# Vibrational Spectroscopic Investigation, Homo-Lumo, Nlo, and NBO Analyses ofAlpha, Alpha- Dibromo – M- Chloro Toluene

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## ABSTRACT

The FTIR and FT-Raman spectra of alpha, alpha- dibromo –m- chloro toluene (AADMCT) have been recorded in the regions 4000-400$cm^{-1}$ and 3500-400$cm^{-1}$, respectively. Utilizing the observed FT-Raman and FTIR data, a complete vibrational assignment and analysis of the fundamental modes of the compound have been carried out and subsequently confirmed by total energy distribution (TEDs). In the calculations performed to determine the optimum molecular geometry, harmonic vibrational frequencies, infrared intensities and Raman scattering activities. The first hyperpolarizability of the molecule have been calculated. The effects of frontier orbitals, HOMO and LUMO and the transition of electron density transfer have been discussed. The chemical interpretation of hyperconjugative interactions and charge delocalization has been analyzed using natural bond orbital (NBO) analysis.

**Keywords :** FTIR, FT-Raman, alpha, alpha- dibromo –m- chloro toluene, NBO.

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## I. INTRODUCTION

Toluene, also known as methylbenzene or phenylmethane, is a clear water-insoluble liquid with the typical smell of paint thinners, redolent of the sweet smell of the related compound benzene. It is an aromatic hydrocarbon that is widely used as industrial feedstock and as a solvent. Like other solvents, toluene is used as an inhalent drug for its intoxicating properties [1,2]. Toluene reacts as a normal aromatic hydrocarbon towards electrophilic aromatic substitution [3,4]. The methyl group in toluene makes it around 25 times more reactive than benzene in such reactions. Toluene can be used to break open red blood cells in order to extract hemoglobin in biochemistry experiments [5]. The complete vibrational analysis of alpha,alpha-dibromo-M-chlorotoulene (AADMCT) was performed by combining the experimental and theoretical information using Pulay's density functional theory (DFT) based on scaled quantum chemical approach [6].

Density functional theory calculations [7] are also reported to provide excellent vibrational frequencies of organic compounds, if the calculated frequencies are scaled to compensate the approximate treatment of electron correction, basis set deficiencies and the anharmonicity effects [8-12]. Electronic structure methods, namely, ab initio HF self consistent field method and density functional methods are increasingly used by spectroscopists for modelling molecular properties that include equilibrium structure vibrational frequencies and intensities [13].

Spectroscopic investigations on isomeric toluidines, nitro toluenes, α-chlorotoluene, α,α-dichlorotoluene and 2-bromo-4-methylaniline are reported in literature [14-17]. The structural stability of toluene molecule has

been investigated in the past years by several workers [18-20]. By combining all those facts into account, the present investigation has been aimed to investigate the vibrational spectra of AADMCT. Investigations have also been carried out to identify the HOMO-LUMO energy gap, NLO property, NBO analysis, thermodynamical properties and delocalization activity of the electron clouds in the optimized molecular structure. All the investigations have been done on the basis of the optimized geometry by using ab initio HF/6-311++G(d,p) and density functional theory (DFT) B3LYP/6-311++G(d,p) level.

## II. EXPERIMENTAL PROCEDURE

The pure sample of alpha, alpha-dibromo-M-chlorotoulene (AADMCT) were purchased from the Lancaster chemical company UK, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The room temperature FT-IR spectra of the title compound was recorded in the region 4000–400 cm$^{-1}$ on BRUKER IFS 66V spectrometer using KBr pellet. The spectral resolution is $\pm$ 1 cm$^{-1}$.

The FT-Raman spectra was recorded in the region 3500 – 50 cm$^{-1}$ with BRUKER RFS 100/s Raman module equipped with Nd: YAG laser source operating at 1064 nm line width 150mW power. The spectra were recorded with scanning speed of 50 cm$^{-1}$ min$^{-1}$ of spectral width 4 cm$^{-1}$. The reported wave numbers are believed to accurate within $\pm$ 1 cm$^{-1}$.

## III. METHODS OF COMPUTATION

Quantum chemical density functional theory calculations were carried out for AADMCT with GAUSSIAN 2009W program software package [21] using standard B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) methods and basis sets. The Cartesian representation of the theoretical force constants has been computed at the optimized geometry by assuming C$_s$ point group symmetry (low symmetry). The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, Raman activity, atomic charges, dipole moment, first-order hyperpolarizability and other thermodynamic parameters were calculated.

Scaling of the force field was performed according to the SQM procedure [22,23] Transformation of the force field and the subsequent normal coordinate analysis (NCA) including the least squares refinement of the scaling factors, calculation of total energy distribution (TED) were done on a PC with the MOLVIB program (version V7.0 – G77) written by Sundius [24,25].

## IV. RESULTS AND DISCUSSION
### 4.1. Molecular Geometry

A complete geometry optimization was performed within the C$_s$ point group symmetry. The optimized molecular structure of AADMCT is shown in Fig. 1. The corresponding global minimum energy obtained by the HF/6-311G(d,p) and B3LYP 6-311++G(d,p) methods and basis sets are −5872.08044 a.u and −5878.15188 a.u respectively.

The structural parameters, bond lengths, bond angles and dihedral angles are calculated using HF / (6-311++G(d,p) and B3LYP/6-311++G(d,p) methods and basis sets are shown in the Table 1. The order of the bond lengths lie as C1- C2 ~ C1- C6 ~C1-C7~C3-C4~C4-C5~C5-C6. The lowest bond length found in C3- C4 is 1.3758 A$^o$ (HF) and 1.387 A$^o$ (DFT). The highest bond length 1.494 A$^o$ (HF) and 1.4029A$^o$ (DFT) is found in C1-C7.The distortion in the benzene ring is found to be evident from the order of bond angle C2-C1-C6 ~ C2-C1-C7 ~ C1-C2-C3~ C3-C4-C5. Benzene ring is unaffected by C4-C5-C6 and C1-C6-C5 ~120$^o$. The breakdown of the symmetry is also due to C2-C3-C4 and C6-C1-C7 ~ 121$^o$. The evaluated bond angle of C2-C1-C6 is 119.4$^o$.
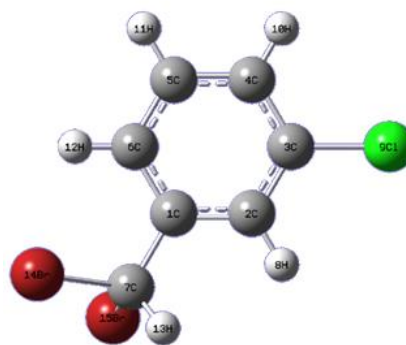


Fig : 1 Molecular structure of alpha, alpha – dibromo – M- Cholorotolune

## 4.2. Vibrational Spectra

The title compound consists of 15 atoms and its leads to 39 normal modes are distributed amongst the symmetry species as:

$$3N - 6 = 27A' \text{ (in-plane)} + 12A'' \text{ (out-of-plane)}$$

All the vibrations are active both in the Raman scattering and absorption. The vibrational spectral assignments performed on the recorded FT-IR and FT-Raman spectra based on the theoretically predicted wave numbers by B3LYP/ 6-311++G(d,p) and HF/6-311++G(d,p) modes of vibrations are presented in Table 2. None of the predicted vibrational spectra has any imaginary wave number, implying that the optimized geometry is located at the local lowest point on the potential energy surface. One knows that DFT potentials systematically overestimate the vibrational wave numbers. Those discrepancies are corrected by introducing proper scale factors [26]. Comparison of the wave numbers calculated with the DFT method using 6-311++G(d,p) basis set with experimental values reveals that the B3LYP method shows very good agreement with experimental observation due to inclusion of electron correlation for this method. The observed experimental FT-IR and FT-Raman spectra of AADMCT are shown in Figs. 2 and 3, respectively.
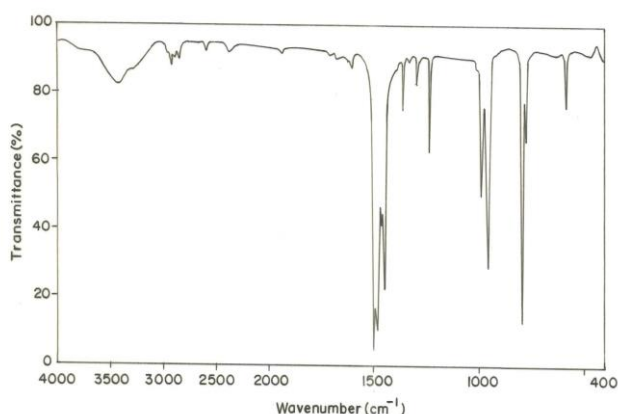


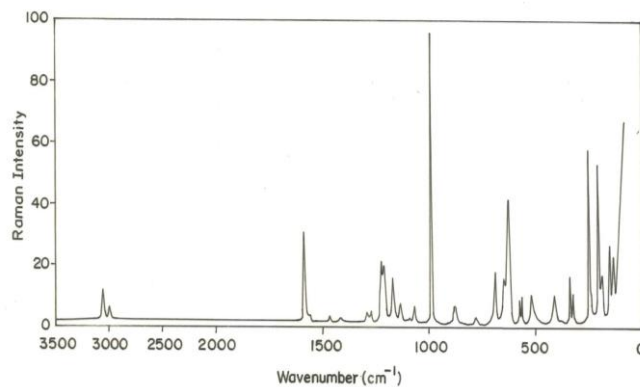**Fig.2:** FT-IR spectrum of Alpha alpha di-bromo-M-chlorotolotune



**Fig.3:** FT-Raman spectrum of Alpha alpha di-bromo-M-chlorotolotune

## 4.3. C–H  Vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 $cm^{-1}$ due to aromatic C–H stretching vibrations [27]. Hence, the infrared and Raman bands appeared at 3077, 3061, 3041, 3009 $cm^{-1}$ and 3150 $cm^{-1}$ in AADMCT have been assigned to C–H stretching vibrations respectively and these modes are confirmed by their TED values. The bands due to C–H in-plane ring bending vibrations, interacting somewhat with C–C stretching vibrations, are observed as a number of sharp bands in the region 1600-1400 $cm^1$ [28]. The C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900-667 $cm^{-1}$. The FTIR bands observed at 1424, 1301, 1286, 1235 $cm^{-1}$ are assigned to C–H in-plane bending vibrations of AADMCT. The out-of-plane bending vibrations of C–H group have also been identified and they are presented in Table 2.

## 4.4. C–C vibrations

Generally the [28-30] C–C stretching vibrations in aromatic compounds are seen in the region of 1430-1650 $cm^{-1}$.  The C–C stretching vibrations of AADMCT are strongly observed at 1693, 1595, 1584, 1574, 1477, 1471, 1432 and 1590 $cm^{-1}$ in FT-IR and FT-Raman spectrum respectively. All bands lie in the expected range when compared to the literature values. The C–C in-plane bending vibrations are observed at 1101$cm^{-1}$ in FT-IR spectrum . The out-of-plane bending vibrations appeared at 439 $cm^{-1}$ in FT-IR spectrum.

## 4.5. C–Cl vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here,

since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule [31]. Generally the C–Cl absorption is obtained in between 850 and 550cm$^{-1}$. For AADMCT, the FT-Raman bands found at 625cm$^{-1}$ have been designated to C–C1 stretching mode of vibration and the corresponding force constant contribute nearly74% to the TED. Most of the aromatic chloro compounds have the band of strong to medium intensity in the region 385-265 cm$^{-1}$ due to C–C1 in-plane bending vibration. Accordingly, the Raman bands identified at 310 cm$^{-1}$ is assigned to the C–C1 in-plane mode of AADMCT. The C–C1 out-of-plane deformation for AADMCT has been established at 170 cm$^{-1}$ in the Raman spectrum.

### 4.6. C-Br vibrations

The assignments of the C-Br stretching and deformation vibrations have been made on the basis of the calculated TED. Bromine compounds absorb strongly in the region 650-485 cm$^{-1}$ [32] due to the C-Br stretching vibrations. The bands identified at 655,639 and 640 cm$^{-1}$ in FT-IR and FT-Raman spectrum, have been assigned to C-Br stretching vibrations respectively. The FT-Raman bands are observed at 420, 340cm$^{-1}$ and 250, 205cm$^{-1}$ for C-Br in-plane and out-of-plane bending vibrations respectively.

## V. NON-LINEAR OPTICAL (NLO) PROPERTIES

The quantum chemistry based prediction of non-linear optical (NLO) properties of a molecule has an important role for the bonding and delocalization of electron density from occupied Lewis-type (donor) NBOs to properly unoccupied non-Lewis type design of materials in modern communication technology, signal processing and optical interconnections [33]. Especially organic molecules are studied because of their larger NLO susceptibilities arising from π-electron cloud movement from donor to acceptor, fast NLO response times, high laser damage thresholds and low dielectric constants. Although the organic molecules have these advantages, they have several NLO disadvantages, too they have generally low thermal stability and they may undergo a facile relaxation to random orientation [34]. The tensor components of the static first

hyperpolarizability (β) were analytically calculated by using the same method as mentioned above. From the computed tensorial components, β is calculated for the title molecule by taking into account the Kleimman symmetry relations and the square norm of the Cartesian expression for the β tensor [33]. The relevant expressions used for the calculation are shown below.

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

where

$$\beta_x= \beta_{xxx}+ \beta_{xyy}+ \beta_{xzz}$$
$$\beta_y= \beta_{yyy}+ \beta_{xxy}+ \beta_{yzz}$$
$$\beta_z= \beta_{zzz}+ \beta_{xxz}+ \beta_{yyz}$$

The components of dipole moment, and the first hyperpolarizability of the title compound can be seen in. The calculated value of the first hyperpolarizability is $5.9664 \times 10^{-30}$ e.s.u. The value of β obtained by Sun et al. [33] with the B3LYP/6-311++G(d,p) method for urea is $0.37289 \times 10^{-30}$ e.s.u. The first hyperpolarizability of AADMCT compound is 16 times greater than that of urea. According to the magnitude of the first hyperpolarizability, the title compound may be a potential applicant in the development of NLO materials.

## VI. 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, estimating their energetic importance by 2$^{nd}$ 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 -> j is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \qquad _____(2)$$

where $q_i$ is the donor orbital occupancy $\varepsilon_j$ and $\varepsilon_i$ are diagonal element orbital energies and $F (i, j)$ is the off diagonal NBO Fock matrix element. The larger the $E^{(2)}$ value, the more intensive is the interaction between electron donors and acceptors i.e., the more the tendency to donate from electron donors to electron

acceptors and the greater the extent of conjugation of the whole system. B3LYP/6-311++G(d,p) and HF/6-311++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 [35].

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 2.0, 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 AADMCT, $\pi$ (C5-C6) $\rightarrow$ $\pi^*$(C3-C4) interaction is seen to give a strong stabilization 23.23 Kcal/mol. This strong stabilization denotes the larger delocalization. The interesting interactions in AADMCT are LP(3) Cl 9 LP (3) Br14 and LP(3)Br15 with that of antibonding C3-C4, C7 – Br 15 and C7-Br 14 . These two interactions result the stabilization energy of 12.56 ,7.36 and 7.42 Kcal/mol respectively. This highest interaction around the ring can induce the large bioactivity in the compound. The calculated values of $E^{(2)}$ are shown in Table 3.

## VII. THERMODYNAMIC PROPERTIES

The values of some thermodynamic parameters (such as zero point vibrational energy, thermal energy, specific heat capacity, rotational constants, entropy and dipole moment) of AADMCT by B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) basis sets are listed in Table 4. The global minimum energy obtained for structure optimization of AADMCT using B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) basis sets are -5878.15187981 and -5872.08044015 Hartrees respectively. The difference in the values calculated by both the methods is only marginal. The same trends have been observed in

entropy calculations. All the above observations were made without any symmetric constrains. The thermal energies are also in same trend with global minimum energy. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. In the present study, the total dipole moment of AADMCT determined by using B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) methods basis set is 1.2898 and 1.2734 Debye, respectively. The variation in zero-point vibrational energies (ZPVEs) seems to be significant.

## VIII. HOMO-LUMO ANALYSIS

For AADMCT compound, the hipsochromic shifts is caused by an increase in the gap between bonding and anti-bonding orbitals. The energy gap between the highest occupied and the lowest unoccupied molecular orbitals, is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. 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 highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). The HOMO energy characterizes the ability of electron giving and the LUMO energy characterizes the ability of electron accepting and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gaps are largely responsible for the chemical and spectroscopic properties of the molecules. This is also used by the frontier electron density for predicting the most reactive position in conjugated system [36]. Here, molecular orbitals (MO) were explained for AADMCT, the HOMO, LUMO, is shown in Figs. 4 and 5 along with the respective energies.

The calculated energy value of HOMO in HF/6-311++G(d,p) is -0.35975 a.u. and energy of LUMO is 0.05340 a.u. Moreover lower in the HOMO and LUMO energy gap ($\Delta E$ = -0.4135 a.u.). The calculated energy value of HOMO in B3LYP/6-311++G(d,p) is -0.27259 a.u. and energy of LUMO is -0.07593 a.u. Moreover lower in the HOMO and LUMO energy gap ($\Delta E$ = -0.19669 a.u.). It explains the eventual charge transfer interactions taking place within the compound, which influences the biological activity of the compound and also energy serves as a measure of excitability of a compound, the smaller the energy gap, the more easily the compound will be excited. Consequently, the lowering of the HOMO-LUMO band gap is essentially a consequence of the large stabilization of the LUMO due to the strong electron-acceptor ability of the electron-acceptor group.

**First Excited State**



$E_{LUMO}$ = 0.05340 a.u.

$\Delta E$ = -0.41315 a.u

$E_{HOMO}$ = -0.35975 a.u
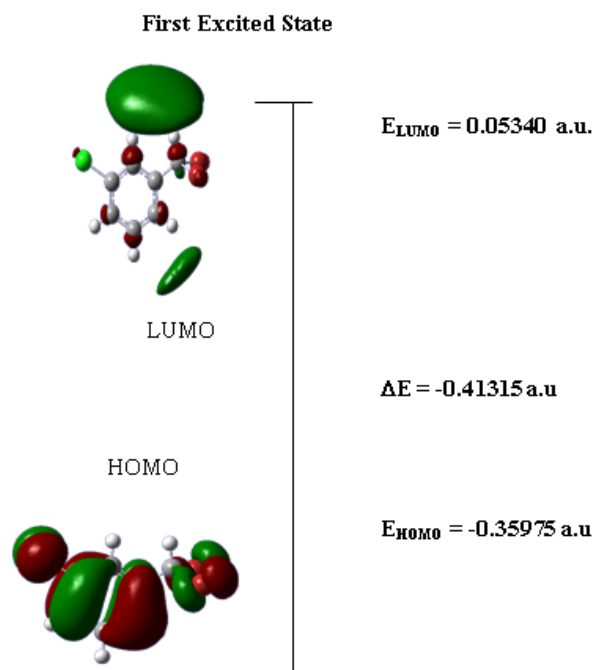
**Fig. 5:** HOMO – LUMO structure for alpha, alpha-dibromo-M-chlorotoluene by HF method

**First Excited State**



$E_{LUMO}$ = -0.07593 a.u.

$\Delta E$= -0.19666 a.u

$_{HOMO}$ = -0.27259 a.u.
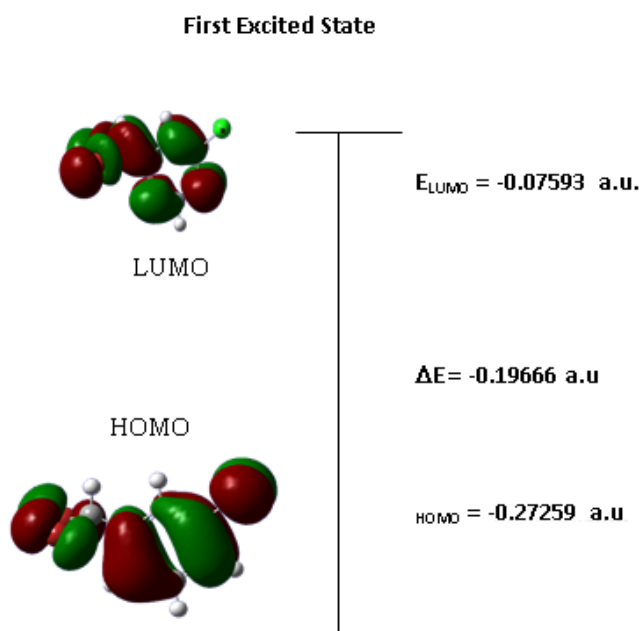
**Fig. 4 :** HOMO – LUMO structure for alpha, alpha-dibromo-M-chlorotoluene by DFT method

## IX. CONCLUSION

In the present investigation, the density functional calculations on alpha,alpha-dibromo-M-chlorotoulene have been performed. The main objective is to reproduce the molecular geometry, investigate delocalization of electron density, energy gap, and non-linear optical properties of alpha,alpha-dibromo-M-chlorotoulene for further studies. The HOMO-LUMO gap reveals that charge transfer may be taking place from the ring to bromine atom. The Natural bond orbital analysis indicates the strong intramolecular interactions of AADMCT confirm that the intramolecular charge transfer caused by $\pi$-electron cloud movement from donor to acceptor must be responsible for the non-linear optical properties compound.

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**Table 1:** Optimized geometrical parameters of alpha alpha –dibromo-M-Chlorotolune obtained by HF and B3LYP methods with 6-311++G(d,p) basis set

| Bond Length | Value (Å) | | Bond Angle | Value (°) | | Dihedral Angle | Value (°) | |
|---|---|---|---|---|---|---|---|---|
| | 6-311++G(d,p) | | | 6-311++G(d,p) | | | 6-311++G(d,p) | |
| | HF | DFT | | HF | DFT | | HF | DFT |
| C1 –C2 | 1.3885 | 1.4028 | C2-C1-C6 | 119.4323 | 119.4818 | C6-C1-C2-C3 | 0.0007 | 0.0053 |
| C1-C6 | 1.3912 | 1.4029 | C2-C1-C7 | 118.2414 | 118.1384 | C6-C1-C2-H8 | -180.004 | 180.0085 |
| C1-C7 | 1.494 | 1.4095 | C6-C1-C7 | 122.3263 | 122.3798 | C7-C1-C2- C3 | 180.0089 | -179.9787 |
| C2-C3 | 1.381 | 1.3904 | C1-C2-C3 | 119.3214 | 119.1158 | C7-C1-C2-H8 | 0.0033 | 0.0245 |
| C2-H8 | 1.0694 | 1.0806 | C1-C2-H8 | 120.9519 | 120.8444 | C2-C1-C6-C5 | 0.0026 | -0.0195 |
| C3-C4 | 1.3758 | 1.3879 | C3-C2-H8 | 119.7267 | 120.0398 | C2-C1-C6-H12 | 180.0056 | 179.9711 |
| C3-CL9 | 1.8061 | 1.8274 | C2-C3-C4 | 121.9752 | 122.1821 | C7-C1-C6-C5 | -180.006 | 179.9638 |
| C4-C5 | 1.3904 | 1.401 | C2-C3-CL9 | 118.7288 | 118.6542 | C7-C1-C6- H12 | -0.0029 | -0.0456 |
| C4-H10 | 1.0685 | 1.0796 | C4-C3-CL9 | 119.2959 | 119.1637 | C2-C1-C7-H13 | -0.001 | -0.0133 |
| C5-C6 | 1.3818 | 1.3923 | C3-C4-C5 | 118.4502 | 118.3523 | C2-C1-C7-Br14 | 117.48 | 117.6532 |
| C5-H11 | 1.07 | 1.0812 | C3-C4-H10 | 120.539 | 120.5672 | C2-C1-C7-Br15 | 117.49 | -117.6069 |
| C7-H13 | 1.0698 | 1.808 | C5-C4-H10 | 121.0108 | 121.0805 | C6-C1-C7-H13 | 180.0094 | 180.0032 |
| C7-Br14 | 1.0675 | 1.0799 | C4-C5-C6 | 120.5584 | 120.6412 | C6-C1-C7Br14 | -62.503 | -62.3303 |
| C7-Br15 | 1.9793 | 2.0115 | C4-C5-H11 | 119.50975 | 119.3869 | C6-C1-C7-Br15 | 62.5178 | 62.4096 |
| | | | C6-C5-H11 | 119.9321 | 119.9719 | C1-C2-C3-C4 | -0.002 | 0.0177 |
| | | | C1-C6-C5 | 120.2625 | 120.2266 | C1-C2-C3-Cl9 | -179.9977 | -180.0055 |
| | | | C1-C6-H12 | 119.8595 | 119.6367 | H8-C2-C3-C4 | 180.0053 | -179.9854 |
| | | | C5-C6-H12 | 119.878 | 120.1366 | H8-C2-C3-Cl9 | 0.0078 | -0.086 |
| | | | C1-C7-H13 | 111.341 | 112.2909 | C2-C3-C4-C5 | -0.0035 | 0.0259 |
| | | | C1-C7-Br14 | 112.6245 | 112.5134 | C2-C3-C4-H10 | -179.9948 | 179.9708 |
| | | | C1-C7-Br15 | 112.6234 | 112.4998 | Cl9-C3-C4-C5 | 179.994 | -180.0026 |
| | | | H13-C7-Br14 | 104.8817 | 104.5739 | CL9-C3-C4-H10 | 0.0027 | -0.0059 |
| | | | H13-C7-Br15 | 104.8857 | 104.5232 | C3-C4-C5-C6 | 0.0068 | 0.0111 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | B r$_{14}$-C$_7$-Br$_{15}$ | 109.9365 | 109.8649 | C3-C4-C5-H11 | -179.997 | -179.9965 |
| | | | | | H10-C4-C5-C6 | 179.998 | 180.0143 |
| | | | | | H10-C4-C5-H11 | -0.0058 | 0.0068 |
| | | | | | C4-C5-C6-C1 | 0.0064 | 0.0112 |
| | | | | | C4-C5-C6-H12 | -180.0094 | -179.9793 |
| | | | | | H11-C3-C6-C1 | 179.9974 | 180.0189 |
| | | | | | H11-C5-C6-H12 | -0.0056 | 0.0284 |
| | | | | | | | |

For numbering of atom refer Fig. 1.

**Table 4.2:** Vibrational assignments of fundamental modes of alpha alpha –dibromo-M-Chlorotolune along with calculated IR intensities, Raman activity and normal mode descriptions (characterized by TED) based on quantum mechanical calculations using HF and DFT methods.

| Sl. No. | Symmetry Species Cs | Observed fundamentals (cm$^{-1}$) | | Calculated values | | | | | | | | Assignment TED% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | HF/6-311++G(d,p) | | | | B3LYP/6-311++G(d,p) | | | | |
| | | FTIR | FT-Raman | Unscaled | Scaled | IR intensity | Raman Activity | Unscaled | Scaled | IR Intensity | Raman Activity | |
| 1 | A´ | - | 3150 | 3380 | 3161 | 5.2668 | 15.166 | 3212 | 3080 | 4.3007 | 171.71 | γCH(98) |
| 2. | A´ | 3077 | - | 3365 | 3085 | 2.8284 | 124.974 | 3198 | 3088 | 3.5001 | 42.6469 | γCH(97) |
| 3. | A´ | 3061 | - | 3364 | 3071 | 2.0946 | 15.096 | 3194 | 3065 | 1.4481 | 42.2324 | γCH(98) |
| 4. | A´ | 3041 | - | 3356 | 3048 | 2.1207 | 4.5884 | 3182 | 3046 | 0.1796 | 27.7710 | γCH(97) |
| 5. | A´ | 3009 | - | 3343 | 3019 | 6.5241 | 46.3955 | 3180 | 3014 | 5.9022 | 51.8996 | γCH(98) |
| 6. | A´ | 1693 | - | 1782 | 1705 | 9.1605 | 89.6436 | 1635 | 1697 | 3.0343 | 125.3909 | γCC(90) |
| 7. | A´ | 1595 | 1590 | 1753 | 1603 | 27.2030 | 10.1681 | 1604 | 1600 | 32.0296 | 21.8494 | γCC(88) |
| 8. | A´ | 1584 | - | 1643 | 1593 | 32.9070 | 3.3772 | 1522 | 1589 | 25.5652 | 10.6212 | γCC(87) |
| 9. | A´ | 1574 | - | 1580 | 1582 | 38.7130 | 3.3252 | 1462 | 157 | 33.836 | 8.5615 | γCC(86) |
| 10. | A´ | 1477 | - | 1468 | 1486 | 3.9866 | 0.9213 | 1357 | 1482 | 1.5884 | 0.8289 | γCC(76) |
| 11. | A´ | 1471 | - | 1409 | 1481 | 18.3213 | 23.9242 | 1344 | 1476 | 3.1246 | 9.6679 | γCC(75) |
| 12 | A´ | 1432 | - | 1343 | 1440 | 30.2642 | 41.1846 | 1266 | 1437 | 58.2856 | 96.2774 | γCC(76) |
| 13. | A´ | 1424 | - | 1325 | 1436 | 52.8848 | 13.0500 | 1231 | 1430 | 24.8994 | 67.6292 | bCH(75) |
| 14. | A´ | 1301 | - | 1317 | 1310 | 4.8078 | 11.849 | 1219 | 1309 | 2.3318 | 6.8786 | bCH(74) |
| 15. | A´ | 1286 | - | 1260 | 1299 | 0.0099 | 6.6573 | 1205 | 1292 | 35.9688 | 6.8629 | bCH(81) |
| 16. | A´ | 1235 | - | 1213 | 1246 | 10.555 | 2.1021 | 1126 | 1242 | 7.2843 | 1.4166 | bCH(79) |
| 17. | A´ | 1225 | - | 1180 | 1240 | 23.9100 | 5.6484 | 1100 | 1232 | 24.8094 | 10.3244 | bCH(74) |
| 18. | A´ | 1180 | - | 1134 | 1191 | 0.0502 | 0.0970 | 1022 | 1188 | 2.4259 | 58.7809 | R trigd (72) |
| 19. | A´ | 1145 | - | 1096 | 1919 | 4.3812 | 3.5748 | 1019 | 1151 | 0.0152 | 0.1293 | R symd (74) |
| 20. | A´ | 1101 | - | 1072 | 1084 | 0.9640 | 2.7380 | 951 | 1107 | 2.3373 | 0.449 | Rassmd(74) |
| 21. | A´ | 1080 | - | 1033 | 1095 | 0.9434 | 4.2660 | 916. | 1087 | 4.7601 | 0.0896 | bcc(72) |
| 22. | A´ | - | 1060 | 950 | 1075 | 18.3425 | 21.9049 | 885 | 1068 | 17.7346 | 32.3787 | ωcH(65) |
| 23. | A´ | 998 | 990 | 916 | 1008 | 18.0909 | 2.4079 | 820 | 1007 | 22.4487 | 1.6278 | ωcH(65) |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24. | A´ | 883 | 880 | 787 | 901 | 123.2561 | 10.435 | 712 | 895 | 70.0741 | 2.9398 | ωcH (64) |
| 25. | A´ | 788 | 782 | 754 | 807 | 18.6613 | 14.0818 | 703 | 799 | 21.0059 | 10.1483 | ωcH(61) |
| 26. | A´´ | 693 | 690 | 736 | 712 | 32.8326 | 20.4627 | 650 | 703 | 51.3498 | 14.8151 | ωcH(62) |
| 27. | A´ | 655 | - | 690 | 667 | 34.1967 | 29.8643 | 633 | 664 | 28.0717 | 38.2003 | γ cBr(75) |
| 28. | A´ | 639 | 640 | 644 | 651 | 17.6376 | 2.6719 | 595 | 645 | 30.3358 | 8.9679 | γcBr(75) |
| 29. | A´´ | - | 625 | 609 | 633 | 52.3047 | 26.3724 | 528 | 628 | 71.8580 | 19.6093 | γccl(74) |
| 30. | A´ | 602 | - | 498 | 620 | 0.1450 | 1.6267 | 448 | 607 | 1.0047 | 2.3791 | τtrigd(61) |
| 31. | A´´ | 570 | 575 | 438 | 588 | 8.337 | 9.3893 | 405 | 576 | 10.8082 | 6.5281 | τsymd(60) |
| 32. | A´´ | 526 | 520 | 363 | 541 | 0.4481 | 8.4353 | 339 | 534 | 0.6141 | 7.9561 | τasgm(62) |
| 33 | A´´ | 439 | - | 270 | 459 | 0.0688 | 0.4456 | 244 | 447 | 0.6362 | 6.3713 | ωcc(62) |
| 34. | A´´ | - | 420 | 221 | 435 | 0.3508 | 11.566 | 201 | 429 | 0.7561 | 12.4834 | bcBr(68) |
| 35. | A´´ | - | 340 | 208 | 352 | 0.1325 | 0.5576 | 186 | 347 | 0.1402 | 0.6187 | bcBr(68) |
| 36. | A´´ | - | 310 | 153 | 321 | 1.9644 | 2.5954 | 138 | 316 | 2.1409 | 2.6041 | bccl(68) |
| 37. | A´´ | - | 250 | 142 | 270 | 1.4154 | 1.8310 | 130 | 256 | 0.9325 | 2.4670 | ωcBr(60) |
| 38. | A´´ | - | 205 | 86 | 223 | 0.3054 | 6.4978 | 78 | 215 | 0.3843 | 7.4931 | ωcBr(60) |
| 39. | A´´ | - | 170 | 21 | 189 | 1.2263 | 3.8903 | 21 | 180 | 1.1174 | 4.3385 | ωccl(61) |

**Abbreviations:** γ – stretching; ss – symmetric stretching; ass – asymmetric stretching; b – bending; ω – out-of-plane bending; R– ring; trigd – trigonal deformation; symd – symmetric deformation; asymd – antisymmetric deformation.

**Table 3:** Second order perturbation theory analysis of fock matrix in NBO basic corresponding to the interamolecular bonds of alpha, alpha-dibromo-M-chlorotolotune

| Donor (i) | Type | Acceptor (j) | Type | [a]E(2) (kJ mol^{-1}) | [b]E(j)–E(i) (a.u.) | [c]F (i,j) (a.u.) |
|---|---|---|---|---|---|---|
| C1-C2 | σ | C3-Cl9 | σ* | 4.84 | 0.83 | 0.057 |
| C2-C3 | σ | C1-C2 | σ* | 3.75 | 1.29 | 0.062 |
| C3-C4 | σ | C1-C2 | σ* | 20.30 | 0.29 | 0.069 |
| C4-C5 | σ | C3-Cl9 | σ* | 5.29 | 0.82 | 0.058 |
| C5-C6 | σ | C3-C4 | σ* | 23.23 | 0.26 | 0.070 |
| C6-C11 | σ | C1-C2 | σ* | 3.54 | 1.27 | 0.060 |
| C1-C7 | σ | C1-C6 | σ* | 2.11 | 1.22 | 0.045 |
| C2-H8 | σ | C1-C6 | σ* | 4.66 | 1.09 | 0.064 |
| C3-Cl9 | σ | C1-C2 | σ* | 2.35 | 1.27 | 0.049 |
| C4-H10 | σ | C2-C3 | σ* | 4.29 | 1.07 | 0.060 |
| C5-H11 | σ | C1-C6 | σ* | 3.72 | 1.08 | 0.057 |
| C6-H12 | σ | C1-C2 | σ* | 4.85 | 1.08 | 0.065 |
| C7-H13 | σ | C1-C6 | σ* | 3.29 | 1.13 | 0.054 |
| C7-Br14 | σ | C1-C2 | σ* | 2.98 | 1.21 | 0.054 |
| C7-Br15 | σ | C1-C2 | σ* | 2.85 | 0.67 | 0.043 |

| LP(3)Cl9 | σ | C3-C4 | σ* | 12.56 | 0.32 | 0.061 |
|----------|---|-------|----|-------|------|-------|
| LP(3)Br14 | σ | C7-Br15 | σ* | 7.36 | 0.36 | 0.046 |
| LP(3)Br15 | σ | C7-Br14 | σ* | 7.42 | 0.69 | 0.025 |

[a]E(2) means energy of hyperconjugative interactions.
[b]Energy difference between donor and acceptor i and j NBO orbitals.

**Table 4:** The thermodynamic parameters of alpha, alpha-dibromo-M-chlorotolotune calculated at HF and B3LYP methods using 6-311++G(d,p) basis set.

| Parameter | Methods/Basis set | |
|-----------|-------------------|---|
| | HF/6-311++G(d,p) | B3LYP/6-311++G(d,p) |
| Optimized global minimum energy, (Hartrees) | -5872.08044015a.u | -5878.15187981a.u |
| Total energy (thermal), $E_{total}$ (k cal mol$^{-1}$) | 72.823 | 68.532 |
| Heat capacity cv. (k cal mol$^{-1}$) | 31.652 | 33.944 |
| Total Entropy(s). (k cal mol$^{-1}$k$^{-1}$) | 102.094 | 104.687 |
| Translational Entropy | 0.889 | 0.889 |
| Rotational Entropy | 0.889 | 0.889 |
| Vibrational Entropy | 71.046 | 66.754 |
| Zero point vibrational energy, (k cal mol$^{-1}$) | 67.08426 | 62.42313 |
| Rotational constants(GHz) | | |
| A | 0.85215 | 0.83003 |
| B | 0.29224 | 0.28800 |
| C | 0.25713 | 0.25246 |
| Dipole moment (Debye) | | |
| $\mu_x$ | -0.4631 | 0.6223 |
| $\mu_y$ | 0.0003 | -0.0045 |
| $\mu_z$ | 1.1862 | 1.1297 |
| $\mu_{total}$ | 1.2734 | 1.2898 |