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Theoretical studies on the structural, vibrational, conformational analysis and nonlinear optic property of 4-(methoxycarbonyl)-phenylboronic acid

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In this paper, the structural, electronic, non-linear optical (NLO) properties and vibrational frequencies of 4-(methoxycarbonyl)-phenylboronic acid have been examined theoretically using ab initio Hartree-Fock (HF) and Density Functional Theory (DFT/B3LYP) methods applying the standard 6-311++G(d,p) basis set. ^{1}H- and ^{13}C NMR chemical shifts are calculated by employing the direct implementation of the gauge including-atomic-orbital (GIAO) method at the B3LYP/6-311++G(d,p) and HF/6-31G(d) levels of the theory. There are two conformers, cis-trans(ct) and trans-cis (tc) for title molecule. The energy difference between ct and tc conformers of studied molecule are of 0.126 kcal/mol with B3LYP/6-311++G(d,p) and 0.138 kcal/mol with HF/6-311++G(d,p), respectively. The conformer ct is more stable than the conformer tc. Also, the energy gap differences between the highest occupied and the lowest unoccupied molecular orbitals, dipole moment, polarizability and first static hyperpolarizability are calculated as a function of both dihedral angle (C3-C4-C7-O3), between methoxycarbonyl group (CH_3-O-CO-) and benzene ring, and dihedral angle (C2-C1-B-O1), between boronic acid group (-$B(OH)_2$) and benzene ring. In the change of the energy gap and polarizability depending on dihedral angles, it is shown that the polarizabilities follow inverse relationship the energy gaps.

Keywords: Nonlinear optical properties, Polarizability, First static hyperpolarizability, DFT/B3LYP

Usually, boronic acids are represented a structural R-B $(OH)_2$, (R= alkyl or aryl) form and they are not naturally occurring, although boronic acids have come along in the literature for over a century[1]. The practicality, reaction ability and versatile reactivity of boronic acids are connected to their unique electronic, structure and chemical properties. The compounds containing boronic acids and their derivatives have an extensive range of uses in material science[2-4], polymer industry[5], medicinal[6,7] and bioorganic[8,9], as well as chemical biology[10-13]. Moreover, they are used boron neutron capture therapy agents, as antibiotics, enzyme inhibitors for treatment of tumors. Because of these unique features, interest in boronic acids and their derivatives continues to increase. There are many studies about the synthesis of new boronic acid derivatives. The structural, electronic and chemical properties of these compounds are studied experimentally and theoretically by a lot of researchers. The molecular structure of phenylboronic acid and substituted phenylboronic acid molecules such as 2,4-difluorophenyboronic acid, 4-phenyboronic acid monohydrate, 4-amino-3-fluorophenylboronic acid and (4-carbamoylpheny) boronic acid have been reported[14-17]. The conformational analyzes of phenylboronic acid, monosubstituted phenylboronic acid molecules and methylboronic acid have been carried out[18]. Experimental (FTIR, FT-Raman, UV-visible ^{1}H and ^{13}C NMR) computational studies of 3-bromophenyboronic acid, 3,5-difluorophenyboronic acid and 2,3-difluorophenyboronic acid have been accomplished[19-21]. Also, the molecular properties studies such as FTIR, FT-Raman, UV-visible and NMR of 2,6-dimethoxyphenyboronic acid, 4-mercaptophenyboronic acid, 5-bromo-2-ethoxyphenyboronic acid, 3-pyridine boronic acid, 4-pyridine boronic acid and 3,4-diclorophenyboronic acid have been presented[22-25]. Although the crystal structure of 4-(methoxycarbonyl)-phenylboronic acid molecule was reported, a comprehensives study on the physical and chemical properties of title molecule has not been reported so far. The present work is aimed to investigate three-dimensional potential energy surface, vibrational frequencies, the dipole moment (μ), mean polarizability (α), the total first static hyperpolarizability (β), the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), ^{1}H and ^{13}C NMR chemical shifts of 4-(methoxycarbonyl)-phenylboronic acid molecule of which is determined solely the molecular structure by Flanagan et al.[26] using DFT/B3LYP and HF level of theory. In this work, potential energy scan, relative energies, rotational barriers, molecular structure, dipole moment, polarizability, first static hyper polarizability, the electronic structure, vibrational frequencies, HOMO-LUMO energies and ^{1}H NMR and ^{13}C NMR chemical shifts of the molecule under investigation have been studied. From the calculation results, it was seen that title molecule has two conformers, cis-trans (ct) and trans-cis (tc). The conformer ct is more stable than the conformer tc. The molecular structure using numbering scheme of 4-(methoxycarbonyl)-phenylboronic acid is given in Fig. 1. These conformers are as a function of the orientation of the hydrogen atoms in the boronic acid group of title molecule. The conformer tc is that H1 atom to the phenyl ring, H2 atom toward reverse direction of H1 atom is orientation. The conformer ct is opposite of this status (see Fig. 1).

Materials and Methods

The quantum chemical calculations of all studied compounds were performed within the framework of ab initio Hartre-Fock (HF) and Density Functional Theory (DFT)[27-28] with Becke's three parameter hybrid functional (B3) and combined with gradient corrected correlation functional of Lee–Yang–Parr (LYP)[29,30] by means of the Gaussian 09 program package and Gauss view 5.0 molecular visualization programs[31,32]. The minima of the potential energy surface have first determined by way of B3LYP/6-311++G(d,p). Secondly the obtained conformers having low energy were optimized at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis set. Then, the structural parameter of conformer ct as an initial geometries are used to calculate the ground state dipole moments (μ), vibrational frequencies, polarizability (α), hyperpolarizability (β), the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) by using ab initio Hartee-Fock method and DFT/B3LYP method with 6-311++G(d,p) basis set. The assignments of fundamental vibrational modes of the studied molecule were performed based on total energy distribution (TED) analysis by using VEDA 4f program[33]. The ^{1}H and ^{13}C NMR chemical shifts were calculated with GIAO approach using B3LYP/6-311+G(2d,p) and HF/6-31G(d).

Results and Discussion

Conformational analysis and torsional barriers

In order to find the structure of low energy conformers, the potential energy surface of title molecule as a function of the two dihedral angles θ_1=C1-B-O1-H1 and θ_2=C1-B-O2-H2 was calculated using DFT/6-311++G(d,p) method.

The dihedral angles θ_1 = C1-B-O1-H1 and θ_2 = C1-B-O2-H2 were varied with increments of 10° starting from 0° throughout 36 steps while entire other structural parameters were optimized and the result of potential energy surface is shown Fig. 2. The potential

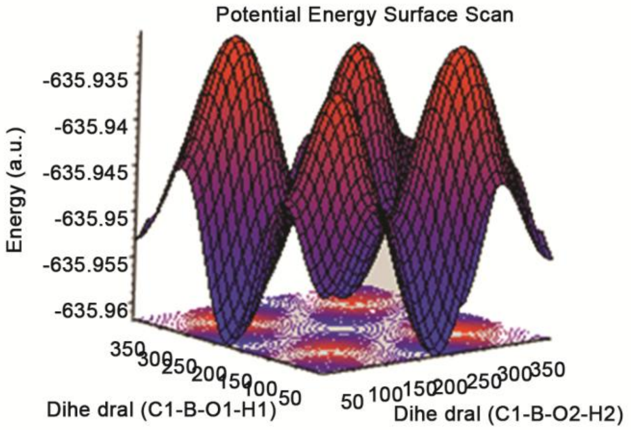

Fig. 2 — The potential energy surface of title molecule calculated at DFT/B3LYP/6–311++G (d,p) level of theory.

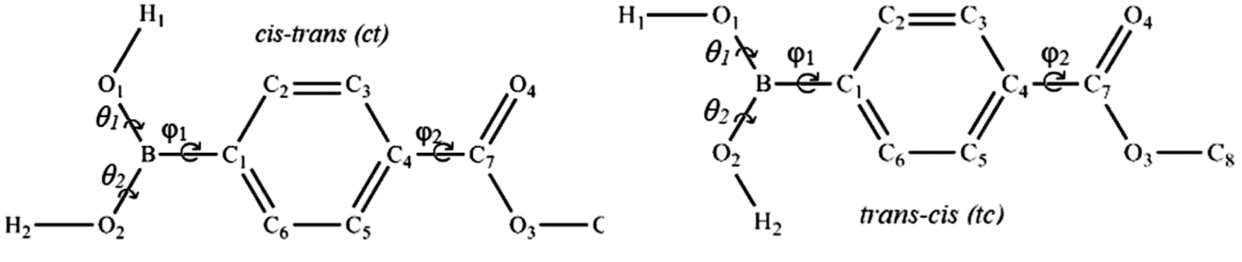

Fig. 1 — Molecular structure of 4-(methoxycarbonyl)-phenylboronic acid numbering scheme.

energy surface displays minima and maxima corresponding to several low and high energy structures[34]. The structures of minimum energies were optimized without any constraints. As a result of these optimizations, these conformations with low energies are converted into two possible conformers (ct and tc). The conformer ct is more stable than the conformer tc. In addition to these, the potential energy curves for internal rotation of the boronic acid $B(OH)_2$ group around C1-B bond and the methoxycarbonyl group around C4-C7 bond of conformers ct and tc of title molecule were obtained by allowing the φ_1 = C2-C1-B-O1 and φ_2 = C3-C4-C7-O3 dihedral angles from 0˚ to 180˚ by steps of 10˚, respectively. Finally, the results of potential energy curves are shown Fig. 3.

Molecular structure

The cis-trans and trans-cis conformers of 4-(methoxycarbonyl)-phenylboronic acid molecule are optimized both B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) level of theory. The structural parameter of conformer ct and tc as an initial geometries are used to calculate polarizability, hyperpolarizability, the highest occupied molecular orbital, the lowest unoccupied molecular orbital by the same methods[35]. The values of calculate dipole moment, electronic energy, polarizability, hyperpolarizability, HOMO, LUMO and energy gap of conformer ct and tc of the molecule are given in Table 1. The selected bond lengths, bond angles and dihedral angles from obtained the geometry optimizations for both conformers are listed in Table 2. As seen from Table 2, the optimized bond lengths of bond in the benzene ring of studied molecule fall in the range of 1.3892-1.4048 and 1.3821-1.3948 in the B3LYP and HF methods, respectively. The observed X-ray diffraction (XRD) data[26] for these bond lengths in title molecule fall in the range from 1.3891 to 1.4035 Å, which are in good agreement with the values obtained using the B3LYP method. The optimized C4-C7 bond lengths between methoxycarbonyl group and benzene ring are 1.4921 and 1.488 in the B3LYP and HF methods, which is consistent with the experiential value 1.488 (13) Å. According to XRD data and the optimized results, it is observed that most of the optimized bond and dihedral angles are slightly shorter as well as longer than the experiential values both models. The inconsistencies between the theoretical and experimental results are due to the fact that theoretical calculation belongs to isolated

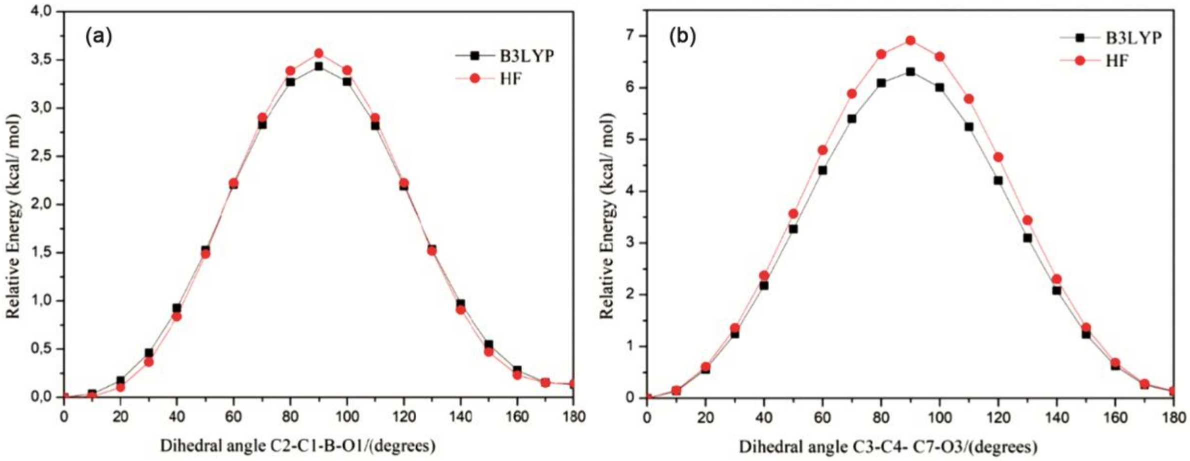

Fig. 3 — The potential energy surface of conformer ct (a) C2-C1-B-O1 and (b) C3-C4-C7-O3 dihedral angles.

Table 1 — The electronic, HOMO, LUMO energy, dipole moment, polarizability, hyperpolarizability, and energy gap (ΔE_g) of conformer ct and tc of title molecule

Conformer	Energy (eV)	μ (D)	α (eV)	β (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_g (eV)
				B3LYP/6-311++G(d,p)			
cis-trans	-17315.305	0.647	3351.27	3842.42	-7.377	-2.009	5.368
trans-cis	-17315.299	2.996	3351.27	3263.11	-7.393	-2.008	5.385
				HF/6-311++G(d,p)			
cis-trans	-17214.586	0.725	2967.87	1029.63	-9.452	1.024	10.476
trans-cis	-17214.580	3.219	2968.14	1465.84	-9.466	0.944	10.410

Table 2 — The selected bond lengths, bond angles and dihedral angles of conformer ct and tc of title molecule

Parameters	*cis-trans*			*trans-cis*	
	B3LYP	HF	Experimental[a]	B3LYP	HF
			Bond lengths (Å)		
O1—B1	1.3726	1.3588	1.3552(13)	1.3661	1.3524
C1—C2	1.4048	1.3942	1.4034(13)	1.4038	1.3936
C1—C6	1.4045	1.3948	1.4035(13)	1.4055	1.3955
C1—B1	1.5700	1.5795	1.5752(14)	1.5701	1.5795
B1—O2	1.3663	1.3526	1.372(13)	1.3727	1.3592
C2—C3	1.3904	1.384	1.3923(13)	1.3906	1.384
O3—C7	1.3500	1.3197	1.3336(12)	1.351	1.3206
O3—C8	1.4390	1.4171	1.4503(12)	1.4391	1.4172
C3—C4	1.3996	1.3882	1.3942(13)	1.399	1.3877
O4—C7	1.2101	1.1864	1.2191(12)	1.2097	1.1858
C4—C5	1.3985	1.3879	1.3992(13)	1.3991	1.3886
C4—C7	1.4921	1.494	1.488(13)	1.4921	1.4941
C5—C6	1.3892	1.3821	1.3891(13)	1.3891	1.3823
			Bond angles (°)		
B1—O1—H1	115.17	116.62	113.1(12)	112.53	113.48
C2—C1—C6	117.63	117.83	118(8)	117.64	117.84
C2—C1—B1	119.82	119.55	122.77(8)	122.54	122.62
C6—C1—B1	122.55	122.62	119.23(8)	119.82	119.54
O1—B1—O2	117.28	117.55	118.16(9)	117.31	117.54
O1—B1—C1	124.36	124.12	118.02(9)	118.32	118.34
O2—B1—C1	118.37	118.34	123.82(9)	124.37	124.12
B1—O2—H2	112.47	113.46	118(12)	115.14	116.58
C3—C2—C1	121.41	121.28	121.43(9)	121.68	121.53
C7—O3—C8	115.89	117.38	115.73(8)	115.83	117.32
C2—C3—C4	119.95	119.87	119.48(9)	119.71	119.66
C3—C4—C5	119.56	119.78	120.15 (9)	119.56	119.77
C3—C4—C7	122.52	122.17	121.91 (8)	122.34	122.03
C5—C4—C7	117.93	118.05	117.91 (8)	118.11	118.21
C6—C5—C4	119.90	119.81	119.75 (9)	120.14	120.04
C5—C6—C1	121.55	121.42	121.19 (9)	121.27	121.16
O4—C7—O3	123.06	123.25	123.30 (9)	123.03	123.20
O4—C7—C4	124.44	123.72	123.32 (9)	124.49	123.79
O3—C7—C4	112.50	113.03	113.37 (8)	112.49	113.01
			Dihedral angles (°)		
C2—C1—B1—O1	179.99	179.99	178.38 (9)	179.98	179.98
C6—C1—B1—O1	-0.01	-0.01	-1.02 (14)	-0.02	-0.02
C2—C1—B1—O2	-0.01	-0.02	-1.88 (15)	-0.02	-0.03
C6—C1—B1—O2	179.99	179.98	178.73 (9)	179.98	179.97
C6—C1—C2—C3	0.00	0.00	-0.29 (14)	0.00	0.00
B1—C1—C2—C3	-180.00	180.00	-179.69 (9)	180.00	180.00
C1—C2—C3—C4	0.00	0.00	-0.52 (14)	0.00	0.00
C2—C3—C4—C5	0.00	0.00	0.82 (14)	0.00	0.00
C2—C3—C4—C7	180.00	-180.00	-177.45 (8)	-180.00	-180.00
C3—C4—C5—C6	0.00	0.00	-0.31 (14)	0.00	0.00
C7—C4—C5—C6	-180.00	-180.00	178.03 (8)	180.00	-180.00
C4—C5—C6—C1	0.00	0.00	-0.52 (14)	0.00	0.00
C2—C1—C6—C5	0.00	0.00	0.81 (14)	0.00	0.00
B1—C1—C6—C5	180.00	-180.00	-179.77 (9)	-180.00	-180.00
C8—O3—C7—O4	0.00	-0.03	-5.45 (14)	0.00	0.00
C8—O3—C7—C4	-180.00	180.03	174.59 (8)	-180.00	-180.00
C3—C4—C7—O4	-180.00	180.03	173.53 (9)	-180.00	180.00
C5—C4—C7—O4	0.00	0.03	-4.78 (14)	0.00	0.00
C3—C4—C7—O3	0.00	-0.03	-6.51(13)	0.00	0.00
C5—C4—C7—O3	-180.00	-180.03	175.18 (8)	180.00	-180.00

[a] Values taken from Ref[26]

molecules in gaseous phase and experimental results belonging to molecule in solid state. The values of dipole moment of conformer ct and tc are found at 0.647 and 2.996 Debye with B3LYP and at 0.725 and 3.219 Debye HF method, respectively. Also, the 3D plots of energy values of HOMO and LUMO orbitals calculated B3LYP using 6-311++G(d,p) basis set for both conformers are presented in the Fig. 4. The ^{1}H and ^{13}C NMR chemical shifts were calculated with GIAO approach using B3LYP/6-311+G(d,p) and HF/6-31G(d) methods and the results are listed in Table 3.

The frontier molecular orbitals (HOMO and LUMO) are very important parameters for quantum chemistry as they are related to the optical and electrical properties of the molecule. The calculated difference between HOMOs and LUMOs energy gaps of conformer ct and tc are found to be 5.368 and 5.384 eV with B3LYP using 6-311++G(d,p), respectively. The difference between conformer ct and tc energy gaps are found to be 0.016 eV.

Electronic and nonlinear optic properties

The materials having nonlinear activity possess a nonlinear response to the electric fields associated with the light of a laser beam. There is a renaissance in the studies of atomically thin two dimensional (2D) layered materials of transition metal dichalcogenides, having unique properties for applications in flexible and transparent optoelectronics, sensors, nonlinear optical (NLO) devices, laser and sustainable energy. The ultrasonication treatment, being simple and having ease of mass production, has been tried for syntheses of 2D layered materials in different organic solvents[36]. It is well known that the higher values of dipole moment, polarizability, and hyperpolarizability are important for more active NLO properties[36-39]. Polarizability and hyperpolarizability provide useful information for frequency changing, optical modulation, optical switching and optical logic for technologies evolving in areas such as nonlinear optical activity, communication, signal processing, and optical interconnection[40-42]. Organic materials are expected to have relatively strong NLO properties, due to the delocalized electrons in the π->π* orbitals[43].

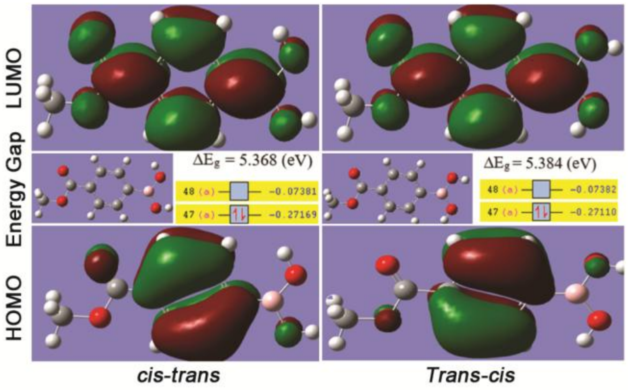

Fig. 4 — The 3D plots of energy values of HOMO (red) and LUMO (blue) orbitals of conformer ct and tc v of title molecule calculated B3LYP using 6-311++G(d,p).

In this study dipole moment, polarizability and first hyperpolarizability of conformer ct of the titled molecule were investigated by using B3LYP method at 6-311++G(d,p) basis set. The following formulas are used for calculating the magnitude of total static dipole moment (μ), polarizability (α) and first hyperpolarizability (β):

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\beta = \sqrt{(\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2}$$

Where, the total static dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) using the *x*, y, *z* components are determined according to literature[44]. The energy gap ΔE$_g$, dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) values of conformer ct of the titled molecule are investigated as a function of the two torsional angle using B3LYP/6-311++G(d,p) level of theory. The obtained results

Table 3 — The ^{13}C NMR and ^{1}H NMR chemical shifts of conformer ct the molecule calculated at B3LYP/6-311+G (d. p) and HF/6-31+G (d)

	^{13}C and ^{1}H NMR								
	C1	C4	C2	C3	C5	C6	C7	C8	
B3LYP/6-311+G(2d. p)	140.05	138.22	140.65	134.17	134.82	135.77	172.56	53.85	
HF/6-31+G(d)	131.65	128.79	132.29	127.54	128.06	126.97	156.60	45.77	
	B-H		Ph-H					OCH_3	
	H1	H2	H4	H3	H5	H6	H7	H8	H9
B3LYP/6-311+G(2d. p)	4.40	3.61	8.45	8.42	8.55	7.70	3.95	3.95	3.65
HF/6-31+G(d)	3.60	3.34	8.33	8.28	8.54	7.27	3.68	3.68	3.53

of energy gap ΔE_g, dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) values of conformer ct of the titled molecule are given in Figs 5-7, respectively. The calculated results showed that behavior of dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) values of conformer ct of the titled molecule as a function of dihedral angles have the same tendency. It means that these values are symmetric with the orthogonal conformation (90º) of the molecules.

As seen from Figs 5 and 6, in the change of the energy gap and polarizability depending on dihedral

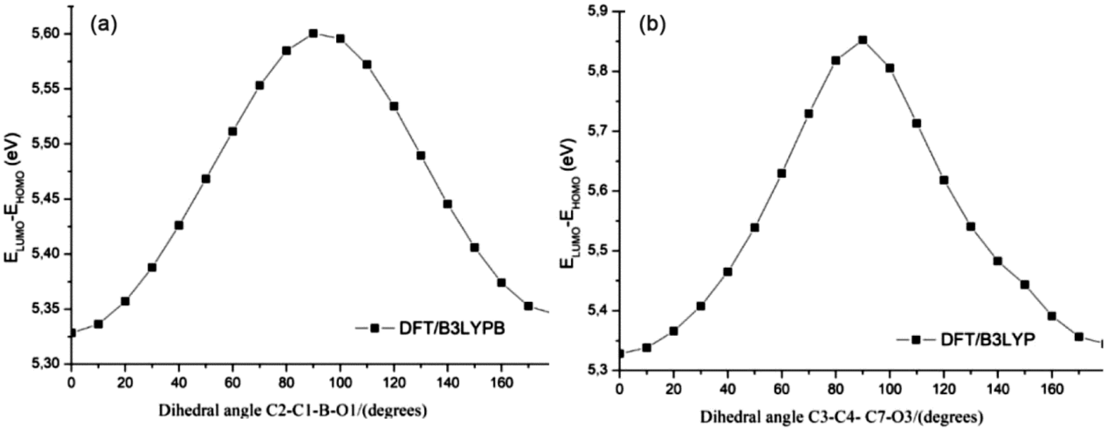

Fig. 5 — The energy gap of conformer ct (a) C2-C1-B-O1 and (b) C3-C4-C7-O3 dihedral angles at the 6-311++G(d,p).

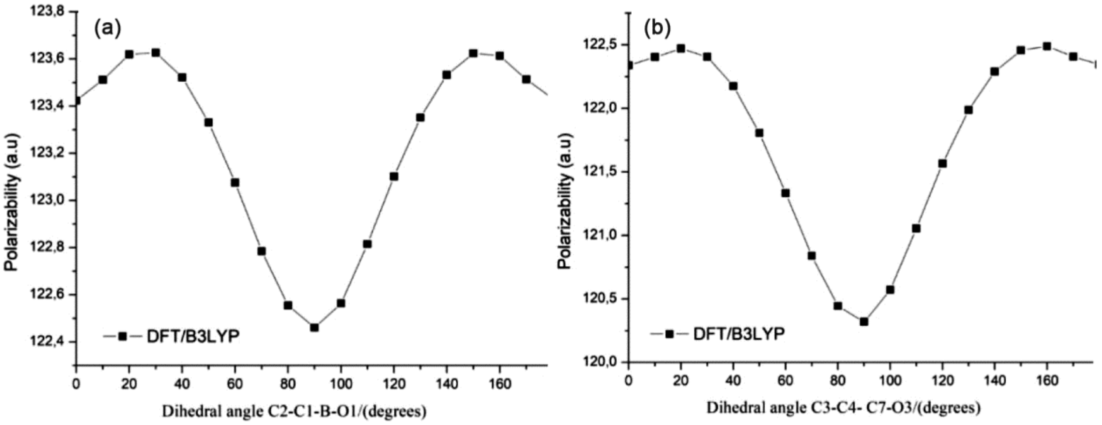

Fig. 6 — Linear polarizability (α) of conformer ct (a) C2-C1-B-O1 and (b) C3-C4-C7-O3 dihedral angles at 6-311++G(d,p).

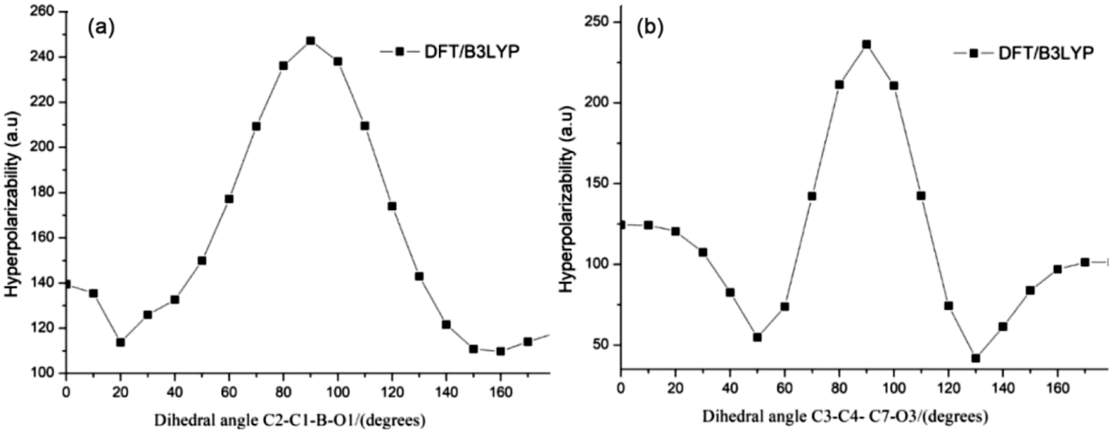

Fig. 7 — Hyperpolarizability (α) of conformer ct (a) C2-C1-B-O1 and (b) C3-C4-C7-O3 dihedral angles at 6-311++G(d,p).

angles, it was shown that the polarizabilities were following inverse relationship the energy gaps. The calculated results showed that behavior of hyperpolarizability values of conformer ct as a function of dihedral angles have almost the same tendency. It means that these values are symmetric with the orthogonal conformation (90°) of conformer ct for both dihedral angles.

Vibrational Spectral Analysis

4-(methoxycarbonyl)-phenylboronic acid molecule consist of 22 atoms, so it has 60 (3N-6) normal vibrational modes. Vibrational spectral assignments were performed at the B3LYP level with the triplet split valence basis set 6-311++G(d,p). A detailed interpretation of the vibrational spectral of title molecule was done based on the calculated potential energy distribution (PED) with vibrational energy distribution program (veda4f). Since theoretical and experimental vibration frequencies studies of title molecule are not available, calculated vibration frequencies have compared with similar molecule[45-48]. The results of the theoretical and spectroscopic[45] studies are given Table 4.

Table 4 — Vibration frequencies (cm^{-1}) of 4-(methoxycarbonyl)-phenylboronic acid molecule

Mode	Experimental[b]		B3LYP/6-311++G(d,p)		Assignments
	IR	Raman	Scaled Freq.	Unscaled.	
1	3496		3710.164	3884.9889	ν OH(100)
2	3343		3673.359	3846.4489	ν OH(100)
3		3064	3063.915	3208.2881	ν CH(91)
4			3055.501	3199.4778	ν CH(99)
5		3041	3042.330	3185.686	ν CH (92)
6		3017	3014.347	3156.3842	ν CH (84)
7	3222		2992.988	3134.0184	ν CH (100)
8	3086		2983.173	3123.7416	ν CH(100)
9	2990	2930	2913.602	3050.8922	ν CH(93)
10			1725.786	1766.4138	ν OC (86)
11	1592	1596	1611.968	1649.9161	ν CC(53), δ HCC(20)
12	1547	1549	1559.379	1596.0894	ν CC(64), δ HCC(11)
13			1503.272	1538.6609	δ HCC(58), δ CCC(29)
14			1463.255	1497.7023	δ HCH(76), β HCOC(11)
15			1448.593	1482.695	HCH(75), HCOC(11)
16	1420	1427	1436.662	1470.4833	δ HCH(77)
17			1396.882	1429.7662	ν CC(24), ν OB(12), δ HCC(29)
18			1353.804	1385.6747	CC(15), ν OB(50), HCC(12), δ CCC(12)
19			1334.222	1365.6319	ν OB(33), ν CB(25), δ HOB(13)
20	1300	1311	1309.156	1339.975	ν CC(18) , δ HCC(68)
21			1281.584	1311.7545	ν CC(59), ν OB(10), HCC(16)
22	1260	1264	1258.269	1287.8906	ν CC(30), ν OC(21), δ OCO(10)
23			1184.107	1211.9827	δ HCH(25), β HCOC(27)
24			1181.310	1209.1196	ν CC(19), δ HCC(73)
25			1143.493	1170.4123	δ HCH(26), HCOC(51)
26			1110.056	1136.1886	ν OC(11), δ HCC(30), δ CCC(20)
27			1105.420	1131.4431	δ HCC(34)
28			1089.037	1114.6744	ν CC(28), δ HOB(13)
29			1014.435	1038.316	δ HCC(13), δ CCC(47)
30	995		998.345	1021.8478	ν OB(15), δ HOB(64)
31			986.969	1010.2036	β HCCC(84)
32			963.939	986.632	β HCCC(71), β CCCC(16)
33			962.230	984.8822	ν CC(12), ν OC(58)
34			955.771	978.2717	ν OB(25), δ HOB(57)
35			860.756	881.0194	β HCCC(58), β CCCC(29), β OCOC(11)
36			837.055	856.7603	β HCCC(82)
37			818.939	838.218	ν CC(14), ν OC(22), δ OCO(18)
38			774.677	792.9141	β HCCC(13), β CCCC(16), β OCOC(30)
39			730.248	747.4394	ν CB(12), δ OCO(17), δ CCC(29)

(*Contd*.)

Table 4 — Vibration frequencies (cm^{-1}) of 4-(methoxycarbonyl)-phenylboronic acid molecule (*Contd.*)

Mode	Experimental^{b}		B3LYP/6-311++G(d,p)		Assignments
	IR	Raman	Scaled Freq.	Unscaled.	
40			703.847	720.4163	β HCCC(26), β CCCC(13), β OCOC(32)
41			641.764	656.8723	C β CCC(25), β OCOB (56)
41			633.708	648.6259	δ CCC(68)
43			563.683	576.9525	ν CC(10), ν CB(18), δ OBO(21)
44			551.883	564.8751	β HOBC (66)
45			482.183	493.5339	δ OCC(32), δ CCC(15)
46			457.618	468.3906	β HOBC (72)
47			435.758	446.0164	β CCCC(19), β HOBC (17)
48			417.954	427.7932	δ OBC(33), δ BCC(10), δ OBO(15)
48			398.141	407.5139	δ OCC(13), δ OBO(25), δ OBC(16)
50			387.748	396.8758	β CCCC(65)
51			314.755	322.1649	δ COC(52), δ OCO(18), δ CCC(22)
52			252.523	258.4677	ν CC(14), ν CB(19), δ OBO(16)
53			239.912	245.5602	β BCCC(25), β COCC18), β CCCC(23)
54			185.970	190.3477	δ COC(10), δ BCC(27), δ OCC(24), δ CCC(12), δ OBC(21)
55			148.314	151.8054	β COCC(36), β HCOC(14), β BCCC(14)
56			123.715	126.6274	β COCC(30), β HCOC(47)
57			106.115	108.6129	δ BCC(33), δ OCC(15), δ OBC(10), δ BCC(33)
58			62.356	63.8237	β CCCC(43), β OCCC(20), β BCCC(19)
59			49.236	50.3947	β OCCC(71)
60			18.063	18.4885	β OBCC(91)

ν = stretching vibration, δ = bending vibration, β = torsion vibration
^{b}Values taken from Ref ^{36}

Conclusions

The molecular structures, vibrational frequencies, ^{1}H and ^{13}C NMR chemicals shifts, HOMO and LUMO analyses, energy gap, dipole moment, linear polarizability and the first hyperpolarizability values of the of 4-(methoxycarbonyl)-phenylboronic acid molecule have been calculated by using DFT/B3LYP and HF methods. The cis-trans and trans-cis conformers of 4-(methoxycarbonyl)-phenylboronic acid possess an energy difference of 0.126 kcal/mol with B3LYP/6-311++G(d,p) and 0.138 kcal/mol with HF/6-311++G(d,p), respectively. In the change of the energy gap and polarizability depending on dihedral angles, it was found that the polarizabilities were follow reverse relationship the energy gaps. The calculated difference between HOMOs and LUMOs energy gaps of conformer ct and tc are found to be 5.368 and 5.384 eV with B3LYP using 6-311++G(d,p), respectively. Comparison of the calculated and experimental bond lengths, and bond and dihedral angles values in literature indicated that the structural parameters (bond lengths, bond and dihedral angles) obtained theoretically are in a very good agreement with the experimental data in the literature.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(10)1504-1512_SupplData.pdf.

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