

Molecular Dynamic Simulations, Geometrical, and Vibrational Spectral studies of $\alpha,\alpha,\acute{\alpha},\acute{\alpha}$ Tetrabromo-m-Xylene

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ABSTRACT

Density functional theory (DFT) approach has become one of the most cost-effective means to investigate the molecular structure and vibrational spectra are finding widespread use in the applications related to biological systems. Investigations (experimental and calculated) on the molecular structure, and characteristics of $\alpha,\alpha,\acute{\alpha},\acute{\alpha}$ tetra bromo-m-xylene are reported in this work. The structure of the molecule was optimized and structural characteristics were determined by DFT using the B3LYP method with 6-311+ G (d, p) and 6-311++G (d, p) basis sets. The detailed vibrational assignments were made on the basis of potential energy distribution. A good coherence between the observed and calculated spectra was achieved. Besides, the HOMO- LUMO, Mulliken analysis and Non-linear optical effects were performed. In this review, the present xylene derivatives for spectral and quantum chemical calculations are also discussed.

KEY WORDS: FT-IR, FT-Raman, B3LYP, HOMO-LUMO, NLO

1. INTRODUCTION

Xylene can be found in three forms: Meta-xylene (m-xylene), Ortho -xylene (o-xylene) and Para-xylene (p-xylene). It consists of Xylene is an aromatic hydrocarbon which has two

methyl groups substituted in benzene at various positions. The xylene is used as a cleaning agent and paint thinner. Small amounts of xylene are also present in airplane fuel and gasoline. m-xylene, used as a thermally stable aramid fibers. It is used as thinners and solvents in paints, varnishes, adhesives and inks [1]. It is a major petrochemical produced by the carbonization of coal in the manufacturing of coke fuel [2]. The p-xylene have intensive health impacts associated with cardiovascular or blood toxicity, developmental toxicity, gastro intestinal or liver toxicity, immune toxicity, Neurotoxicity, respiratory toxicity and skin sensitivity [3]. M-xylene also used as varnish solvent in varnish and wood stains industries dyes, organic synthesis, Insecticide and aviation fuel. The bromine compounds are the main key of manufacturing such pharmaceutical drug. It is also used in many areas such as agricultural chemicals, dyestuffs and chemical intermediates [4]. Though the present compound has rich pharmaceutical and industrial impact, same of the physical and chemical properties related to its pharmaceutical importance of $\alpha,\alpha,\alpha,\alpha$, Tetra bromo-m-Xylene(4 α TBX) due to its bromination, extensive experimental and theoretical quantum chemicals studies were carried out to obtain a complete consistent and precise vibrational study and structural characteristics of the compound. The assignments of band in the vibrational spectra of molecule are an essential step in the application of vibrational spectroscopy for solving various structural chemical problems. In the present study, the detailed vibrational analysis of 4 α TBX was performed by combining the experimental and theoretical information using density functional theory (DFT).

In the framework of DFT approach, different exchange and correlation functional are routinely used. Among these B3LYP combination is the most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and standard basis sets 6-311+G (d, p) and 6-311++G(d, p) provide an excellent agreement between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The aim of this work is to check the performance of B3LYP density functional force field of 4 α TBX with the use of the standard 6-311+G (d, p) and 6-311++G(d, p) basis sets. The HOMO-LUMO and Mulliken analysis have been computed with same level of calculations to get charge transfer information of the molecule.

2. EXPERIMENTAL DETAILS

The compound under investigation namely 4 α TBX is purchased from sigma-Aldrich chemicals, U.S.A., which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FTIR spectrum of the compound were recorded in the range of 4000-400 cm^{-1} using a BRUKER IFS-66V FTIR spectrometer equipped with a cooled MCT detector, a KBR beam splitter and a global arc source. The spectral resolution is $\pm 1 \text{ cm}^{-1}$.

The FT-Raman spectrum of the title compound have been recorded in the stokes region (3500-50 cm^{-1}) on a computer interfaced BRUKER IFS model interferometer equipped with FRA-106 FT-Raman accessory using Nd: YAG laser source operating at 1.064 μm excitation wavelength line width with 200mW power. The reported wave numbers are expected to be accurate within $\pm 1 \text{ cm}^{-1}$.

3. COMPUTATIONAL DETAILS

The molecular structure optimization of the title molecule and corresponding vibrational frequencies were performed using DFT with Becke-3-Lee-Yang-Parr (B3LYP) combined with 6-311+G(d, p) and 6-311++G(d, p) basis sets using GAUSSIAN09W program package. Initial geometry generated from the standard geometrical parameters was minimized without any constraint in the potential energy surface at B3LYP level, adopting the standard 6-311++G (d, p) basic set. This geometry was then re-optimized again at DFT level employing the Becke 3LYP keyword, which invokes Becke's three-Parameter hybrid method using the correlation function of Lee et.al [5] .implemented with the same basic set. Vibrational bonds were assigned by visual inspection of the vibrations using both the frequency sequence and the intensity pattern and by comparison with other studies. The calculated vibrational frequencies were compared with experimental frequencies were also analyzed in detail. The calculated vibrations frequencies obtained by quantum chemical calculations are typically larger than their experimental details and they have to be scaled by empirical scaling factors B3LYP using MOLVIB 7.0 version written by Tomsundius [6]. These scaling factors depend on both the method and basis sets and they are determined and experimental frequencies [7].

The optimized geometrical parameters, fundamental vibrational frequencies, Atomic charge displacement, HOMO-LUMO, Natural bond orbital analysis and NLO parameters were

calculated [8-16]. By combining the results of the GAUSSVIEW [17] program with symmetry consideration vibrational frequency assignment were made with a high degree of accuracy. However, the defined coordinates forms complete set and matches quite well with motions were observed using the Gauss View program.

4. RESULT AND DISCUSSIONS

4.1Molecular geometry

The Optimized molecular structure has been obtained from Gaussian 09W Program. The title molecule 4 α TBX belongs to C_s point group symmetry. In the benzene base, four hydrogen atoms of two methyl groups were replaced by bromine atoms (tetra substitution) were connected in meta positions. The optimization of geometry was achieved by DFT model theories, the zero point vibrational energy of the compound at B3LYP/6-311++G(d, p) and 6-311+G(d, p) were 73.30 and 73.44 kcal/mol respectively. The benzene of the title molecular structure was much fractured multiply by methyl groups and tetra addition of Br atoms. The most important feature that has greater influence upon determining molecular parameters found to be bond angle (BA) and dihedral angle (DA). The title molecule 4 α TBX contained exactly 18 bond lengths, 30 bond angles and 36 dihedral angles. The complete geometry of the title molecule was shown in Fig.1. In most of the cases, the physical and chemical properties of substitutional groups and atoms were dominated on the substituent and the entire properties are driven through the ligand properties. So the altered chemical properties of the brominated xylene enable the pharmaceutical use. The optimized structure of 4 α TBX indicates that the inclusion of methoxy groups and bromine atom known for their strong electron-donating and electron withdrawing nature, respectively. This is the cause for enlarge in bond length of C7-BR15 (1.968 and 2.012 Å by lower and higher basis sets, respectively). The carbon and hydrogen atoms are bonded with the σ -bond in benzene [18, 19]. The substitution of methoxy groups and bromine atom for hydrogen changes the electron density. From the bond lengths, bond angles and dihedrals angles are given in Table.1, the benzene rings seems to be indistinct due to the substituent's and is differing from the angle of 120°. For bromine atom, at third position of the benzene ring, the angles C1-C2-C3 are found as

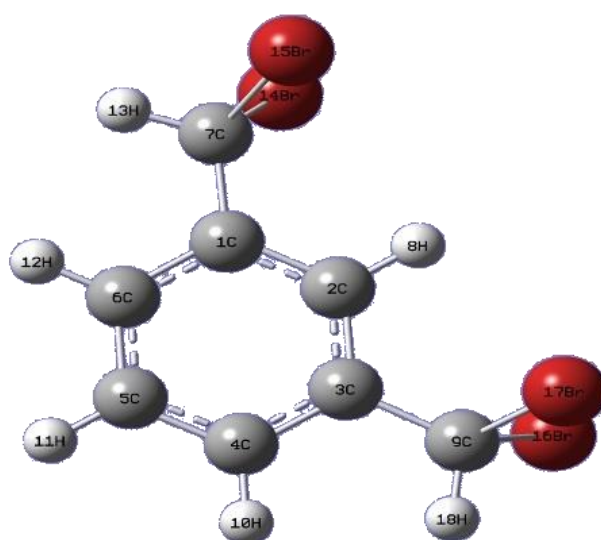


Fig.1: Molecular structure of $\alpha,\alpha,\alpha,\alpha$ tetra bromo-m-xylene along with numbering of atoms

Table.1: Optimized geometrical structural parameters of $\alpha,\alpha,\alpha,\alpha$ tetra bromo-m-xylene obtained by density functional calculations

Bond Length	Values(Å)		Bond Angle	Values(°)		Dihedral Angle	Values(°)	
	B3LYP	B3LYP		B3LYP	B3LYP		B3LYP	B3LYP
	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	1.394	1.397	C2-C1-C6	119.4	119.6	C6-C1-C2-C3	-0.013	-0.005
C1-C6	1.401	1.404	C2-C1-C7	122.0	120.5	C6-C1-C2-H8	-180.0	179.9
C1-C7	1.492	1.490	C6-C1-C7	118.5	119.8	C7-C1-C2-C3	179.9	-179.9
C2-C3	1.394	1.397	C1-C2-C3	120.6	120.5	C7-C1-C2-H8	0.007	0.008
C2-H8	1.085	1.080	C1-C2-H8	119.6	119.7	C2-C1-C6-C5	0.004	0.004
C3-C4	1.401	1.404	C3-C2-H8	119.6	119.7	C2-C1-C6-H12	-179.9	-179.9
C3-C9	1.492	1.490	C2-C3-C4	119.4	119.6	C7-C1-C6-C5	179.9	179.9
C4-C5	1.395	1.394	C2-C3-C9	122.0	120.5	C7-C1-C6-H12	-0.005	-0.009
C4-C10	1.086	1.082	C4-C3-C9	118.5	119.8	C2-C1-C7-H13	-179.9	-179.9
C5-C6	1.395	1.394	C3-C4-C5	120.2	120.1	C2-C1-C7-BR14	61.09	62.41
C5-H11	1.085	1.081	C3-C4-H10	119.8	119.9	C2-C1-C7-BR15	-61.10	-62.37
C6-H12	1.086	1.082	C5-C4-H10	119.8	119.9	C6-C1-C7-H13	0.003	0.032
C7-H13	1.085	1.079	C4-C5-C6	120.0	120.0	C6-C1-C7-BR14	-118.8	-117.5
C7-BR14	1.968	2.012	C4-C5-H11	119.9	120.0	C6-C1-C7-BR15	118.8	117.6
C7-BR15	1.968	2.012	C6-C5-H11	119.9	120.1	C1-C2-C3-C4	0.021	0.003
C9-H16	1.968	2.012	C1-C6-C5	120.2	119.9	C1-C2-C3-C9	179.9	179.9
C9-H17	1.968	2.012	C1-C6-H12	119.8	119.9	H8-C2-C3-C4	-179.9	-179.9
C9-H18	1.085	1.079	C5-C6-H12	119.8	113.4	H8-C2-C3-C9	-0.019	-0.007
			C1-C7-H13	112.2	111.7	C2-C3-C4-C5	-0.028	-0.009
			C1-C7-BR14	112.5	111.7	C2-C3-C4-H10	179.9	179.9

			C1-C7-BR15	112.5	105.3	C9-C3-C4-C5	-179.9	-179.9
			H13-C7-BR14	104.5	105.3	C9-C3-C4-H10	0.016	0.008
			H13-C7-B15	104.5	108.8	C2-C3-C9-BR16	-61.09	-62.43
			BR14-C7-BR15	109.8	111.7	C2-C3-C9-BR17	61.10	62.35
			C3-C9-BR116	112.5	112.5	C2-C3-C9-H18	-179.9	179.9
			C3-C9-BR17	112.5	112.5	C4-C3-C9-BR16	118.8	117.5
			C3-C9-H18	112.2	112.2	C4-C3-C9-BR17	-118.8	-117.6
			BR16-C9-B17	109.8	109.8	C4-C3-C9-H18	-0.022	-0.045
			BR17-C9-H18	104.5	104.5	C4-C3-C9-C6	0.012	0.000
						C3-C4-C5-H11	-179.9	-179.9
						H10-C4-C5-C6	-179.9	180.00
						H10-C4-C5-H11	-0.004	-0.001
						C4-C5-C6-C1	-0.004	-0.002
						C4-C5-C6-H12	179.9	-180.0
						H11-C5-C6-C1	-179.9	179.9
						H11-C5-C6-H12	0.004	-0.001

120.6 and the angles C3-C4-C5, and C2-C1-C7 are calculated as 120.2 and 122.0 respectively.

4.2 Vibrational Assignments

The observed and calculated vibrational frequencies along with assignments have been summarized in Table.2. The observed infrared and Raman spectra of title compound were presented in Fig.2 and Fig.3, which is convenient to discuss the vibrational spectra of the title molecule as described below. The molecule belongs to C_s point group symmetry which contains 18 atoms in different planes, so it has 48 normal vibrational modes out of that fundamental vibrations of the present molecule are distributed as 33 in plane vibrations denoted by A' species and 15 out of plane vibrations denoted by A'' species, i.e., $vib=33A'+15A''$. The observed FT-TR and FT-Raman frequencies and calculated fundamentals at B3LYP with 6-311++G(d, p) and 6-31+G(d, p) have been presented in Table.2 and were displayed as Fig.2 and Fig.3 respectively. Comparison of calculated frequencies with the experimental values reveal the over estimation of the calculated vibrational modes due to the neglect of a harmonicity in real system.

C-H vibrations

Generally, in aromatic benzene and its related derivatives, the C-H stretching vibrations are observed in the appropriate region of $3000-3100\text{cm}^{-1}$ [20]. But due to the substitutional effect. The observed range is fluctuated [21]. The title molecule consists of two methyl groups. The compound of this study was the bromine and methyl substituted benzene derivative where the aromatic C-H vibrations, were observed with medium and strong intensity at 2900cm^{-1} and 2972cm^{-1} in IR and Raman spectra respectively.

The C-H in-plane bending vibrations are expected to occur as a number of strong to weak intensity bands in the region $1000-1300\text{cm}^{-1}$ [22]. In the present work the C-H stretching vibrations are observed at 3090,3030,3010,2940,2920 cm^{-1} in FT-IR spectrum, where as in the FT Raman spectrum, it is found at 2900,2942 cm^{-1} . All the six stretching vibrations are within the expected range. The C-H in-plane bending vibrations and out-of-bending vibrations are normally expected in the region $1000-1300\text{cm}^{-1}$ and $750-1000\text{cm}^{-1}$ respectively in the aromatic compounds.

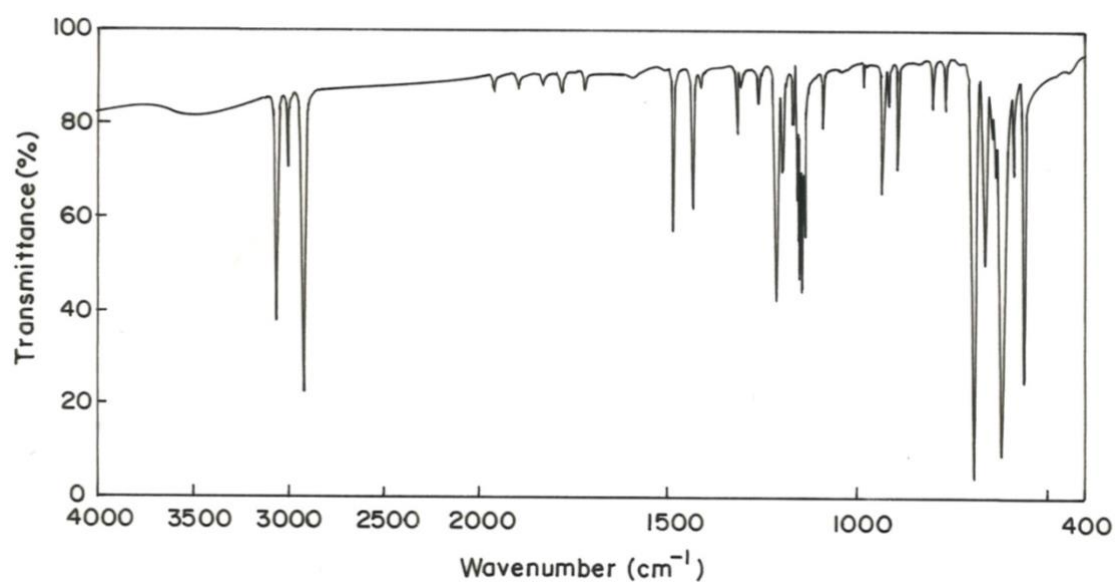
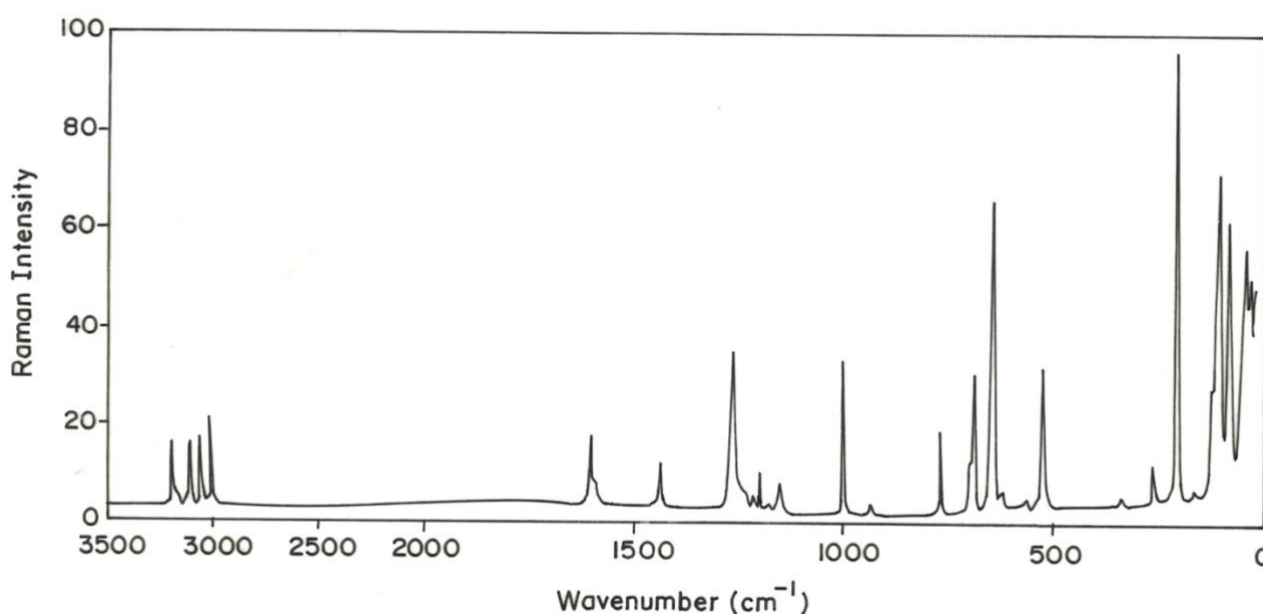


Fig.2: FTIR spectrum of $\alpha,\alpha,\alpha,\alpha$ tetra bromo-m-xylene

Fig.3: FT-Raman spectrum of $\alpha,\alpha,\alpha,\alpha$ tetra bromo-m-xylene



For the title molecule the frequencies found at 1180, 1175, 1015cm⁻¹ and 1160, 1135cm⁻¹ are assigned to C-H in-plane bending vibrations and the bands observed at 850,848,845,660,575 cm⁻¹ and 790,530 cm⁻¹ are designated to C-H out-of-plane bending vibrations. In this work all the assigned vibrations are not affected by the substitution in the ring and are in good agreement with theoretically calculated values.

C=C and C-C Vibrations

The C-C stretching vibrations in the aromatic ring are generally observed at 1600 – 1460 cm^{-1} [23] in which two types of vibrations C=C and C-C are found. In the present case the phenyl ring C=C stretching vibrations were observed at 1605, 1560, 1550, 1410, 1390, and 1330 cm^{-1} in IR spectrum and Raman bands at 1450, 1290 cm^{-1} have been assigned to C-C stretching modes of 4 α TBX. The observed three vibrations were found in the expected range and no more in libration taking place in the π bonds of the ring.

Similarly, the stretching vibrations of C-C are normally expected in the range 1450-1360 cm^{-1} . The in-plane and out of plane ring breathing CCC vibrations are occurred one below 800 cm^{-1} [24]. The CCC in-plane and out-of-plane vibrations of the molecule are found at 960, 850, 430 in IR spectrum and Raman bands 1000, 980, 960, 850, 450, 445, 350, 310 cm^{-1} respectively. The observed vibrations are very much below the expected region. Thus, it was concluded that the CCC bending vibrations were affected much due to the loading of Br atoms

C-Br vibrations

The present studies of four hydrogens of two methyl groups were strongly replaced by Br atoms. Normally, the strong characteristic absorption due to the C-Br stretching vibration for organic bromide was found in the region 650-485 cm^{-1} [26]. In accordance with the literature. Four very strong bands observed in the IR and Raman spectra at 540, 515, 480 cm^{-1} and 530 cm^{-1} . The C-Br in plane and out-of-plane bending modes of 4 α TBX have been identified and listed in Table 2.

5. FRONTIER MOLECULAR ANALYSIS

The electronic reconfiguration and electronic excitations in frontier molecular orbitals are very much useful for studying the electric and optical properties of the organic molecules. The stabilization of the bonding and destabilization of the anti bonding of molecular orbital

Table.2: The observed (FT-IR and FT-Raman) and calculated (unscaled and scaled) frequencies, and assignments of $\alpha,\alpha,\alpha,\alpha$ tetra bromo-m-xylene using B3LYP with 6-311+G(d,p) and 6-31++G(d,p) basis set

		Calculated frequency (cm^{-1})	
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Sl.No	Symmetry Species (Cs)	Observed Frequency (cm ⁻¹)						Vibrational Assignments with TED(%)
				B3LYP/6-311++G(d,p)		B3LYP/6-311+G(d,p)		
		FTIR	FT Raman	Unscaled	Scaled	Unscaled	Scaled	
1.	A'	3090	-	3211	3098	3221	3095	vC-H(98)
2.	A'	3030	-	3206	3035	3209	3020	vC-H(99)
3.	A'	3010	-	3192	3015	3191	3007	vC-H(99)
4.	A'	2970	2972	3191	2975	3188	2968	vC-H(97)
5.	A'	2940	-	3189	2944	3186	2938	vC-H(98)
6.	A'	-	2900	3184	2905	3183	2902	vC-H(97)
7.	A'	1605	-	1658	1608	1656	1603	vC=C(87)
8.	A'	1560	-	1632	1565	1632	1562	vC=C(87)
9.	A'	1550	-	1519	1555	1517	1552	vC=C(87)
10.	A'	1450	1450	1484	1455	1486	1452	vC-C(85)
11.	A'	1410	-	1398	1416	1369	1412	vC-C(87)
12.	A'	1390	-	1347	1395	1344	1392	vC-C(87)
13.	A'	1330	-	1303	1335	1302	1332	vC-C(85)
14.	A'	-	1290	1231	1295	1242	1292	vC-C(87)
15.	A'	-	1270	1218	1280	1230	1274	bC-H(71)
16.	A'	1180	-	1176	1185	1204	1182	bC-H(72)
17.	A'	1175	-	1197	1178	1199	1176	bC-H(71)
18.	A'	-	1160	1195	1165	1198	1162	bC-H(72)
19.	A'	-	1135	1171	1139	1167	1137	bC-H(71)
20.	A'	1015	-	1117	1019	1124	1017	bC-H(72)
21.	A'	-	1000	1012	1005	1012	1002	Rsymd(70)
22.	A''	-	980	983	990	975	982	Rasymd(70)
23.	A''	960	-	980	955	979	952	Rtrigd(78)
24.	A''	-	930	923	928	925	932	bcc(77)
25.	A''	850	-	901	856	878	852	bcc(76)
26.	A''	848	-	782	852	814	846	ωC-H(65)
27.	A''	845	-	781	850	789	844	ωC-H(65)
28.	A''	-	790	666	795	732	792	ωC-H(65)
29.	A''	750	-	646	756	688	753	ωC-H(65)
30.	A''	660	-	632	666	687	662	ωC-H(65)
31.	A''	575	-	619	576	631	573	ωC-H(65)
32.	A'	540	-	585	546	603	543	vC-BR(86)
33.	A'	-	530	578	539	588	532	vC-BR(87)
34.	A'	515	-	570	520	573	517	vC-BR(87)

35	A'	480	-	515	487	516	482	vC-BR(87)
36	A''	-	450	425	453	447	448	tRtrigd(57)
37	A''	-	445	302	449	304	442	tRsymd(58)
38	A''	430	-	267	437	269	432	tRsymd(56)
39	A''	-	420	259	428	245	423	bCBR(66)
40	A''	390	390	251	396	235	393	bCBR(77)
41	A''	-	350	195	360	182	355	bCC(65)
42	A''	-	310	153	318	150	314	bCC(65)
43	A''	-	280	142	288	147	283	bC-BR(76)
44	A''	-	240	92	248	72	243	bC-BR(76)
45	A''	-	220	80	226	69	222	ωC-BR(56)
46	A''	-	200	54	210	59	205	ωC-BR(54)
47	A''	180	-	31	188	17	183	ωC-BR(55)
48	A''	150	-	27	158	13	152	ωC-BR(56)

can be made by the overlapping of molecular orbitals. The stabilization of the bonding molecular orbital and destabilization of the anti bonding can increases when overlap of two orbitals increases [27].

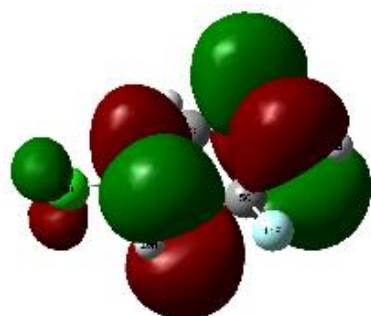
In molecular interaction, there are the two important orbitals that interact with each other. One is the highest energy occupied molecular orbital is called HOMO represents the ability to donate an electron. The other one is the lowest energy unoccupied molecular orbital is called LUMO as an electron acceptor. These orbitals are also called the frontier orbitals. The interaction between them is much stable and is called filled empty interaction. When the two same sign orbitals overlap to form a molecular orbital, the electron density will occupy at the

region between two nuclei. The molecular orbital resulting from in phase interaction is defined as the bonding orbital which has lower energy than the original atomic orbital. The out of phase interaction forms the anti bonding molecular orbital.

The 3D plots of the frontier orbitals, HOMO and LUMO for present molecule are in gas, shown in figure. According to such figure, the HUMO is mainly localized by a charge distribution connects the carbon and hydrogen bond interaction taking place. From this observation, it is clear that, the in and out of phase interaction are present in HOMO and LUMO respectively. The HOMO-LUMO transition implies an electron density transferred within the molecule. The HOMO-LUMO energy gap of 4αTBX was calculated at the DFT (B3LYP)/6-311++G (d, p) levels and reveals that the energy gap reflects the chemical activity of the molecule. The HOMO and LUMO energy are -9.5424eV and 1.0117 eV in gas phase. Energy difference between HOMO and LUMO orbital is called as energy gap (Kubo gap) that is an important stability for structures. The calculated energy gap is 8.53eV, show the medium energy gap and reflect the high electrical activity of the molecule.

6. MULLIKEN ANALYSIS

The reactive atomic charges [28] play an important role in the application of quantum chemical calculation to molecular system. Because of atomic charges affects dipole moment, polarisability, electronic structure and more properties of molecular system.



LUMO $E_{LUMO} = 1.011742$ eV
<http://annalsofrscb.ro>

LUMO PLOT (First excited state)

Energy gap $\Delta E = 8.5307$ eV

Fig.4: Frontier molecular orbitals and their energies of $\alpha,\alpha,\alpha,\alpha$ tetra bromo-m-xylene

The corresponding Mulliken's plot title compounds using B3LYP with 6-311++G (d, p) and 6-311+G(d,p) basis sets are shown in Fig 5. For 4 α TBX molecule the atomic charge on C₄, C₅, C₆, and BR atoms are negative where as the remaining atoms are positively charged. Due to strong negative charges are accommodate higher positive charge and become more acidic. The negative values on atoms in the aromatic ring leads to a redistribution of electron density. For instance, atomic charge has been used to describe the processes of electro negativity equalization and charge transfer in chemical reactions [29].

7. NON-LINEAR OPTICAL (NLO) EFFECTS

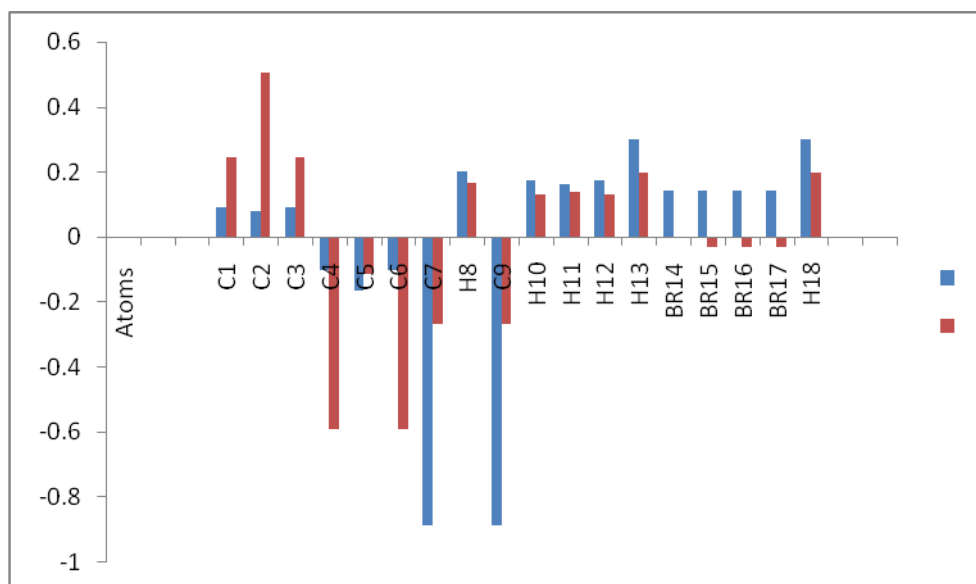
In the recent trends, a large number research of new materials exhibiting efficient NLO features has been of great interest because of potential applications as modern communication technology, telecommunication and optical signal Processing [30]. Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. The significance of the polarizability and the first hyper polarizability of molecular systems is dependent on the efficiency of electronic communication between acceptor and the donor groups as that will be the key of intra molecular charge transfer mechanism. The acceptor and donor groups have an important role in the polarizability and first hyperpolarizability measured of the NLO activity of the molecular system is associated with the resulting from the electron cloud movement through π -Conjugated frame work from electron donor to electron acceptor groups [31]

The first hyper polarizability (β_0) of 4 α TBX are calculated using the B2LYP/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. 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. It can be given in the lower tetrahedral.

The first hyper polarizability (β_0) using the x, y, z components they are defined as follows

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

Fig. 5



:Mulliken plot by B3LYP with 6-311++G(d, p) and 6-311+G(d, p) basis set of $\alpha, \alpha, \alpha, \alpha$

tetra bromo-m-xylene

Table.3 Mulliken atomic charge of $\alpha,\alpha,\acute{\alpha},\acute{\alpha}$ tetra bromo-m-xylene performed by density functional calculations

Atoms	Mulliken Charges	
	B3LYP/ 6-311+G (d, p)	B3LYP/ 6-311++G (d, p)
C1	0.093053	0.244496
C2	0.079397	0.505183
C3	0.093087	0.244650
C4	-0.100523	-0.591250
C5	-0.165029	-0.113025
C6	-0.100497	-0.591306
C7	-0.887379	-0.267672
H8	0.200138	0.166176
C9	-0.887368	-0.267764
H10	0.173343	0.131070
H11	0.162813	0.137850
H12	0.173344	0.131069
H13	0.299014	0.196529
BR14	0.141904	-0.30634
BR15	0.141897	-0.030625
BR16	0.141844	-0.030688
BR17	0.141950	-0.030593
H18	0.299013	0.196534

$$\beta_y = (\beta_{yyy} + \beta_{xyy} + \beta_{yzz})$$

$$\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yzz})$$

$$\beta_0 = [\beta_x^2 + \beta_y^2 + \beta_z^2]^{1/2}$$

The calculated first hyper polarizability (β_0) values of 4 α TBX are 3.3318×10^{-30} esu. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore it was used frequently as a threshold value for comparative purposes. The calculated value of β_0 for the title compound is relatively higher than that of Urea. Hence, from the results of the present molecule 4 α TBX refined that it supports in the development of new effective material for NLO applications.

CONCLUSION

The vibrational frequencies analysis by B3LYP method agrees satisfactorily with experimental results, assignments of all the fundamental vibrational modes of 4 α TBX were examined and proposed. Therefore, the assigned made at higher level of the theory with basis set reasonable deviations from the experimental values, seems to be correct. HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule which are responsible for the bioactivity property of the molecule. FTIR and FT-Raman spectra of 4 α TBX are recorded and the detailed vibrational assignments were obtained. The Mulliken charge calculations have identified the negatively and positively charged atoms in the molecule, in order to stabilize the structure. The NLO activity of the present compound was also confirmed by the predicted large value of first order hyperpolarizability. The result of this study will help researchers to design and synthesis new materials.

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