Structural And Spectroscopic Evaluations Of Quantum Chemical Investigations On 1,3,5-Tribromobenzene

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Abstract— A combined experimental and theoretical studies were conducted on the molecular structure and vibrational, spectra of 1,3,5-tribromobenzene (TBB). The FT-IR and FT-Raman spectra of (TBB)were recorded in the solid phase. The molecular geometry and vibrational frequencies of TBB in the ground state have been calculated by using density functional methods (B3LYP) invoking 6-31++G (d,p) basis set. The optimized geometric bond lengths and bond angles obtained by (B3LYP)method shows best agreement with the experimental values. Comparison of the observed fundamental vibrational frequencies of TBB with calculated results by density functional methods indicates that B3LYP is superior. A detailed interpretation of the FT-IR, FT-Raman, NMR spectra of TBB was also reported Natural bond orbital analysis has been carried out to explain the change transfer or delocalization of change due to the intra-molecular interactions. The HOMO and LUMO energies and electronic charge transfer (ECT) confirms that local reactivity and global reactivity descriptors. High field indicates that this molecule exhibit considerable electrical conductivity in atomic charges.The ESP map is found to be positive throughout the backbone of the molecule. The negative charges have a tendency to drift from left to right. Thermodynamic parameters like heat capacities ($C^{o}_{p,m}$), entropies (S^{o}_{m}) and enthalpies changes (H^{o}_{m}) are used for various electrical field.

Key words— TBB,NMR, HOMO – LUMO, NBO, ESP.

I.INTRODUCTION

Aromatic bromo compounds or their derivatives are used as solvents, analytical reagents, and are important intermediates in organic synthesis of perfumes, drugs, pesticides, and explosives[1–4].Aromatic nitro compounds are convertible by reduction into primary amines, which in turn are valuable intermediates in the synthesis of dyes, pharmaceuticals, photographic developers and antioxidants [5]. The organic hydro carbons having one or more Br groups bonded to the carbon framework, are versatile intermediate in organic synthesis. The bromo ion in hydrogen compounds is trigonally planar with 120° angles. There are two resonance bonds so that the three H are equivalent. Bromo compounds are strongly basic due to electron withdrawing both inductively and mesomerically. Historically, they are abundant in dyes and explosives. Both 1,3,5-tribromobenzene (TBB) and 1,3,5-tribromo-2,4,6-trifluoro-benzene are used as an intermediate for organic compounds; pharmaceuticals, pesticides and dyes. Both the compounds are pale yellow in colour and insoluble in water. It is harmful by inhalation, in contact with skin and if swallowed, and it also irritates to eyes, respiratory system and skin. 1,3,5-tribromobenzene is useful as an intermediate in the preparation. Haloaromatic compounds are well known building blocks in the synthesis of pharmaceuticals and agrochemicals. Traditionally, the halogen has normally been chlorine but bromo aromatics are assuming greater importance as the cost-effectiveness of biologically active fluorine containing products and the synthesis value of H substituents becomes more widely acknowledged [6-8]. The photoelectron spectra of tribromobenzene studied only the conventional infrared and Raman spectra with normal coordinate analysis. The complete FT-IR and FT-Raman vibrational studies on the fundamental modes and the electronic property investigations by NMR spectrum, NBO analysis, FMO's and thermodynamic properties are not found in the literature. The resulting demand of bromo aromatics has led to search for commercially attractive, flexible and to investigate the entire properties of TBB. Thus, a detailed investigation have been attempted using B3LYP/6-311G++(d,p) basis sets to provide more satisfactory and valuable informations on electronic stability, molecular orbitals, potential energy distribution and NMR spectral characteristics of TBB. The atomic charges, distribution of electron density (ED) in various bonding and antibonding orbitals and stabilisation energies, $E^{(2)}$ have been calculated by natural bond orbital (NBO) analysis. The optimised geometry, frontier molecular orbital (FMO) and their energy gaps, molecular electrostatic potential map (MESP), total density region and electrostatic potential contour (ESP) map have been constructed at B3LYP/6-311G++(d,p) level to understand the electronic properties, electrophilic and nucleophilic active centers of TBB. The temperature dependence of the thermodynamic functions and their correlations were performed at B3LYP/6-311G++(d,p).

II.EXPERIMENTAL METHODS

The pure compound 1-amino-2,6-dimethyl piperidine was purchased from Lancaster chemical company U.K., and used as such without any further purification. The room temperature fourier transform infrared (FTIR) spectrum of the title molecule was recorded in the region 4000-400 cm^{-1} at a resolution of ±1cm^{-1} using a BRUKER IFS 66V FTIR spectrophotometer equipped with a cooled MCT detector. Boxcar apodization was used for the 250 averaged interferograms collected for both the samples and background. The FT-Raman spectrum was recorded on a computer interfaced BRUKER IFS model interferometer, equipped with FRA 106 FT-Raman accessory in the 3500-50 cm^{-1} stokes region, using the 1064 nm line of Nd:YAG laser for excitation operating at 200mW power.The reported wave numbers are believed to be accurate within ±1cm^{-1}.

III. COMPUTATIONAL METHODS

DFT-B3LYP is adopted using 6-311G++(d,p) as basis set to give complete information concerning the structural characteristics and the fundamental vibrational modes of the title compounds. The calculations of geometrical parameters in the ground state are performed using GAUSSIAN09W[9]program.Thefirst hyperpolarizability, HOMO-LUMO and ESP analyses under various electric fields, NBO analysis are carried out by B3LYP/6-311G++(d,p) method. The thermodynamic functions such as entropy, enthalpy and the heat capacity are investigated for the different temperatures. Molecular structure is specified in Fig 1. But the geometrical parameters such as bond lengths, bond angles are the important factors in determining the electronic properties of the molecules that are listed in Table 1. This study explains the internal coordinates for TBB (Table 2). The non-redundant set of local symmetry coordinates are constructed by linear combinations of internal coordinates using Table 3 for TBB.

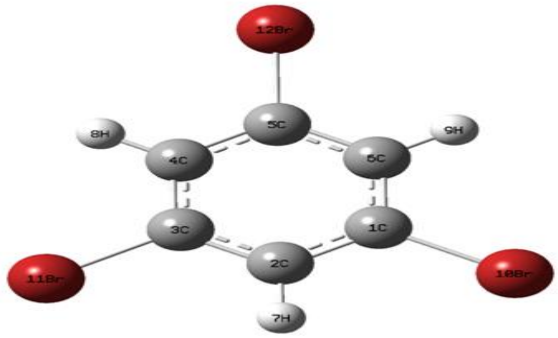

Fig.1:Molecular structure of 1,3,5-tribromobenzene

IV. RESULTS AND DISCUSSIONS

A.Molecular geometry

The molecular structure of TBB belongs to C_1 point group symmetry. The molecule consists of 12 atoms and expected to have 30 normal modes of vibrations of the same a species under C_1 symmetry. These modes are found to be IR and Raman active suggesting that the molecule possesses a non-centrosymmetric structure, which recommends the TBB for non-linear optical applications. Schematic view of the reaction pathway from 1,3,5-tribromobenzene monomers to dimmers structure is specified in Fig 2.

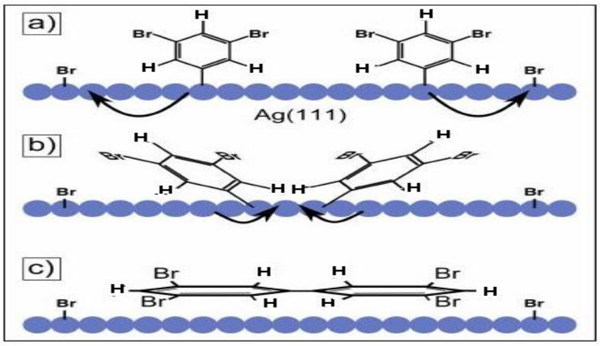

Fig 2:Schematic view of the reaction pathway from 1,3,5-tribromobenzene monomers to dimmers.

B. Vibrational assignments

The spectral analysis of title compounds is done by DFT/B3LYP method using the basis set 6-311G++(d,p). The FT-IR and FT-Raman spectra of the title compounds are figured out in Figs.3, and 4 respectively and the theoretical and experimental fundamental modes of vibrations of TBB are presented in Table 4, respectively.

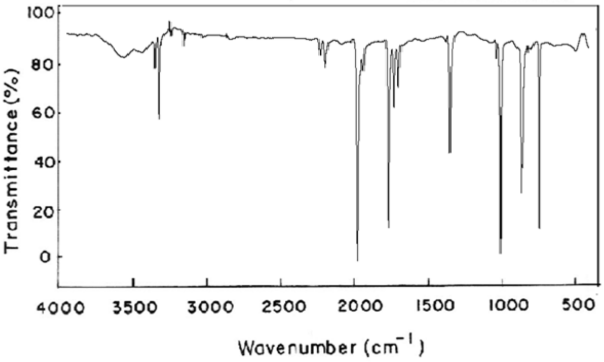

Fig.3: Experimental FTIR spectra of 1,3,5-tribromobenzene

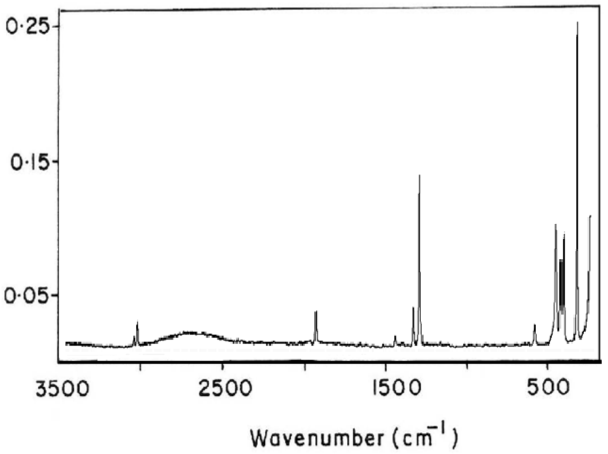

Fig.4: Experimental FT-Raman spectra of 1,3,5-tribromobenzene

C–H vibrations

The aromatic C–H stretching vibrations are usually established between 3100 and $3000cm^{-1}$. The peaks identified at 3099,3056,2075 cm^{-1} (FTIR)and(Raman) 3057 cm^{-1} are due to CH stretching vibrations of TBB, respectively [10]. The total energy (TED) contribution of these modes specifies that these are also highly pure modes like CC stretching modes. The aromatic C–H in-plane bending modes of benzene and its derivatives are observed in the region $1300–1000cm^{-1}$. The peaks seen at (FTIR) 1472, 1424, $1411cm^{-1}$ are attributed to the aromatic C–H in-plane bending vibrations of TBB, respectively [11]. The C–H out of plane bending modes of benzene derivatives are observed in the region 1000–$600cm^{-1}$.The aromatic C–H out of plane bending vibrations have also seen at(FTIR) 645, 632, $612cm^{-1}$ for TBB. In the present case these bands are occurred in the said region. The aromatic C–H in-plane and out of plane bending vibrations have substantial overlapping with the ring C–C–C in-plane and out of plane bending modes, respectively. Theoretical Positive field and negative field showed excellent agreement with recorded spectrum.

Carbon vibrations

The aromatic ring carbon–carbon stretching modes are expected in the range from 1650 to $1200cm^{-1}$. The observed peaks of TBB at 1804, 1794, 1781, 1770, 1765,1753cm^{-1} are recognized as the C–C stretching modes, respectively [10,11]. All the bands lie in the expected range when compared to the literature values. These observed frequencies show that, the substitutions in the ring to some extend affect the ring mode of vibrations. The comparison of the theoretically (Positive field and negative field) values are good agreement with B3LYP/6-311++G(d,p) method.The in-plane and out-of-plane bending vibrations of C-C group are also listed out in the Table 4 for TBB.

C-Br Vibrations

The vibrations that are 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 presence of heavy atoms on the periphery of the compound [11].C-X bond show lower absorption frequencies as compared to C-H bond due to the decreased negative field and increase in positive field. Further, Br causes redistribution of charges in the ring. Bromine compounds absorbed in the region 650-485cm^{-1}due to the C-Br stretching vibrations. In C-Br stretching vibrations are observed at IR and Raman spectrum 684 cm^{-1} and 670,631 cm^{-1} are assigned for TBB. The observed C-Br in-plane-bending and C-Br out-of-plane bending modes show consistent agreement with Positive field and negative field.

V.HOMO–LUMO energy gap

The analysis of the wave function is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital. The HOMO–LUMO analysis of these two compounds is done at B3LYP/6- 311++G(d,p) level of theory for the zero field and fields of 0.05, 0.15 and 0.25 VA^{-1}. Fig. 5 illustrates the orbital distributions of HOMO and LUMO levels of the title compounds for the zero field and biasing steps of 0.05, 0.15 and 0.25 VA^{-1}. In TBB, HOMO is delocalized mainly on ring carbons and there is no distribution of HOMO on bromine of phenyl ring [12]. Fig.5 shows that there is no electronic projection in HOMO and LUMO over the ring hydrogen atoms of the both the compounds in zero field. The values of HOMO energy, LUMO energy and HOMO–LUMO energy gap are used as an indicator of kinetic stability of the molecule. They are nearly same which shows that substituted bromine would have no effect on the title compound. When the field increases (0.0 - 0.20 VA^{-1}), the HOMO-LUMO gap (HLG) extensively decreases from 0.0853 eV to 0.1508eV for 1,3,5-tribromobenzene, respectively (as shown in Table 5). This large decrease in the HLG implies that the possibility of having reasonable conduction through the molecule, hence the conductivity increases with decreases in HLG.

VI. NBO analysis

NBO analysis gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra- and intermolecular interactions. The larger the E$^{(2)}$ (energy of hyperconjugative interactions) value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor–acceptor interaction. NBO analysis has been performed on the title molecule at the DFT level in order to elucidate the intra-molecular, re-hybridization and delocalization of electron density within the molecule. These interactions can reveal the electron transfer (hyperconjugative effect) between the orbital localized in these atoms. NBO analysis is carried out for the most stable form of the title compounds by DFT/B3LYP method using the basis set 6-311G++(d,p). The interaction energies between donor and acceptor orbital for both compounds are shown in Table 6, respectively. By analyzing these data, an effective energy interaction between the lone pair LP(1)Br11 π -antibonding orbitals of (C3 – Br10) bond is observed in the compound. This implies that an electron transport from nitrogen LP to antibonding orbital (hyperconjugative effect) [13]. The electron donation from the LP(2) Br10, LP(1) Br12 to the anitbonding acceptor σ* (C5- Br12), π*C3 - C4 is observed which leads to moderate stabilization energy in the compound as shown in Table 6.

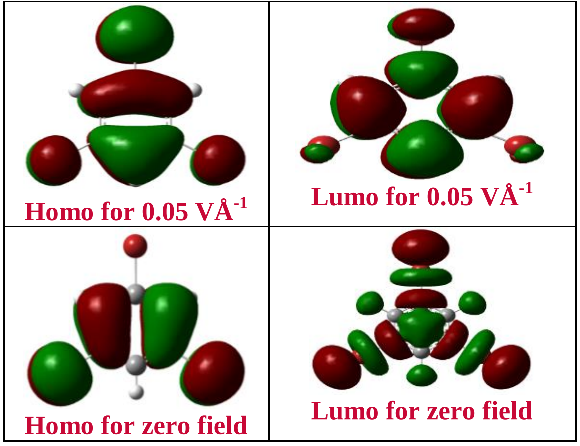

Fig 5:Isosurface representation of molecular orbitals of 1,3,5-tribromobenzene.

VII. NMR studies

The ^{1}H and ^{13}C theoretical and experimental chemical shifts and the assignments of the title molecule are presented in Table 7. The observed ^{1}H and ^{13}C NMR spectra of the title molecule are given in Fig. 6. Electronegative group can increase the electron cloud density of hydrogen, and then increases chemical shift. So, the chemical shift of C1 atom observed at 187.473ppm is calculated at 118.009 ppm for B3LYP/6-311++G(d,p) levels, respectively. Due to the deshielding effect of electronegative H7 atom, the chemical shift value of C2 is also shifted to the downfield NMR signals -34.8453and 172.158ppm, respectively. Aromatic carbons give signals with chemical shift values in the range 100–200 ppm. All of the aromatic protons are responsible for the peaks at the range of 158.93–114.20 ppm in observed NMR spectrum. The H proton peak is calculated at downfield region of -34.8453and 137.53ppm for B3LYP/6-311++G(d,p) levels, respectively. This Experimental peak is observed at 6.49 ppm in FT-NMR. From Table 7, there is general correlation between the experimental and theoretical NMR chemical shift calculations, that is, theoretical values can replace the experimental ones for the title molecule.

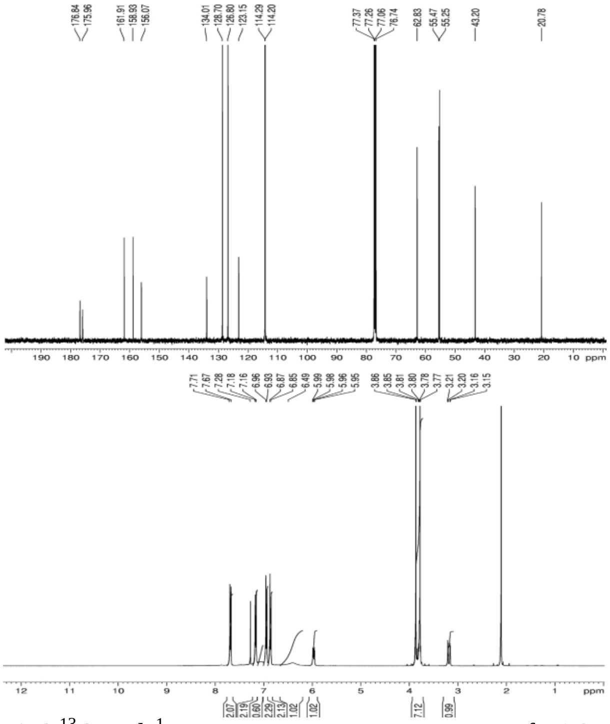

Fig6:^{13}C and ^{1}H NMR spectra NMR spectra of 1,3,5-tribromobenzene.

VIII. Electrostatic Potentials

Analysis of electrostatic potential (ESP) derived from the deformation electron densities on the molecular surfaces was performed to highlight the effect of crystalline environment and also to point out the differences and the similarities between the two polymorphic forms. The construction of a three-dimensional ESP map plotted over the molecular surfaces from experimental charge densities clearly brings out the differences of electrostatic nature of the three forms (Fig.7-8). The electropositive and electronegative surfaces are well separated in the forms. It displays a larger electronegative surface in ESP mapping. This is due to the conformational difference at the C-Br side chain and additionally due to the involvement of the π electrons of three bonded atoms C1-C2-H7 in C-H… π type of contacts and the presence of π ….π contacts. The electronegative surface is mainly seen around the Br atoms, which are involved in C-H…Br type of intermolecular contacts. However, the atom Br10 shown to have less prominent electronegative surface compared to other H atom in the structures. This is because the atom Br10 is not involved in any intermolecular contacts, whereas the corresponding atom in the H is seen to interact remotely with the neighbour molecule. The corresponding maps from the theoretical analysis revealed similar features. The ESP maps clearly emphasize the preferred binding sites to form the networks of interactions and also highlight the difference in nature of interactions [13,14].

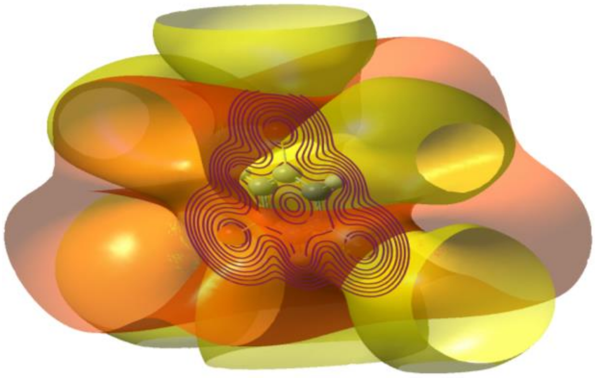

Fig.7:The total electron density surface of 1,3,5-tribromobenzene .

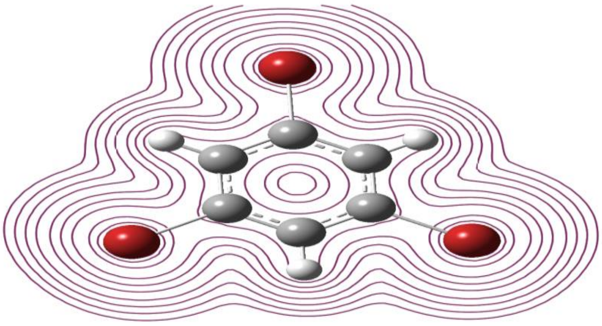

Fig.8:The molecular electrostatic potential surface of 1,3,5-tribromobenzene .

IX. TWO ROTOR PES SCAN STUDIES

Conformational analysis was performed to determine the stable conformers, thereby sampling points on the potential energy surface (PES). In this PES scan process, the potential energy surface is built by varying the H7-C2-C1-Br10 and C3-C4-C5-C6 dihedral angle from 0° to 360° in every 10°, while all of the other geometrical parameters have been simultaneously relaxed. The title molecule has several minima and maxima on the potential energy surface, and these minima and maxima are given in Fig. 9 The dark blue regions represent the more stable molecules with low total energy, while the dark red regions represent the unstable molecules with high total energies.

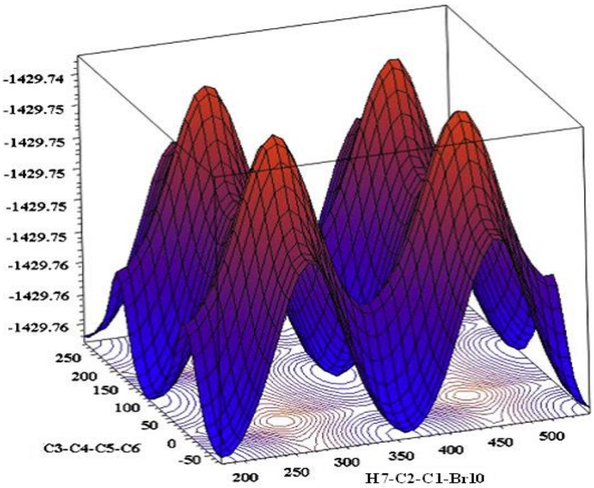

Fig 9.Two Rotor PES Scan of 1,3,5-tribromobenzene

X. Conclusion

The molecular structural parameters, thermodynamic properties and fundamental vibrational frequencies of the optimized geometry of 1,3,5-tribromobenzene have been obtained from DFT calculations. The theoretical results are compared with the experimental vibrations. Although this types of calculations are useful to explain vibrational spectra of 1,3,5-tribromobenzene, for DFT-B3LYP/6-311++G(d,p) level calculation methods. On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of 1,3,5-tribromobenzene have been made for the first time in this investigation. The electric field influence is noticed TED calculation regarding the normal modes of vibration provides a strong support for the frequency assignment. Therefore, the assignments proposed at higher level of theory with higher basis set with only reasonable deviations from the experimental values seem to be correct. NMR, NBO analysis have been performed in order to elucidate charge transfers or conjugative interaction, the intra-molecule rehybridization and delocalization of electron density within the molecule. The electric field influence is noticed in HOMO-LUMO gaps for 1,3,5-tribromobenzene. The HOMO-LUMO gap extensively decreases from 0.0853 eV to 0.1508eV for 1,3,5-tribromobenzene, respectively as the electric field increases. Thus the present investigation is providing the complete vibrational assignments, structural information and electronic properties of the title compounds which may be useful to raise the knowledge on phenyl derivatives. MEP study shows that the electrophilic attack takes place at the Br position of 1,3,5-tribromobenzene.

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Table 1 Optimized parameters of 1,3,5-tribromobenzene using B3LYP/6-311++G(d,p) method

Bond Length	**Values (Å)**		**Bond Angle**	**Values (˚)**	
	Monomer	Dimer		Monomer	Dimer
C1-C2	1.3941	1.3951/ 1.3955	C2-C1-C6	115.0	117.11/ 117.12
C1-C6	1.0838	1.0839/ 1.0839	C2-C1-Br12	125.0	126.13/ 126.14
C1-Br10	1.3859	1.3990/ 1.3991	C6-H1-Br11	114.4	115.22/ 115.23
C2-C3	1.088	1.098/ 1.0982	C1-C2-C3	120.4	121.67/ 121.68
C2-H7	1.3632	1.3720/ 1.3721	C1-C2-H7	132.7	135.22/ 135.71
C3-C4	1.0843	1.0943/ 1.0944	C3-C2-H7	112.9	114.21/ 114.22
C3-Br10	1.4693	1.4799/ 1.4799	C2-C3-C4	114.0	116.13/ 116.14
C4-C5	1.3882	1.3920/ 1.3921	C2-C3-Br10	123.5	124.86/ 124.89
C4-H8	1.411	1.4523/ 1.4554	C4-C3-Br10	122.4	123.56/ 123.57
C5-C6	1.3865	1.3955/ 1.3958	C3-C4-C5	117.1	119.31/ 119.32
C5-H9	1.4157	1.4278/ 1.4288	C3-C4-H8	127.7	128.19/ 128.20
C6-Br11	1.0783	1.0883/ 1.0893	C5-C4-H8	111.9	113.32/ 113.33
Br10-H9	1.4116	1.4236/ 1.4246	C4-C5-C6	130.1	132.16/ 132.17
Br11-H7	1.4582	1.4882/ 1.4892	C4-C5-H9	117.9	118.88/ 118.89
Br12-H8	1.3923	1.3933/ 1.3933	C6-C5-H9	115.1	117.54/ 117.55

Table 2:Definition of internal coordinates of 1,3,5-tribromo benzene.

No	Symbol	Type	Definition
1-3	P	CH	C2-H8,C4-H10,C6-H12
4-6	S	CBr	C1-Br7,C3-Br9,C5-Br11
7-12	Q	CC	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1
13-18	β	Ring	C1-C2-C3,C2-C3-C4,C3-C4-C5,C4-C5-C6,C5-C6-C1,C6-C1-C2
19-24	α	CBr	Br7-C1-C2,Br7-C1-C6,Br9-C3-C4,Br9-C3-C2,Br11-C5-C6, Br11-C5-C4
25-30	ϕ	CH	H8-C2-C1,H8-C2-C3,H10-C4-C3,H10-C4-C5,H12-C6-C5, H12-C6-C1
31-36	α	Ring	C1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6,C4-C5-C6-C1, C5-C6-C1-C2,C6-C1-C2-C3
37-39	Δ	CH	H8-C2-C3-C1,H10-C4-C5-C3,H12-C6-C1-C5
40-42	τ	CBr	Br7-C1-C2-C6, Br9-C3-C4-C2, Br11-C5-C6-C4

[a] *For numbering of atoms refer Fig.1*

Table 3:Definition of local symmetry coordinates of 1,3,5-tribromo benzene.

No	Type	Definition[b]
1-3	CH	P_1,P_2,P_3
4-6	CBr	S_9,S_{10},S_{11}
7-12	CC	$Q_7,Q_8,Q_9,Q_{10},Q_{11},Q_{12}$
13	Rtrigd	$(\beta_{13}-\beta_{14}+\beta_{15}-\beta_{16}+\beta_{17}-\beta_{18})/\sqrt{6}$
14	Rsymd	$(-\beta_{13}-\beta_{14}+2\beta_{15}-\beta_{16}-\beta_{17}+2\beta_{18})/\sqrt{12}$
15	Rasymd	$(\beta_{13}-\beta_{14}+\beta_{16}-\beta_{17})/2$
16-18	bCBr	$(\alpha_{19}-\alpha_{20})/\sqrt{2}$, $(\alpha_{21}-\alpha_{22})/\sqrt{2}$, $(\alpha_{23}-\alpha_{24})/\sqrt{2}$
19-21	bCH	$(\phi_{25}-\phi_{26})/\sqrt{2}$,$(\phi_{27}-\phi_{28})/\sqrt{2}$,$(\phi_{29}-\phi_{30})/\sqrt{2}$

22	tR trigd	$(\tau_{31}-\tau_{32}+\tau_{33}-\tau_{34}+\tau_{35}-\tau_{36})/\sqrt{6}$
23	tRSymd	$(\tau_{31}-\tau_{33}+\tau_{35}-\tau_{36})/\sqrt{2}$
24	tRasymd	$(-\tau_{31}+2\tau_{32}-\tau_{33}-\tau_{34}+2\tau_{35}-\tau_{36})/\sqrt{6}$
25-27	ωCH	$\Delta_{37},\Delta_{38},\Delta_{39}$
28-30	ωCBr	$\tau_{40},\tau_{41},\tau_{42}$

Table 4: The observed (FT-IR and FT-Raman) frequencies (cm^{-1}) for various applied electric fields ($VÅ^{-1}$) assignments for 1,3,5-tribromo benzene using B3LYP methods.

Observed frequencies (cm^{-1})		Assignments with TED (%) among types of internal co-ordinates				
FT-IR	FT-Raman	0.01 $VÅ^{-1}$		0.02 $VÅ^{-1}$		
		Positive field	Negative field	Positive field	Negative field	
1804 s	-	3358	3196	3656	3356	νCC (99)
1794 s	-	3357	3184	3615	3351	νCC (97)
1781 vs	-	3346	3181	3290	3244	νCC (96)
1770 vs	-	3342	3172	3267	3231	νCC (94)
1765 vs	-	3338	3166	3142	3125	νC C(92)
1753 s	-	3331	3151	3107	3100	νCC (89)
1299 w	1298 w	1632	1617	1711	1701	νCF (89)
1283 w	1282 w	1591	1553	1620	1605	νCF (89)
1270 vs	-	1553	1518	1561	1545	νCF (89)
1259 vs	-	1527	1509	1490	1456	bCF(71)
1237 vs	-	1475	1461	1450	1423	bCF(70)
1204 vs	-	1425	1415	1417	1401	bCF(75)
961vs	-	1394	1382	1329	1319	Rtrigd (73)
-	934vs	1348	1332	1279	1255	Rsymd (69
925vs	-	1340	1312	1248	1232	Rasym (68)
684vs	-	1291	1287	1205	1195	νCBr(63)
-	670vs	1266	1256	1170	1152	νCBr(60)
-	631s	1206	1200	1118	1103	νCBr(62)
564s	-	1141	1132	1075	1056	bCBr(67)
-	530s	1123	1114	1069	1031	bCBr (68)
-	512s	1052	1041	1020	1007	bCBr (60)
-	475s	1009	1000	969	954	tRtrigd(57)
-	461w	998	988	947	931	tRsymd(51)
-	412w	995	976	909	897	tRasym(52)
-	312s	947	931	906	863	ωCBr(51)
-	301s	929	913	841	825	ωCBr(50)
-	286s	889	857	769	754	ωCBr(55)
-	212w	831	821	731	722	ωCF
-	169w	811	801	660	643	ωCF
-	145w	774	753	644	622	ωCF

Abbreviations: *ν - stretching; ss - symmetric stretching; ass - asymmetric stretching; b - bending; ω - out-of-plane bending; R - ring;*

Table: 5 Electronic Properties with various Electric Field's of 1,3,5-tribromobenzene

Parameters	**0.00 $VÅ^{-1}$**	**0.05 $VÅ^{-1}$**	**0.1$VÅ^{-1}$**	**0.2$VÅ^{-1}$**
HOMO(a.u)	-0.2717	-0.2112	-0.2379	-0.3860
LUMO(a.u)	-0.1864	-0.1098	-0.2169	-0.2352
Energy Gap (Eg) (a.u)	0.0853	0.1014	0.0211	0.1508
Chemical Hardness(η) (a.u)	0.08531	0.03890	0.06451	0.04580
Chemical Potential (μ) (a.u)	-0.23910	-0.54701	-0.92704	-0.86071
Electronegativity (χ) (a.u)	+0.239	+0.524	+0.9240	+0.8661
Softness(S) (a.u)	12.8920	13.4036	32.3398	24.7899
Electrophilicity Index (ω) (a.u)	0.72986	0.24327	0.91235	0.77374

Table 6
Selected second order perturbation energies E(2) associated with i->j delocalization in gas phase. 1,3,5-tribromobenzene.

Donor (i)	Type	Acceptor (j)	Type	$E^{(2)}$[a] ($kJmol^{-1}$)	$\varepsilon_{(j)}-\varepsilon_{(i)}$[b] (a.u.)	F(I,j)[c] (a.u.)
C1- C2	π	C3 - C4	π*	16.4	0.27	0.060
		C5 - C6	π*	23.8	0.28	0.074
			π*	19.4	0.31	0.071
C3- C4	π	C1 - C2	π*	26.3	0.29	0.078
		C5 - C6	π*	14.25	0.29	0.058
C5- C6	π	C1 - C2	π*	14.3	0.29	0.059
		C3 - C4	π*	23.51	0.28	0.074
LP(2)Br10	n_2	C5-Br12	σ*	18.3	0.69	0.102
		C1-Br11	σ*	24.7	0.68	0.117
LP(1)Br11	n_1	C3-Br10	π*	34.93	0.35	0.100
LP(1)Br12	n_1	C3 - C4	π*	29.3	0.32	0.093

[a] E (2) means energy of hyperconjugative interactions
[b] The energy difference between donor and acceptor i and j NBO orbitals
[c] F(i, j) is the Fock matrix element between i and j NBO orbitals.

Table 7
The calculated shifts of carbon and hydrogen atoms of 1,3,5-tribromobenzene using B3LYP method

Atom position	**Theoretical**	**Expt**[a]	**Δ**
	6-311++G(d,p		
C1	118.009	187.473	69.464
C2	-172.158		
C3	162.033	123.56	-38.473
C4	31.7285	42.456	10.7275
C5	123.043	140.56	17.517
C6	76.798	82.734	5.936
H7	-34.8453		
H8	62.357	66.430	4.073
H9	137.53	153.671	16.141
Br10	41.11	43.67	2.56
Br11	21.66	25.635	3.975
Br12	96.235	99.89	3.655

[a] Taken from Ref [15] and $\Delta(\delta_{exp}-\delta_{the})$; difference between respective chemical shifts.