

# Vibrational Spectra, DFT Calculations, Electronic and Optical Properties of 3-bromo-o-xylene

S. Jeyavijayan, Palani Murugan, M. S. Revathy, S. Kokila, K. Gurushankar

**Abstract:** The vibrational spectra of 3-bromo-o-xylene have been studied by FTIR and FT-Raman spectra in the regions 4000-400  $\text{cm}^{-1}$  and 3500-50  $\text{cm}^{-1}$ , respectively. The geometrical parameters, frequencies and spectral intensities were calculated by density functional theory (DFT/B3LYP) method with 6-31+G(d,p) and 6-311++G(d,p) basis sets. The experimental and theoretical spectra are compared. The UV-Vis spectral analysis and the HOMO-LUMO of the molecule has been calculated which confirms the charge shift of the molecular system. The natural bond orbital investigation has been found for different bonding, antibonding and lone pair interactions and mapped molecular electrostatic potential (MEP) have also been reported.

**Index Terms:** FTIR, FT-Raman, DFT calculations, 3-bromo-o-xylene, NBO.

## I. INTRODUCTION

Xylene can be found in three forms; meta-xylene (m-xylene), ortho-xylene (o-xylene) and para-xylene (p-xylene). It consists of a benzene ring with two methyl chains and occurs in coal tar, petroleum. It is used as thinners and solvents in paints, varnishes, adhesives and inks. Particularly, o-xylene is used to produce phthalic anhydride, which can be utilized for drugs, materials and other chemicals [1]. Xylene is the main precursor to dimethyl terephthalate and terephthalic acids, both of them are used to manufacture polyethylene terephthalate (PET) plastic bottles and polyester clothing [2]. Because of their wide applications, the vibrational, spectral properties of xylene derivatives have been studied by many researchers [3-7]. More recently, Ramalingam et al [8] investigated the vibrational studies on pharmaceutical activity of m-xylene-4-sulphonic acid. In this study, the compound 3-bromo-o-xylene (BOX) is effective raw material and mediator for many organic synthesis, agrochemicals and pharmaceuticals. Owing to these industrial importances of xylene and its bromo derivatives, the detailed structural, spectral and DFT computations have been investigated in this study.

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## II. EXPERIMENTAL

The FTIR spectra of BOX was recorded in the region 4000-400  $\text{cm}^{-1}$  at a resolution of  $\pm 1 \text{cm}^{-1}$  using Perkin Elmer FTIR spectrometer and the FT-Raman spectrum of BOX have been recorded in the Stokes region (3500-50  $\text{cm}^{-1}$ ) on a computer interfaced BRUKER RFS-66V model interferometer operating at 1064 nm excitation wavelength using Nd:YAG laser. In the quantum chemical calculations, DFT calculations were carried out for BOX with GAUSSIAN 09W program package [9] using the Becke's parameter combined with the Lee-Yang-Parr correlation (B3LYP) functional [10,11] with lower and higher basis sets. The total energy distribution (TED) associated with each vibration is calculated by the MOLVIB program [12]. The electron density (ED) redistribution and hyperconjugative interactions energies have been calculated by natural bond orbital analysis. The UV-Vis and HOMO-LUMO analyses have been computed with same level of calculations to get charge transfer information of the molecule.

## III. RESULTS AND DISCUSSION

### A. Molecular Geometry

The molecular structure of BOX is shown in Fig. 1. The most optimized structural parameters calculated by DFT/B3LYP with lower and higher basis sets are compared with X-ray diffraction experimental data [13] and represented in Table I. The optimized structure of BOX 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 C3-Br15 (1.921 and 1.932 Å by lower and higher basis sets, respectively). The carbon and hydrogen atoms are bonded with the  $\sigma$ -bond in benzene. The substitution of methoxy groups and bromine atom for hydrogen changes the electron density. From the bond angles given in Table I, the benzene ring seems to be indistinct due to the substituents and is differing from the angle of  $120^\circ$ . For bromine atom, at third position of the benzene ring, the angles C2-C3-C4 are found as  $122.76^\circ$  and the angles C6-C1-C2, C1-C2-C3 are calculated as  $120.06^\circ$  and  $117.24^\circ$  for methoxy groups at first and second position of the benzene ring.

# Vibrational Spectra, DFT Calculations, Electronic and Optical Properties of 3-bromo-o-xylene

Table I. Optimized geometrical parameters of 3-bromo-o-xylene by DFT method

Bond Length	Value (Å)		Expt <sup>a</sup>	Bond angle	Value (°)		Expt <sup>a</sup>
	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)			B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)	
C1-C2	1.418	1.415	1.393	C2-C1-C6	120.05	120.06	119.5
C1-C6	1.398	1.395	1.401	C2-C1-C7	120.36	120.25	120.4
C1-C7	1.511	1.510	1.496	C6-C1-C7	119.60	119.69	117.6
C2-C3	1.402	1.400	1.377	C1-C2-C3	117.39	117.24	119.0
C2-C11	1.509	1.508	1.508	C1-C2-C11	119.35	119.39	119.5
C3-C4	1.396	1.393	1.371	C3-C2-C11	123.26	123.37	121.5
C3-Br15	1.921	1.932	1.896	C2-C3-C4	122.60	122.76	122.6
C4-C5	1.392	1.389	1.380	C2-C3-Br15	120.97	121.19	121.2
C4-H16	1.084	1.082	0.930	C4-C3-Br15	116.44	116.04	116.2
C5-C6	1.395	1.392	1.352	C3-C4-C5	119.15	119.02	119.1
C5-H17	1.086	1.084	0.930	C3-C4-H16	120.01	120.08	122.8
C6-H18	1.087	1.085	0.930	C5-C4-H16	120.84	120.90	119.5
C7-H8	1.097	1.095	0.960	C4-C5-C6	119.69	119.75	120.0
C7-H9	1.097	1.095	0.960	C4-C5-H17	119.84	119.81	120.0
C7-H10	1.093	1.091	0.960	C6-C5-H17	120.47	120.44	120.0
C11-H12	1.097	1.095	0.960	C1-C6-C5	121.13	121.17	121.6
C11-H13	1.097	1.095	0.960	C1-C6-H18	119.16	119.14	121.6
C11-H14	1.089	1.087	0.960	C5-C6-H18	119.71	119.69	123.2
				C1-C7-H8	111.75	111.68	109.5
				C1-C7-H9	111.74	111.68	109.5
				C1-C7-H10	110.82	110.77	109.5
				H8-C7-H9	106.77	106.81	109.5
				H8-C7-H10	107.77	107.84	109.5
				H9-C7-H10	107.77	107.84	109.5
				C2-C11-H12	110.99	110.90	109.5
				C2-C11-H13	111.00	110.90	109.5
				C2-C11-H14	111.74	111.94	109.5
				H12-C11-H13	106.93	106.93	109.5
				H12-C11-H14	108.00	107.99	109.5
				H13-C11-H14	108.00	107.99	109.5

<sup>a</sup>Experimental values are taken Ref. 13.

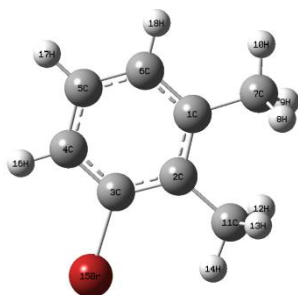


Figure 1. Molecular structure of 3-bromo-o-xylene

## B. Thermodynamic Properties

The thermodynamic parameters of BOX by DFT/B3LYP method are listed in Table II. The global minimum energy obtained for BOX by DFT/B3LYP using 6-31+G(d,p) and 6-311++G(d,p) basis sets are -2882.0354448 and -2884.5064629 Hartrees, respectively. In this study, the dipole moment molecule of BOX is found to be 2.0888 and 2.1015 Debye, for lower and higher basis sets, respectively. The thermodynamic data [14] listed in Table II will be useful to get further information of BOX.

## C. Vibrational Spectra

The molecule possesses  $C_1$  point symmetry and contains 18 atoms which give 48 normal vibrations. The observed and computed FTIR and FT-Raman spectra of BOX are represented in Figs. 2 and 3, respectively and the complete vibrational assignment of BOX are given in Table III. The calculated frequencies are larger than the experimental ones because of the nonharmonic nature and hence it is essential to scale the calculated values by the proper scale factor [15] of 0.96 for B3LYP method.

Table II. The thermodynamic parameters of 3-bromo-o-xylene

Parameters	Method/Basis set	
	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)
Optimized global minimum Energy (Hartrees)	-2882.0354448	-2884.5064629
Total energy (thermal), $E_{total}$ (kcal mol <sup>-1</sup> )	97.886	96.083
Heat capacity, $C_v$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	32.276	31.450
Entropy, $S$ (cal mol <sup>-1</sup> K <sup>-1</sup> )		
<i>Total</i>	94.243	90.851
<i>Translational</i>	41.535	41.535
<i>Rotational</i>	30.268	30.270
<i>Vibrational</i>	22.440	19.045
Vibrational energy, $E_{vib}$ (kcal mol <sup>-1</sup> )	96.108	94.305
Zero point vibrational energy, (kcal mol <sup>-1</sup> )	92.3689	90.8842
Rotational constants (GHz)		
<i>A</i>	2.1714	2.1776
<i>B</i>	0.7391	0.7366
<i>C</i>	0.5552	0.5542
Dipole moment (Debye)	2.0888	2.1015

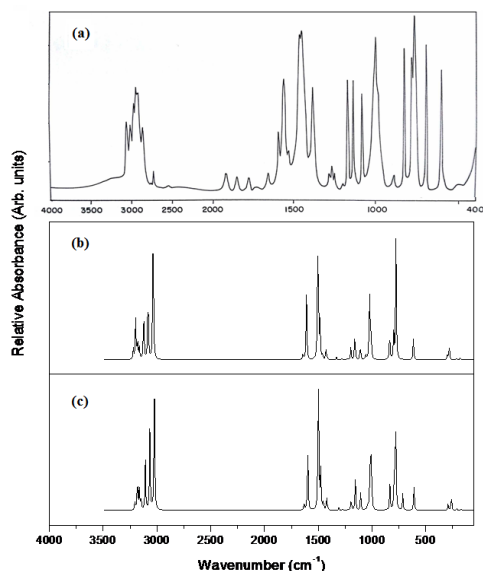


Figure2. FTIR spectra of 3-bromo-o-xylene

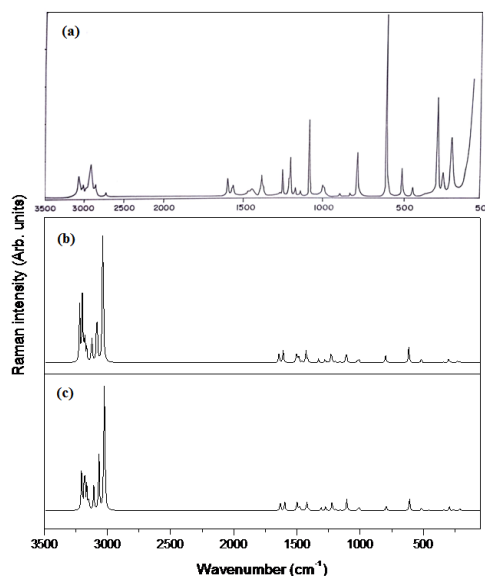


Figure 3. FT-Raman spectra of 3-bromo-o-xylene

### C-H Vibrations

The experimental C–H stretching bands appear in the range 3100–3000  $\text{cm}^{-1}$  [16]. Hence, the IR frequencies of BOX are assigned at 3102 and 3010  $\text{cm}^{-1}$  for C–H stretching modes. The C–H Raman frequencies are observed at 3035 and 3012  $\text{cm}^{-1}$ , which are confirmed by the energy distribution around 100%. The IR band at 1300, 1262, 1200  $\text{cm}^{-1}$  and Raman band at 1260, 1202  $\text{cm}^{-1}$  are assigned to C–H in-plane vibrations of BOX.

### C-C Vibrations

The spectral range from 1650 to 1400  $\text{cm}^{-1}$  gives rise to the C–C aromatic stretching vibrations [17]. As a result, the C–C stretching vibrations of BOX are observed at 1640, 1594, 1543, 1460, 1448, 1388  $\text{cm}^{-1}$  in FTIR and 1580, 1561, 1450  $\text{cm}^{-1}$  in the FT-Raman spectrum and they are also established by their TED contribution. Also, the bands observed at 790, 684  $\text{cm}^{-1}$  and 782  $\text{cm}^{-1}$  in the FTIR and Raman spectra, respectively, have been assigned to ring in-plane bending modes.

### C-Br Vibrations

Since mixing of vibrations is possible due to the presence of heavy atoms, the vibrations corresponding to C–Br bonds are quite interesting [18] and they appear in the lower frequencies i.e. 650–485  $\text{cm}^{-1}$  and their deformation arise in the region 300–140  $\text{cm}^{-1}$ . In the present investigation, the band is observed at 750  $\text{cm}^{-1}$  in FTIR spectrum for C–Br stretching vibration. The deformation vibrations of C–Br are listed in Table III.

### CH<sub>3</sub> Group Vibrations

In the title molecule, there are nine fundamentals associated to each CH<sub>3</sub> group. The asymmetric and symmetric modes of CH<sub>3</sub> groups are observed around 2980 and 2870  $\text{cm}^{-1}$ , respectively [19,20]. The IR and Raman spectra of BOX have CH<sub>3</sub> out-of-plane stretching bands at 2890, 2730 and 2894, 2732  $\text{cm}^{-1}$ , respectively. The CH<sub>3</sub> in-plane stretching vibrations are designated at 2962, 2946  $\text{cm}^{-1}$  in IR and 2944  $\text{cm}^{-1}$  in the Raman spectra and they are in excellent conformity with the calculations by B3LYP/6-311++G(d,p) method. The CH<sub>3</sub> ss frequencies are established at 3054 and 3065  $\text{cm}^{-1}$  in the FTIR and Raman spectra, respectively, and confirmed with the TED results. The bands at 1240, 1148 and 1242, 1150  $\text{cm}^{-1}$  in IR and Raman, respectively, are ascribed to CH<sub>3</sub> out-of-plane bending modes of BOX. The bands obtained at 1100  $\text{cm}^{-1}$  in Raman and 1190  $\text{cm}^{-1}$  in both spectra are allocated to CH<sub>3</sub> in-plane rocking modes, respectively, and they show reliable conformity with the computed values. The twisting modes and out-of-plane rocking modes of methyl groups are also assigned and given in Table III.

### D. UV-Vis and HOMO-LUMO Analysis

The molecular orbitals play a significant role in the electric and optical properties and chemical reactions [21,22]. The electronic behavior of BOX has been evaluated by TD-DFT/B3LYP/6-311++G(d,p) calculations in methanol, benzene and chloroform. The wavelengths ( $\lambda$ ), oscillator strengths ( $f$ ) and energies for excitation ( $E$ ) are listed in Table IV and the theoretical ultraviolet spectrum of BOX in different phases is revealed in Fig. 4. From the Frank–Condon principle, the maximum absorption peak ( $\lambda_{\text{max}}$ ) in UV–vis spectra corresponds to the vertical excitation. The TD-DFT calculations expect three transitions for BOX molecule. The transitions at 5.1879 eV (238.99 nm) with an oscillator strength  $f = 0.0003$  is strong in methanol phase. Similarly, transitions found at 5.1783 eV (239.43 nm) with an oscillator strength  $f = 0.0003$  and at 5.1815 eV (239.28 nm) with an oscillator strength  $f = 0.0003$  in benzene and chloroform, respectively. They are assigned to  $\pi \rightarrow \pi^*$  transitions and their major contributions were calculated with the help of SWizard program [23]. The absorption wavelength corresponds to the transition from HOMO to LUMO (70%) and from HOMO-1 to LUMO+2 (97%) are assigned to  $\pi \rightarrow \pi^*$  type. The 3D plots of frontier molecular orbitals for BOX are shown in Fig. 5. In BOX, the HOMO is located over the ring system, bromine atom and LUMO is delocalized over the C–C bond of the ring; hence the HOMO  $\rightarrow$  LUMO transition explains an electron density transfer to the C–C bond of the benzene ring and methyl groups from the bromine atom, which affects the biological and chemical activity of BOX.

Table III. Vibrational assignments of fundamental modes of 3-bromo-o-xylene along with calculated IR intensities and Raman activities based on DFT force field calculation

Sl.No.	Observed wavenumber (cm <sup>-1</sup> )		Calculated frequencies (cm <sup>-1</sup> )								TED% among types of coordinates
			B3LYP/6-31+G(d,p)				B3LYP/6-311++G(d,p)				
	FTIR	FT Raman	Unscaled	Scaled	IR intensity <sup>a</sup>	Raman activity <sup>b</sup>	Unscaled	Scaled	IR intensity <sup>a</sup>	Raman activity <sup>b</sup>	
1	3102(ms)	-	3220	3095	4.38	134.03	3204	3080	3.43	127.71	vCH(98)
2	-	3065(s)	3199	3075	16.10	1554.48	3181	3058	14.59	156.93	CH <sub>3ss</sub> (92)
3	3054(w)	-	3180	3057	8.84	74.54	3164	3042	7.75	69.50	CH <sub>3ss</sub> (91)
4	-	3035(vw)	3165	3043	4.75	33.16	3147	3025	4.76	32.45	vCH(95)
5	3010(vw)	3012(vw)	3124	3003	19.31	68.90	3108	2988	18.81	66.24	vCH(94)
6	2962(w)	-	3086	2967	2.43	14.14	3069	2950	0.84	5.46	CH <sub>3ips</sub> (90)
7	2946(w)	2944(s)	3083	2964	28.95	137.53	3067	2948	30.36	148.08	CH <sub>3ips</sub> (89)
8	2890(s)	2894(s)	3038	2920	29.86	207.42	3027	2910	26.82	221.57	CH <sub>3ops</sub> (86)
9	2730(w)	2732(w)	3034	2917	27.59	173.20	3023	2906	25.56	196.12	CH <sub>3ops</sub> (85)
10	1640(vw)	-	1643	1579	2.45	18..2792	1633	1570	2.67	17.91	vCC(85)
11	1594(ms)	-	1609	1547	26.37	19.83	1598	1536	25.02	19.26	vCC(84)
12	-	1580(ms)	1506	1448	18.42	6.11	1502	1444	14.94	7.00	vCC(82)
13	-	1561(w)	1504	1446	16.93	5.62	1498	1440	16.91	6.99	vCC(88)
14	1543(ms)	-	1500	1442	22.47	6.80	1496	1438	25.40	5.51	vCC(86)
15	-	1474(vw)	1486	1428	0.80	11.07	1480	1423	0.68	9.14	CH <sub>3ipb</sub> (83)
16	1460(w)	-	1484	1427	13.59	1.21	1477	1420	14.39	1.38	vCC(82)
17	1448 (w)	1450(w)	1460	1403	1.98	2.77	1453	1397	3.54	1.91	vCC(81)
18	-	1463(vw)	1429	1374	4.01	18.52	1423	1368	4.91	16.46	CH <sub>3ipb</sub> (84)
19	1388(s)	-	1416	1361	0.87	6.91	1411	1356	0.75	4.57	vCC(80)
20	-	1378(ms)	1360	1307	1.22	5.57	1309	1258	1.10	5.30	CH <sub>3sb</sub> (79)
21	-	1370(w)	1278	1229	0.66	6.87	1273	1224	0.56	6.95	CH <sub>3sb</sub> (78)
22	1300(vw)	-	1229	1181	0.70	19.96	1222	1175	0.40	19.59	bCH(77)
23	1262(s)	1260(vw)	1216	1169	0.02	0.60	1194	1148	4.47	2.19	bCH(76)
24	1240(s)	1242(s)	1197	1151	4.91	2.14	1135	1091	11.77	1.56	CH <sub>3opb</sub> (75)
25	1200(vs)	1202(ms)	1160	1115	11.22	1.87	1105	1062	6.66	19.36	bCH(76)
26	1190(vs)	1190(s)	1109	1066	6.42	19.36	1067	1026	0.21	0.26	CH <sub>3ipr</sub> (78)
27	1148(vs)	1150(w)	1060	1019	2.27	0.15	1040	1000	2.39	0.24	CH <sub>3opb</sub> (72)
28	-	1100(w)	1023	983	28.01	2.64	1018	979	23.50	3.74	CH <sub>3ipr</sub> (74)
29	-	991(w)	1011	972	14.17	6.22	1006	967	20.73	5.10	CH <sub>3opr</sub> (71)
30	892(vw)	890(vw)	1004	965	0.54	0.06	980	942	0.15	0.00	CH <sub>3opr</sub> (74)
31	874(vw)	-	956	919	0.07	0.01	908	873	0.00	0.17	bCC(72)
32	-	820(w)	916	881	0.04	0.38	834	802	10.76	0.52	bCC(74)
33	790(vs)	-	836	804	11.94	0.33	794	763	14.55	9.46	Rsymd(70)
34	-	782(vs)	799	768	11.10	10.15	780	750	43.14	0.24	Rtrigd(69)
35	765(s)	-	777	747	48.46	0.73	714	686	6.27	0.05	ωCH(65)
36	750(vs)	-	676	650	0.17	0.35	610	586	9.47	19.02	vCBr(74)
37	684(vw)	-	615	591	8.49	5.40	525	505	0.01	0.04	Rasynd(70)
38	678(vs)	-	549	528	0.25	0.01	516	496	0.04	5.09	ωCH (68)
39	-	602(vs)	516	496	0.05	19.82	511	491	0.00	0.01	ωCH (66)
40	590(vs)	-	466	448	0.22	0.84	457	439	0.19	0.78	ωCC(67)
41	550(vw)	-	341	328	0.23	1.15	338	325	0.24	1.18	ωCC (68)
42	-	510(s)	299	287	2.05	5.11	293	282	2.34	5.54	tRsymd (67)
43	502(vw)	-	283	272	6.60	1.39	262	252	6.16	1.47	tRtrigd (69)
44	-	450(ms)	228	219	0.03	2.23	212	204	0.16	1.84	tRasynd (65)
45	-	304(vs)	214	206	0.47	1.58	211	203	0.52	1.72	bCBr(70)
46	-	278(s)	181	174	0.89	0.05	171	164	0.77	0.09	ωCBr (64)
47	-	270(s)	123	118	0.02	0.39	107	103	0.02	0.54	tOCH <sub>3</sub> (60)
48	-	205(vs)	52	50	0.09	0.38	55	53	0.08	0.52	tOCH <sub>3</sub> (59)

Table IV. The calculated absorption wavelength ( $\lambda$ ), excitation energies (e) and oscillator strengths (f) of 3-bromo-o-xylene calculated by the TD-B3LYP/6-311++G(d,p) method

TD-B3LYP/6-311++G(d,p)									Major Contribution	Assignment
Methanol			Benzene			Chloroform				
$\lambda$ (nm)	E (eV)	f	$\lambda$ (nm)	E (eV)	f	$\lambda$ (nm)	E (eV)	f		
243.56	5.0906	0.0002	244.51	5.0707	0.0005	244.03	5.0807	0.0003	H $\rightarrow$ L (70%)	$\pi \rightarrow \pi^*$
238.99	5.1879	0.0003	239.43	5.1783	0.0003	239.28	5.1815	0.0003	H $\rightarrow$ L+2 (96%)	$\pi \rightarrow \pi^*$
226.69	5.4694	0.0002	225.04	5.5095	0.0002	225.93	5.4877	0.0002	H-1 $\rightarrow$ L+2 (97%)	$\pi \rightarrow \pi^*$

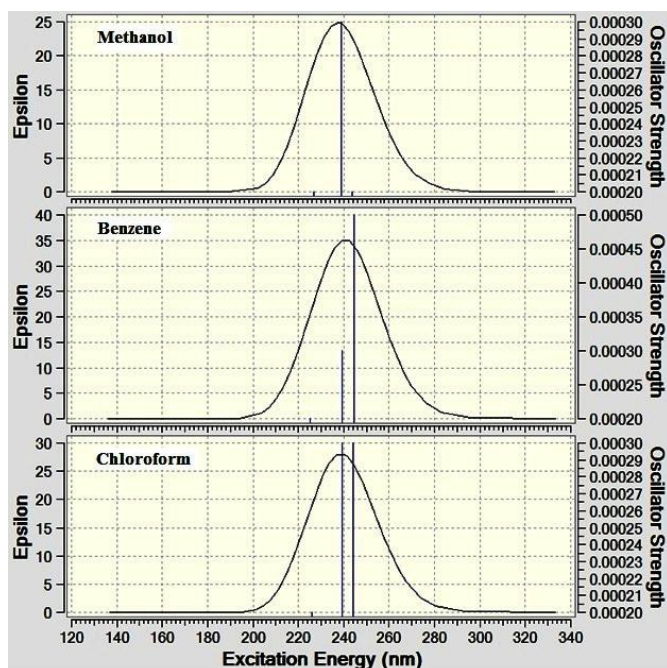


Figure 4. Theoretically calculated UV spectra for 3-bromo-o-xylene

### E. NBO Analysis

From the second-order perturbation approach [24], hyperconjugative interaction energy of BOX was deduced. The donor, acceptor orbitals and their interaction energies for BOX are listed in Table V. The larger the interaction energy  $E(2)$  value shows the stronger interaction between electron-donors and electron-acceptors. The intramolecular interaction of the  $\pi$  electrons of C-C bonding and antibonding of the ring system gives the stabilization of several portion of the ring. In BOX, the intramolecular hyperconjugative interaction of  $\pi(C1-C6) \rightarrow \pi^*(C2-C3)$  and  $\pi(C1-C6) \rightarrow \pi^*(C4-C5)$  leading to stabilization of 20.81 and 21.28 kJ/mol, respectively. These interactions are found as boost in electron density (ED) of C-C, C-Br antibonding orbital that affects the respective bonds. The energies for the interaction  $n3(Br15) \rightarrow \pi^*(C1-C6)$  and  $n2(Br15) \rightarrow \pi^*(C2-C3)$  are 9.55 and 3.34 kJmol<sup>-1</sup>, respectively, represents the interaction between the bromine atom and benzene ring for BOX. There is also a strong interaction from  $\pi(C2-C3) \rightarrow \pi^*(C4-C5)$  that weakens the respective bond (C4-C5 = 1.389 Å by B3LYP/6-311G++(d,p)) with stabilization of 19.88 kJ mol<sup>-1</sup>. The pharmaceutical and biological properties of BOX mainly depend on these charge transfer interactions.

Table V. Second-order perturbation theory analysis of fock matrix in nbo basis for 3-bromo-o-xylene

Donor (i)	ED (i) (e)	Acceptor (j)	ED (j) (e)	<sup>a</sup> E(2) (kJ mol <sup>-1</sup> )	<sup>b</sup> E(j)-E(i) (a.u.)	<sup>c</sup> F (i,j) (a.u.)
$\pi(C1-C6)$	1.660	$\pi^*(C2-C3)$	0.392	20.81	0.27	0.068
		$\pi^*(C4-C5)$	0.328	21.28	0.28	0.069
$\pi(C2-C3)$	1.684	$\pi^*(C1-C6)$	0.335	17.81	0.30	0.066
		$\pi^*(C4-C5)$	0.328	19.88	0.29	0.069
$\pi(C4-C5)$	1.677	$\pi^*(C1-C6)$	0.335	18.87	0.29	0.066
		$\pi^*(C2-C3)$	0.392	19.67	0.28	0.067
$n2(Br15)$	1.972	$\pi^*(C2-C3)$	0.392	3.34	0.86	0.048
$n3(Br15)$	1.941	$\pi^*(C1-C6)$	0.335	9.55	0.31	0.053

<sup>a</sup>E(2) means energy of hyperconjugative interactions.

<sup>b</sup>E(j)-E(i) Energy difference between donor and acceptor i and j NBO orbitals.

<sup>c</sup>F(i,j) is the Fock matrix element between i and j NBO orbitals.

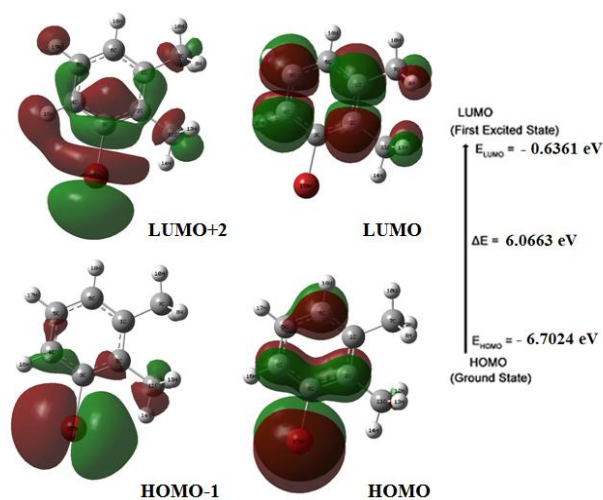


Figure 5. Frontier molecular orbital for 3-bromo-o-xylene

### F. Electrostatic Potential, Total Electron Density and Molecular Electrostatic Potential

The electrophilic and nucleophilic attack [25] for BOX can be predicted from the MEP analysis by B3LYP/6-311++G(d,p) method and the pictorial representation is given in Fig. 6. Here, the negative ESP is distributed over the benzene ring, bromine atom and is reflected as a yellowish blob, the positive ESP is contained on the rest of the molecule. The potential energy increases from red < orange < yellow < green < blue in the MEP figure. In the present study, the MEP map indicates that the negative potential sites are on bromine atom (Red) and the positive potential sites are around the hydrogen atoms of the molecule (Blue). In BOX, the

H atoms indicate the strongest attraction and bromine atom indicate the strongest repulsion.

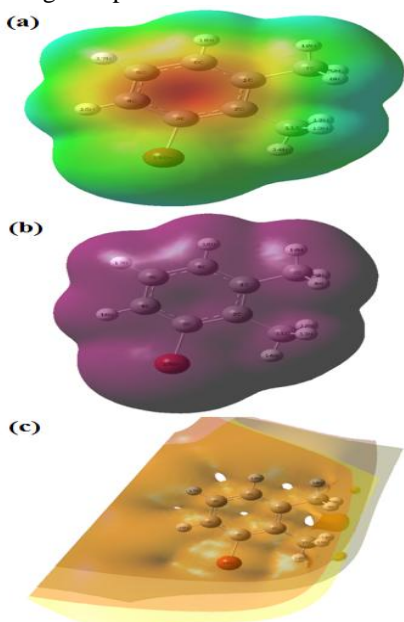


Figure 6.(a) Electrostatic potential (ESP); (b) electron density (ED) and (c) the molecular electrostatic potential (MEP) map for 3-bromo-o-xylene

#### IV. CONCLUSION

The optimized parameters and complete vibrational bands of 3-bromo-o-xylene have been determined using DFT-B3LYP method. The frequency assignment for normal modes is supported by the TED calculation. The NBO analysis explains the hyper conjugative interaction of BOX. The MEP surface drawn and decrease in HOMO-LUMO gap may lead to the understanding of electronic properties and chemical activity of the molecule. The theoretical UV-vis spectrum supports the energy gap of the molecule. These results will be evidence for 3-bromo-o-xylene in pharmaceuticals, reaction intermediates and polymer science.

#### REFERENCES

1. J. Fabri, U. Graeser, and T. A. Simo, "Xylenes". Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2000.
2. R. A. F. Tomás, J. C. M. Bordado, and J. F. P. Gomes, "p-Xylene oxidation to terephthalic acid: a literature review oriented toward process optimization and development," *Chem. Rev.*, vol. 113(10), 2013, pp. 7421-7469.
3. V. Arjunan, P. S. Balamourougane, I. Saravanan, and S. Mohan, "Investigation of the structural and harmonic vibrational properties of 2-nitro-, 4-nitro- and 5-nitro-m-xylene by ab initio and density functional theory," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 74, 2009, pp. 798-807.
4. M. Govindarajan, and M. Karabacak, "Analysis of vibrational spectra (FT-IR and FT-Raman) and nonlinear optical properties of organic 2-chloro-p-xylene," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 94, 2012, pp. 36-47.
5. M. Arivazhagan, and R. Meenakshi, "Vibrational spectroscopic studies and DFT calculations of 4-bromo-o-xylene," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 91, 2012, pp. 419-430.
6. M. Manzoor ali, G. George, S. Ramalingam, S. Periandy, and V. J. Gokulakrishnan, "Spectroscopic investigation and chemical properties analysis on anticancer compound;  $\alpha, \alpha, \alpha, \alpha$ -Tetrabromo-p-Xylene with computational analysis," *J. Mol. Struct.*, vol. 1106, 2016, pp. 37-52.
7. G. Venkatesh, M. Govindaraju, C. Kamal, P. Vennila, and S. Kaya, "Structural, electronic and optical properties of 2,5-dichloro-p-xylene: experimental and theoretical calculations using DFT method," *RSC Adv.*, vol. 7, 2017, pp. 1401-1412.

8. S. Ramalingam, M. Manzoor Ali, G. George, A. A. Manthiri, and S. Periandy, "Vibrational investigation on pharmaceutical activity of m-xylene-4-sulphonic acid by quantum computational and experimental support," *J. Taibah Univ. Sci.*, vol. 12(1), 2018, pp. 87-103.
9. H. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, R. Nakajima, Y. Honda, O. Kikao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas and J. B. Foresman, Gaussian O.G., Revision A.02, Gaussian Inc., Wallingford, CT, 2009.
10. A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.*, vol. 98, 1993, pp. 5648-5652.
11. C. Lee, W. Yang, and R. R. Parr, "Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density," *Phys. Rev. B.*, vol. 37, 1988, pp. 785-789.
12. MOLVIB (V.7.0): Calculation of Harmonic Force Fields and Vibrational Modes of Molecules, QCPE Program No. 807, 2002.
13. S. Dai, and Y. Wang, Crystal structure of 1-bromo-4-methanesulfonyl-2,3-dimethylbenzene, *Acta Cryst.*, vol. E71, 2015, pp. o973.
14. R. Zhang, B. Du, G. Sun, and Y. Sun, "Experimental and theoretical studies on o-, m- and p-chlorobenzylideneaminoantipyridines," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 75, 2010, pp. 1115-1124.
15. D. C. Young, Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems (Electronic), 2001, John Wiley & Sons Ltd., New York.
16. E. Gobinath, S. Jeyavijayan, and R. John Xavier, "Spectroscopic investigations, DFT computations and other molecular properties of 2,4-dimethylbenzoic acid," *Indian J. Pure & Appl. Phys.*, vol. 55, 2017, pp. 541-550.
17. S. Jeyavijayan, "Molecular structure, vibrational spectra, NBO analysis, first hyperpolarizability, and HOMO-LUMO studies of 2-amino-4-hydroxypyrimidine by density functional method," *J. Mol. Struct.*, vol. 1085, 2015, pp. 137-146.
18. Socrates G. Infrared and Raman Characteristic Group Frequencies - Tables and Charts, 2001, third ed., Wiley, Chichester.
19. S. Ramalingam, S. Periandy, B. Narayanan, and S. Mohan, "FTIR and FT-Raman spectroscopic investigation of 2-bromo-4-methylaniline using ab initio HF and DFT calculations," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2010, vol. 76(1), pp. 84-92.
20. N. Y. Sugirtha Suni, L. Guru Prasad, and R. Ganapathi Raman Rajendran, "Vibrational Analysis and Non Linear Optical Activity of 3-fluoro-4-methylbenzotrile," *Orient. J. Chem.*, vol. 34(3), 2018, pp. 1638-1645.
21. I. Fleming, Frontier Orbitals and Organic Chemical Reactions, 1976, Wiley, London.
22. S. Jeyavijayan, "Molecular structure, spectroscopic (FTIR, FT-Raman,  $^{13}\text{C}$  and  $^1\text{H}$  NMR, UV), polarizability and first-order hyperpolarizability, HOMO-LUMO analysis of 2,4-difluoroacetophenone," *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol. 136, 2015, pp. 553-566.
23. S. I. Gorelsky, SWizard Program Revision 4.5, 2010, University of Ottawa, Ottawa, Canada.
24. J. Choo, S. Kim, H. Joo, and Y. Kwon, "Molecular structures of (trifluoromethyl)iodine dihalides CF<sub>3</sub>IX<sub>2</sub> (X=F, Cl): ab initio and DFT calculations," *J. Mol. Struct. (Theochem.)*, vol. 587, 2002, pp. 1-8.
25. J. S. Murray, and K. Sen, "Molecular Electrostatic Potentials, Concepts and Applications," Elsevier, Amsterdam, 1996, pp. 7-624.

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