbicides, dyestuffs, and rubber. Chlorobenzene is also used as high-boiling solvent in many industrial applications as well as in the laboratory [6]. Interestingly, dinitrobenzene belongs to the group of organic halogen compounds and used in the fumigant and insecticide, solvent, chemical intermediate to manufacture dyes, agrochemical, pharmaceuticals and other organic synthesis.

As a continuation of the recent studies on structural and theoretical investigations of some substituted benzene derivatives, the main aspects of this investigation are: Structural analysis, molecular geometries and vibrational spectra of penta chloro nitrobenzene (PCNB) are calculated by applying density functional theory (DFT) and *ab initio* (HF)

computations and thermodynamical parameters, NBO, NLO and Mulliken Charge analyses have been used to give more information regarding charge transfer within the molecules.

2. Experimental Methods

The pure sample of PCNB obtained from Lancaster chemical company, UK and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of the title compound was recorded in the region 4000 - 400 cm^{-1} , at a resolution of $\pm 1 \text{ cm}^{-1}$ using a BRUKER IFS-66 V FTIR spectrometer equipped a cooled MCT detector using KBr pellets. Boxcar apodization is used for the 250 averaged interferograms collected for both the sample and background. The FT-Raman spectra is recorded on a computer interfaced BRUKER IFS 66V model interferometer equipped with FRA-106 FT-Raman accessory in the 3500-100 cm^{-1} stokes region. For that, Nd:YAG laser operating at 200 mw power with 1064 nm excitation is used as source.

2.1. Computational Procedure

Density functional calculations are carried out for PCNB with the 2009 version (G09-DFT) of the GAUSSIAN suite program [7] at the Becke-3-Lee-Yang-Parr (B3LYP) functional [8,9] implemented with the standard 6-31+G(d,p) large basis set. All the parameters are allowed to relax and all the calculations converged to an optimized geometry which

Table 1. Optimized geometrical parameters of Penta Chloro Nitro Benzene obtained by B3LYP and HF methods.

Bond Length	Values		Bond Angle	Values		Dihedral Angle	Values	
	B3LYP	HF		B3LYP	HF		B3LYP	HF
	6-31+ G (d,p)	6-31+ G (d,p)		6-31+ G (d,p)	6-31+ G (d,p)		6-31+ G (d,p)	6-31+ G (d,p)
C1-C2	1.3937	1.3782	C2-C1-C6	122.2563	121.6405	C6-C1-C2-C3	0.0001	0.0001
sC1-C6	1.3937	1.3782	C2-C1-N12	118.8718	119.1797	C6-C1-C2-C17	179.9995	-180.0008
C1-N12	1.483	1.4605	C6-C1-N12	118.8719	119.1797	N12-C1-C2-C3	-180	180.0001
C2-C3	1.4041	1.3825	C1-C2-C3	118.9332	119.184	N12-C1-C2-C17	-0.0006	-0.0008
C2-C17	1.7324	1.7783	C1-C2-C17	119.651	119.4084	C2-C1-C6-C5	0.0001	0.0001
C3-C4	1.4075	1.3861	C3-C2-C17	121.4158	121.4076	C2-C1-C6-C11	179.9994	-180.0008
C3-C18	1.7315	1.7784	C2-C3-C4	119.6922	119.7471	N12-C1-C6-C5	180.0001	180.0001
C4-C5	1.4075	1.3861	C2-C3-C18	119.8334	119.8021	N12-C1-C6-C11	-0.0005	-0.0008
C4-C19	1.7322	1.779	C4-C3-C18	120.4744	120.4508	C2-C1-N12-O13	-89.989	-89.9829
C5-C6	1.4041	1.3825	C3-C4-C5	120.493	120.4972	C2-C1-N12-O14	90.011	90.0171
C5-C110	1.7315	1.7784	C3-C4-C19	119.7535	119.7514	C6-C1-N12-O13	90.0109	90.0171
C6-C111	1.7324	1.7783	C5-C4-C19	119.7535	119.7514	C6-C1-N12-O14	-89.9891	-89.9829
N12-O13	1.2246	1.2205	C4-C5-C6	119.6922	119.7471	C1-C2-C3-C4	-0.0001	-0.0001
N12-O14	1.2246	1.2205	C4-C5-C110	120.4744	120.4508	C1-C2-C3-C18	179.9998	-180.0003
			C6-C5-C110	119.8334	119.8021	C17-C2-C3-C4	-179.9995	180.0008
			C1-C6-C5	118.9332	119.184	C17-C2-C3-C18	0.0004	0.0006
			C1-C6-C111	119.651	119.4084	C2-C3-C4-C5	0.0001	0.0001
			C5-C6-C111	121.4158	121.4076	C2-C3-C4-C19	180.0001	180.0001
			C1-N12-O13	116.6132	117.2055	C18-C3-C4-C5	180.0001	180.0002
			C1-N12-O14	116.6132	117.2055	C18-C3-C4-C19	0.0001	0.0002
			O13-N12-O14	126.7736	125.5891	C3-C4-C5-C6	0.0001	0.0001
						C3-C4-C5-C110	-179.9999	180.0002
						C19-C4-C5-C6	-179.9999	-179.9999
						C19-C4-C5-C110	0.0001	0.0002
						C4-C5-C6-C1	-0.0001	-0.0001
						C4-C5-C6-C111	-179.9995	180.0008
						C110-C5-C6-C1	179.9998	-180.0003
						C110-C5-C6-C111	0.0005	0.0006

corresponds to a true energy minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming the molecule belongs to C_1 point group symmetry. The transformation of force field from Cartesian to internal, local symmetry coordinates, the scaling, the subsequent normal coordinate analysis (NCA), calculation of total energy distribution (TED) are done on a PC with the version V7.0-G77 of the MOLVIB program written by Sundius [10-12].

3. Result and Discussion

3.1. Molecular geometry

The molecular structure of PCNB is shown in Fig.1. The global minimum energy obtained by DFT structure optimization for PCNB is calculated as -763.8140 Hartrees. Detailed description of vibrational modes can be given by means of normal coordinate analysis.

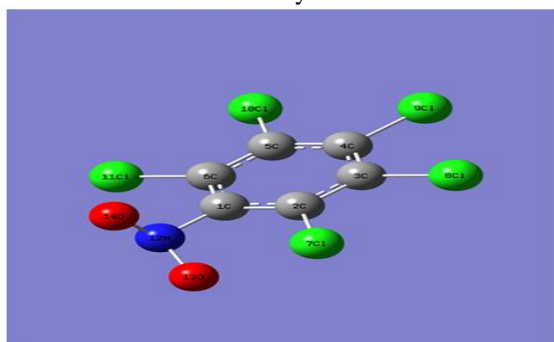


Fig 1. Optimized molecular structure of Penta Chloro Nitro Benzene.

3.2. Vibrational Spectra

The title compound consists of 14 atoms and its 36 normal modes of vibrations. The detailed vibrational assignments of fundamental modes of PCNB along with the calculated IR and Raman frequencies and normal mode descriptions (Characterized by TED) are presented in Table 2.

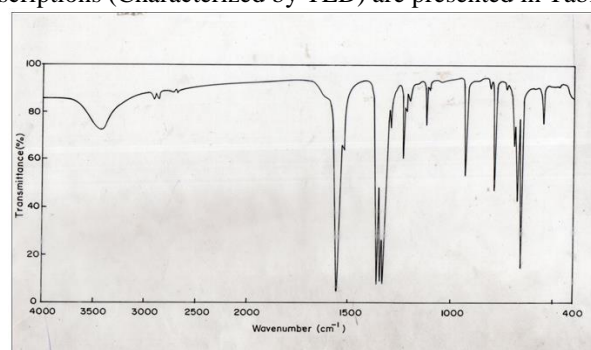


Fig 2. FT-IR Spectrum of Penta Chloro Nitro Benzene.

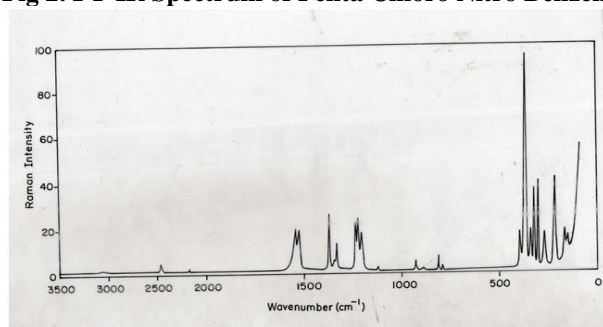


Fig 3. FT-Raman Spectrum of Penta Chloro Nitro Benzene.

The FTIR and FT-Raman spectra of PCNB are shown in Figs. 2-3. From the theoretical values, it is found that most of the optimized bond lengths are slightly lesser than the experimental values.

C-C vibrations

The bands between 1400 and 1650 cm^{-1} in the aromatic and hetero aromatic compounds are assigned to C-C stretching vibrations [13,14]. Therefore, the C-C stretching vibrations of PCNB are observed at 1365, 1347, 1336 cm^{-1} and 1647, 1628 and 1377 cm^{-1} in IR and Raman spectra, respectively. The in-plane and out-of-plane bending vibrations of C-C group are also listed in Table 2.

C-N vibrations

The C-N stretching frequencies in the side chain are found to be a rather difficult task, since there are problems in identifying these frequencies from other vibrations. The C-N stretching usually lies in the region 1400–1200 cm^{-1} . Since, mixing of bands is possible in this region. However, with the help of force field calculations the C-N vibrations are identified [15]. In this investigation, the C-N stretching vibrations of PCNB are found at 1323 cm^{-1} in FT-IR spectrum. The C-N bending vibrations and deformations of PCNB are summarized in Table 2.

Table 2. Vibrational Assignments of fundamental frequencies in cm^{-1} and wave numbers obtained for Penta Chloro Nitro Benzene using B3LYP/6-31+G (d,p) and HF/6-31+G (d,p) level.

S. No	Observed Frequencies		Calculated Values				TED% Among Types Internal Co-Ordinates
	FT-IR	FT-Raman	B3LYP/6-31+G (d,p)		HF/6-31+G (d,p)		
			Frequencies		Frequencies		
			Unscaled	Scaled	Unscaled	Scaled	
1	1661	–	1643	1665	1753	1669	NO ₂ assy (86%)
2	–	1647	1577	1652	1751	1656	γ C-C (99%)
3	–	1628	1558	1632	1584	1638	γ C-C (99%)
4	1527	–	1415	1532	1554	1538	NO ₂ symm(88%)
5	–	1377	1375	1382	1518	1389	γ C-C(98%)
6	1365	–	1368	1369	1484	1373	γ C-C(97%)
7	1347	–	1281	1350	1347	1356	γ C-C(99%)
8	1336	–	1225	1341	1279	1346	γ C-C(98%)
9	1323	–	1115	1328	1236	1334	γ C-N(96%)
10	1297	–	933	1305	1021	1309	b C-C(85%)
11	–	1239	886	1246	998	1252	b C-C(84%)
12	1236	–	809	1242	941	1250	b C-C(83%)
13	1224	1226	793	1231	868	1241	b NO ₂ (70%)
14	–	1208	718	1212	859	1220	b NO ₂ (71%)
15	1204	–	676	1207	842	1217	b C-N(83%)
16	1123	–	656	1128	760	1131	γ C-Cl(75%)
17	1109	–	645	1113	698	1118	γ C-Cl(74%)
18	932	–	584	935	686	942	γ C-Cl(72%)
19	789	–	560	793	601	800	γ C-Cl(71%)
20	694	–	466	699	562	706	γ C-Cl(73%)
21	677	–	386	687	406	692	ω C-C(68%)
22	663	–	360	674	405	679	ω C-C(67%)
23	659	–	334	671	376	676	ω C-C(66%)
24	–	580	323	588	348	592	b C-Cl(65%)
25	–	505	297	512	329	518	b C-Cl(64%)
26	–	430	262	436	310	444	b C-Cl(63%)
27	–	396	234	401	250	411	b C-Cl(62%)
28	–	368	219	372	233	380	b C-Cl(61%)
29	–	340	218	350	231	358	ω C-N(58%)
30	–	325	203	336	216	344	ω C-Cl(57%)
31	–	303	155	315	172	323	ω C-Cl(55%)
32	–	271	141	281	162	286	ω C-Cl(53%)
33	–	231	87	242	97	247	ω C-Cl(52%)
34	–	220	68	232	76	237	ω C-Cl(50%)
35	–	169	60	179	68	187	ω NO ₂ (45%)
36	–	155	39	166	16	174	ω NO ₂ (42%)

Abbreviations: γ – stretching; b – bending; ω – out-of-plane bending; t – torsion; R – ring; trigd – trigonal deformation; symd – symmetric deformation; asymd – antisymmetric deformation.

NO₂ group vibrations

The characteristic group frequencies of the nitro group are relatively independent of the rest of the molecule which makes this group convenient to identify. Aromatic nitro compounds

have strong absorptions due to the asymmetric and symmetric stretching vibrations of the NO₂ group at 1570-1485 cm^{-1} and 1370-1320 cm^{-1} , respectively [16]. Hence, the asymmetric stretching mode of nitro group for PCNB is identified at 1661

cm^{-1} in FT-IR spectrum and in good agreement with TED output. The symmetric stretching mode of nitro group is assigned at 1527 cm^{-1} in IR spectrum. The deformation vibrations of NO_2 group (rocking, wagging and twisting) contribute to several normal modes in the low frequency region [17].

C-Cl vibrations

The vibrations belonging to the bond between the ring and halogen atoms are discussed here as mixing of vibrations is possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule. Generally, the C-Cl absorption is obtained in the broad region between $850\text{-}550 \text{ cm}^{-1}$ [18]. Therefore, the bands found at $1123, 1109, 932, 789$ and 694 cm^{-1} in IR is assigned to C-Cl stretching vibrations of PCNB. Most of the aromatic chloro compounds have the region $385 - 265 \text{ cm}^{-1}$ due to C-Cl in-plane bending vibration. Accordingly, the bands identified $580, 505, 430, 396$ and 368 cm^{-1} in Raman is assigned to the C-Cl in-plane mode of PCNB respectively. The C-Cl out-of-plane deformation for the title compound is established at $325, 303, 271, 231$ and 220 cm^{-1} in the Raman spectrum.

4. Prediction of First Hyperpolarizability

The first hyperpolarizability (β_0) of this novel molecular system and the related properties (β_0, α_0) of PCNB are calculated using the B3LYP/6-31+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. The first hyperpolarizability is a third-rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [19,20]. It can be given in the lower 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 homogenous, this expansion becomes

$$E = E_0 - \mu_a F_a - 1/2 \alpha_{ab} F_a F_b - 1/6 \beta_{abc} F_a F_b F_c + \dots$$

where E_0 is the energy of the unperturbed molecules, F_a is the field at the origin and μ_a, α_{ab} and β_{abc} are the components of dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment μ , the mean polarizability α_0 and the mean first hyperpolarizability β_0 , using the x, y, z components they are defined as:

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

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

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

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

$$\beta_{\text{vec}} = 3/5 [(\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}]$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$$

The β_0 components of GAUSSIAN 09W output are reported in atomic units and therefore the calculated values are converted into e.s.u. units ($1 \text{ a.u.} = 8.3693 \times 10^{-33} \text{ e.s.u.}$). The calculated value of hyperpolarizability and polarizability of PCNB are tabulated in Table 6.6. The title molecule (PCNB) are an attractive object for future studies of non-linear optical properties.

5. Mulliken Population Analysis

The charge distributions calculated by the Mulliken method for the equilibrium geometry of PCNB with DFT/6-

31+G(d,p) are listed in Tables 3. The charge distribution on the molecule has an important influence on the vibrational spectra. The corresponding Mulliken's plot is shown in Fig.4.



Fig 4. Plot of Mulliken's atomic charges of Penta Chloro Nitro Benzene.

Table 3. The Mulliken charge analyses of Penta Chloro Nitrobenzene calculated by B3LYP and HF methods.

S. No	Atoms	Mulliken Charges	
		B3LYP 6-31+G (d,p)	HF 6-31+G (d,p)
1	C ₁	-0.468061	-1.79742
2	C ₂	0.005988	0.193662
3	C ₃	0.251675	0.307613
4	C ₄	-0.670798	-1.100168
5	C ₅	-0.19906	-0.306298
6	C ₆	-0.438458	-0.375622
7	Cl ₇	0.327777	0.571584
8	Cl ₈	0.363052	0.680189
9	Cl ₉	0.320625	0.615598
10	Cl ₁₀	0.362125	0.679111
11	Cl ₁₁	0.284914	0.521766
12	N ₁₂	-0.087345	-0.016738
13	O ₁₃	0.031222	0.118162
14	O ₁₄	-0.083654	-0.091439

From the results it is clear that the substitution of Cl, NO_2 atoms in the heterocyclic ring leads to a redistribution of electron density. The σ -electron withdrawing character of the NO_2 and Cl atom in this title compound is demonstrated by the decrease of electron density on Cl and NO_2 atom. The atomic charges in the NO_2 group are almost identical. The atomic charges obtained from 6-31+G(d,p) basis set shows that common atoms of NO_2 and Cl of PCNB is more acidic due to more positive charge whereas C₁, C₄, C₅, C₆, N₁₂ and O₁₄ are more negative.

6. NBO ANALYSIS

The NBO analysis is carried out by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating their energetic important by 2nd order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOS of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as delocalization corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j) with delocalization $i \rightarrow j$ is estimated as

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

where q_i is the donor orbital occupancy ϵ_j and ϵ_i are diagonal elements orbital energies and $F(i, j)$ is the off

diagonal NBO Fock matrix element. The larger $E^{(2)}$ value, the more intensive is the interaction between electron donors and acceptors, i.e., the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system.

DFT/6-31+G(d,p) level computation is used to investigate the various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the delocalization or hyper-conjugation [21]. NBOs are localized electron pair orbitals for bonding pairs and lone pairs. The hybridization of the atoms and the weight of each atom in each localized electron pair bond are calculated in the idealized Lewis structure. A normal Lewis structure would not leave any antibonding orbitals, so the presence of antibonding orbitals shows deviations from normal Lewis structures. Anti bonding localized orbitals are called non-Lewis NBOs. If the occupancy is not 8.0, then there are deviations from an ideal Lewis structure. In order to study the small deviations from idealized Lewis structure, the Donor-Acceptor interaction approach is adopted. In PCNB, $\pi(C_1-C_6) \rightarrow \pi^*(C_2-C_3)$ interaction is seen to give a strong stabilization 19.46 kJ/mol. This strong stabilization denotes the larger delocalization. The interesting interactions in PCNB molecule are LP(2)Cl₇ and LP(3)Cl₁₀ with that of antibonding C₂-C₃ and C₄-C₅. These two interactions result the stabilization energy of 13.89 and 14.01 kJ/mol respectively. This highest interaction around the ring can induce the large bioactivity in the molecule. The p character of chlorine lone pair orbital LP(2)Cl₇ and LP(3)Cl₁₀ are 99.99% and 99.98%, respectively. This shows that the lone pair orbital participates in electron donation in the molecule. The calculated values of $E^{(2)}$ are shown in Table.4 for PCNB.

7. Thermodynamical Properties

In addition to the vibrational assignments, several thermodynamic parameters are also calculated on the basis of vibrational analysis at B3LYP/6-31+G(d,p) and HF/6-

31+G(d,p). The calculated thermodynamic properties of PCNB are presented in the Table 5. The self consistent field (SCF) energy, zero-point vibrational energies (ZPVE), rotational constants, dipole moment and entropy $S_{vib}(T)$ are calculated to the extent of accuracy and the variations in the ZPVEs seem to be insignificant. The total energies and change in total entropy of PCNB at room temperature are only marginal.

Table 5. The Thermodynamic parameters of Penta Chloro Nitro Benzene calculated by B3LYP and HF methods.

Parameters	Method/Basis Set	
	B3LYP 6-31+G(d, p)	HF 6-31+G(d, p)
Total Energy Etotal	42.168	45.045
Heat Capacity (Cv)	45.035	42.263
Entropy (S)	119.077	117.108
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	40.39	43.268
Zero Point vibrational Energy	33.8412	37.22386
Rotational Constant(GHZ)		
A	0.44399	0.43847
B	0.3942	0.39388
C	0.21564	0.21412
Dipole Moment		
μ_x	2.7446	-3.2194
μ_y	0	0
μ_z	0	0
μ_{total}	2.7446	3.2194
Molecular mass	292.83717 amu	292.83717 amu
Rotational Temperature (Kelvin)		
T1	0.02131	0.02104
T2	0.01892	0.0189
T3	0.01035	0.01028

Table 4. Second order perturbation theory analysis of Fock matrix in NBO basic corresponding to the intermolecular bonds of Penta Chloro Nitro Benzene.

S. No	Donor	Acceptor	E(2)	Ej-Ei	F(i,j)
1	$\sigma(C_1-C_2)$	$\sigma^*(C_1-C_6)$	3.9	1.28	0.063
2	$\sigma(C_1-C_6)$	$\sigma^*(C_1-C_2)$	3.84	1.29	0.063
	π	$\pi^*(C_2-C_3)$	19.46	0.27	0.067
3	$\sigma(C_1-N_{12})$	$\sigma^*(N_{12}-O_{14})$	1.87	1.05	0.041
4	$\sigma(C_2-C_3)$	$\sigma^*(C_1-C_2)$	4.25	1.29	0.066
	π	$\pi^*(C_4-C_5)$	18.63	0.28	0.066
5	$\sigma(C_3-C_4)$	$\sigma^*(C_2-C_{17})$	3.51	0.89	0.05
6	$\sigma(C_3-C_{18})$	$\sigma^*(C_1-C_2)$	2.58	1.23	0.051
7	$\sigma(C_4-C_5)$	$\sigma^*(C_6-Cl_{11})$	3.55	0.9	0.05
	π	$\pi^*(C_1-C_6)$	18.65	0.28	0.066
8	$\sigma(C_4-Cl_9)$	$\sigma^*(C_2-C_3)$	2.57	1.23	0.05
9	$\sigma(C_5-C_6)$	$\sigma^*(C_4-C_5)$	3.42	1.28	0.059
10	$\sigma(C_5-Cl_{10})$	$\sigma^*(N_{12}-O_{13})$	2.38	3.58	0.092
11	$\sigma(C_6-Cl_{11})$	$\sigma^*(C_1-C_2)$	2.88	1.23	0.053
12	$\sigma(N_{12}-O_{13})$	$\pi^*(N_{12}-O_{14})$	2.19	1.34	0.053
13	$\sigma(N_{12}-O_{14})$	$\pi^*(N_{12}-O_{14})$	87.46	1.11	0.296
	π	$\sigma^*(N_{12}-O_{14})$	62.07	0.53	0.167
14	$\pi^*(C_1-C_6)$	$\sigma^*(N_{12}-O_{14})$	1.98	0.24	0.036
15	$\sigma(N_{12}-O_{14})$	$\pi^*(N_{12}-O_{13})$	15.51	2.66	0.342
16	$\pi^*(N_{12}-O_{14})$	$\sigma^*(C_1-C_6)$	6.22	0.04	0.03
17	$\pi^*(N_{12}-O_{14})$	$\pi^*(N_{12}-O_{13})$	112.11	2.41	0.742

$E^{(2)}$ means energy of hyper conjugative interaction (stabilization energy).

Energy difference between donor and acceptor i and j NBO orbitals.

$F(i,j)$ is the Fock matrix element between i and j NBO orbitals.

Table 6. Hyperpolarizability (β), electric dipole moment (μ) and the polarizability (α_0) at the B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) basis set of Penta Chloro Nitro Benzene.

Parameters	B3LYP/6-31+G(d,p)	HF/6-31+G(d,p)
β_{xxx}	21.9161	10.6315
β_{xyx}	0.9162	-26.3431
β_{xyy}	8.2783	-6.0970
β_{yyy}	32.5758	48.0707
β_{zxx}	-9.3648	-4.7663
β_{xyz}	4.3023	22.6950
β_{zyy}	2.8154	18.9111
β_{xzz}	12.8221	18.6983
β_{yzz}	3.0676	-1.9812
β_{zzz}	-14.9328	-25.7256
β_{total}	0.5055x10 ⁻³⁰ esu	0.2729x10 ⁻³⁰ esu
α_{xx}	-122.8412	-131.4178
α_{xy}	0	0
α_{yy}	-107.7952	-113.7422
α_{xz}	0	0
α_{yz}	0	0.0015
α_{zz}	-115.4247	-118.8468
α_0	0.3214x10 ⁻³⁰ esu	0.3523x10 ⁻³⁰ esu
μ_x	2.7446	-3.2194
μ_y	0	0
μ_z	0	0
μ_{total}	2.7446 Debye	3.2194 Debye

Conclusion

The vibrational properties of PCNB have been investigated by FT-IR and FT-Raman spectroscopies and are based on DFT calculations. The vibrational frequencies analysis by B3LYP method agrees satisfactorily with experimental results. On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of PCNB are examined and proposed. Therefore, the assignments made at higher level of the theory with higher basis set with reasonable deviations from the experimental values, seems to be correct. NBO study

reveals that lone pair orbital participates in electron donation to stabilize the compound.

NLO property has also been observed by predicting the first hyperpolarizability for the title compound due to the substitution in the benzene.

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