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Theoretical Studies of the Molecular Structure, Conformational and Nonlinear Optical Properties of (2-Benzyloxy-Pyrimidin-5-Yl) Boronic Acid

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Abstract: In this study, ab initio Hartree-Fock (HF) and Density Functional Theory (DFT), using Becke-3–Lee–Yang–Parr (B3LYP) hybrid density functional, calculations have been performed to characterize the ground state geometrical energy, the dipole moment (μ), polarizability (α), the hyperpolarizability (β) of (2-benzyloxy-pyrimidin-5-yl) boronic acid molecule. The ^{1}H and ^{13}C NMR chemical shifts were calculated by GIAO approach by using B3LYP/6-311+G (2d, p) and HF/6-31G (d) level of theory. The potential energy surface of title molecule has been investigated as a function dihedral angles (C3-B-O1-H1 and C3-B-O2-H2). Also, using the calculated the highest occupied molecular orbital energies (E_{HOMO}) and the lowest unoccupied molecular orbital energies (E_{LUMO}), electronic properties of the studied molecules such as energy gap ΔEg (E_{LUMO}-E_{HOMO}), chemical potential μ, electrophilic index ω, ionization potential IP, electron affinity EA, electronegativity χ, molecular softness S, molecular hardness η were obtained. The dipole moment title molecule are calculated at 1.20 Debye at DFT/B3LYP/6-311++G (d, p) and 1.58 Debye at HF/6-311++G (d, p), respectively. Structural parameters of title molecules compared with the experimental data in the literature. All computational studies have been performed with the Gaussian 09W program.

Keywords: (2-benzyloxy-pyrimidin-5-yl) boronic acid molecule, Density functional theory, Hyperpolarizability polarizability

Introduction

Boronic acids (Lulinski et al. 2007; Maly et al. 2006) have recently attracted a wide range of researches due to their applications in organic synthesis biology and even lithium-ion batteries (Wang, et al., 2008; Bebeda, et al., 2015).The structural parameters of phenylboronic acid were investigated experimentally (Rettig and Trotte ,1977). Heterocyclic boronic acid have found application as Suzuki-Miyaura cross-coupling partners. However, pyrimidylboronic acids have been largely neglected, although some derivatives were synthesized (Clapham et al., 2007; Durka et al., 2012; Liao et al., 1964; Saygili et al., 2004). Crystal structure of (2-benzyloxy-pyrimidin-5-yl) boronic acid molecule were determined experimentally using X-ray structure analysis and spectroscopic methods (Durka et al., (20014). In this work, molecular structure, dipole moment, relative energies, rotational barriers, polarizability, first static hyper polarizability, potential energy scan, the electronic structure and HOMO-LUMO energies of above-mentioned molecule have been studied. ^{1}H NMR and ^{13}C NMR chemical shifts calculations have been performed. The molecular structure using numbering scheme of the (2-benzyloxy-pyrimidin-5-yl) boronic acid molecule is given in Figure 1.

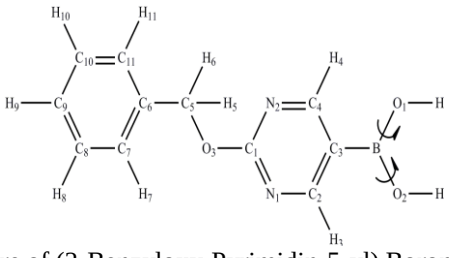

Figure 1. Molecular structure of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid numbering scheme

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Method

Theoretical calculations on the isolated (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule were performed by the aid of Gaussian 09W program package and Gauss view 5.0 molecular visualization programs (Frisch et al., 2010; Dennington et al., 2009) in the gas phase. The geometric parameters of 3-bromo-4-(2-pyridyl) thiophene molecule in the equilibrium state were optimized at HF (Moller et al., 1934) and DFT with Becke's three parameter hybrid functional (B3) (Becke et al., 1988) and combined with gradient corrected correlation functional of Lee–Yang–Parr (LYP) (Lee et al., 1988; Becke, 1993) and employing 6-311++G (d,p) basis set (Francl et al., 1982; Rassolov et al., 2001). After optimization, at all optimized structures of the title compounds obtained B3LYP/6-311++G (d,p) and HF/6-311++G (d,p) level of theory, dipole moment (μ), polarizability (α), hyperpolarizability (β) based on finite field approach and energy differences of ELUMO –EHOMO were calculated in the same as level of theory. The ^{1}H and ^{13}C NMR chemical shifts were calculated by GIAO approach by using B3LYP/6-311+G (2d, p) and HF/6-31G (d) level of theory (McLean et al., 1980; Krishnan et al., 1980).

Results and Discussion

The potential energy surface of (2-Benzyloxy-Pyrimidin-5-Yl) Boronic Acid molecule has been investigated as a function dihedral angles (C3-B-O1-H1 and C3-B-O2-H2). The optimized geometry and Molecular electrostatic potential (MEP) surface values of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule obtained B3LYP/6-311++G (d. p) level are presented Figure 2 (a) and (b)

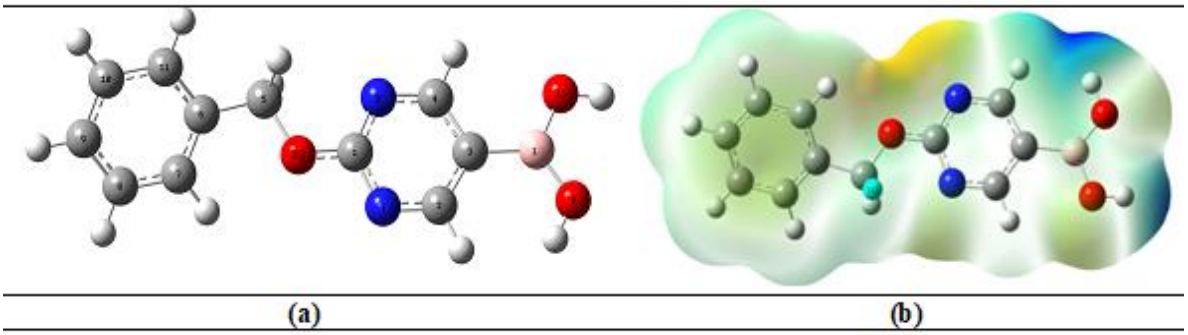

Figure 2. (a)The optimized geometry, (b) Molecular electrostatic (MEP) potential surface (PES) of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule

Potential Energy surface (PES) and electrostatic potential curves of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule obtained B3LYP/6-311++G (d. p) level are presented Figure 3 (a) and (b)

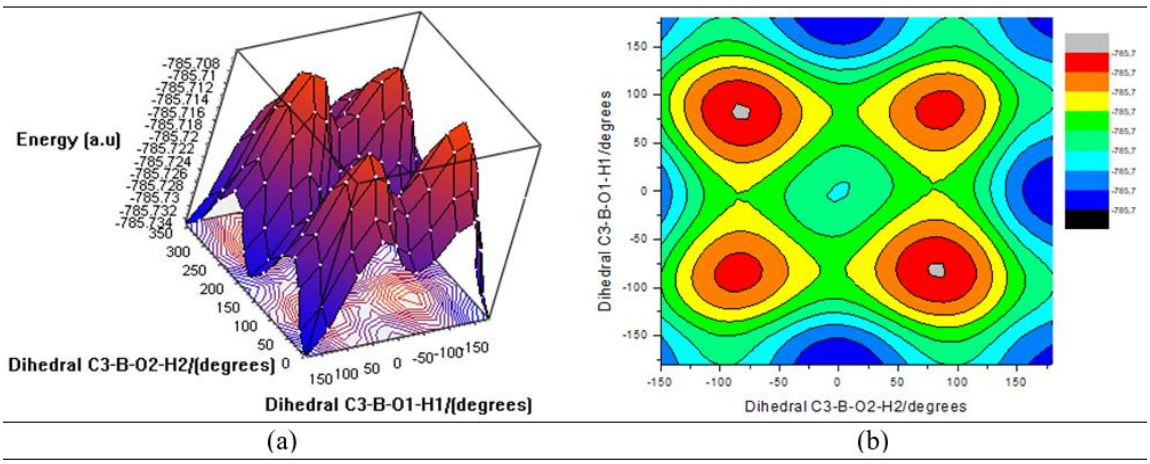

Figure 3. (a) Potential Energy surface (PES) (b) electrostatic potential curves of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule obtained B3LYP/6-311++G (d. p) level

The calculated values of the electronic, dipole moment, polarizability, hyperpolarizability, HOMO, LUMO energy and energy gap (ΔEg) at the ground-state equilibrium geometry of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid are listed in Table 1. As seen from Table 1, dipole moment values of obtained B3LYP/6-311++G (d. p) level is lower than that of HF/6-311++G (d. p) level.

Table 1. The electronic, HOMO, LUMO energy, dipole moment, polarizability, hyperpolarizability, and energy gap (ΔEg) of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule

B3LYP/6-311++G(d. p)						
Electronic Energy (a.u)	μ (Debye	α (a.u)	β(a.u)	EHOMO (a.u)	ELUMO (a.u)	ΔEg (eV)
-786.160372266	1.20	169.18	652.41	-0.254716	-0.058358	5.34
HF/6-311++G(d,p)						
-781.461269575	1.58	150.98	247,21	-0.330525	0.036124	9.98

The X-ray crystal structures for studied molecule is available in the literature and (Durka et al., (20014) and the calculated parameter studied molecule of both at the B3LYP/6-311++G (d, p) and HF/6-311++G (d, p) methods in the ground state are tabulated in the Table 2.

Table 2. Selected structural parameters of (2-Benzyloxy-Pyrimidin-5-Yl) Boronic Acid molecule

	DFT	**HF**	Exp.	HF	Exp[a].	DFT	HF
Atoms		Bond lenght/Å		Atoms		Bond angle/(˚)	
C1-N1	1.3387	1.3227	1.3375 (15)	O3-C1-N2	119.2	119.1	118.63 (10)
C1-N2	1.3352	1.3165	1.3336 (15)	N1-C1-N2	126.8	126.5	127.51 (11)
C2-C3	1.4034	1.395	1.3957 (17)	C3-C2-N1	124.4	124.4	
C2-N1	1.3268	1.3102	1.3407 (16)	C2-C3-C4	113.8	113.2	114.36 (11)
C3-C4	1.3999	1.3894	1.3898 (16)	C2-C3-B	124.7	125.3	125.58 (11)
C3-B	1.5608	1.5641	1.5775 (19)	C4-C3-B	121.5	121.4	120.05 (10)
C4-N2	1.3346	1.32	1.3415 (16)	C3-C4-N2	123.7	123.7	
C5-C6	1.5074	1.5099	1.5028 (18)	C6-C5-O3	108.7	109.1	110.46 (10)
C5-O3	1.4423	1.4137	1.4412 (14)	C7-C6-C11	119.1	119.1	119.14 (11)
C6-C7	1.3979	1.3867	1.3898 (17)	C6-C7-C8	120.3	120.2	119.86 (11)
C6-C11	1.3973	1.3901	1.3972 (16)	C8-C9-C10	119.6	119.5	119.09 (12)
C7-C8	1.393	1.3874	1.3912 (18)	C1-O3-C5	118.3	119.8	
C8-C9	1.3945	1.3837	1.3870 (18)	B-O1-H	112.6	113.6	121.3 (12)
C9-C10	1.3933	1.3864	1.3933 (19)	B-O2-H	115.8	117.2	117.4 (12)
C10-C11	1.3939	1.3836	1.3856 (18)	C3-B-O1	117.9	117.9	123.67 (11)
O1-B	1.3664	1.3542	1.3475 (16)	C3-B-O2	124.6	124.5	116.12 (11)
O2-B	1.3728	1.3601	1.3602 (16)	O3-C1-N1	114.0	114.3	113.86 (10)
			Dihedral angle/(˚)				
		DFT	HF	Exp.		-	-
N1-C1-O3-C5		-178.2	-178.5	-175.72 (10)		-	-
N2-C1-O3-C5		1.9	1.6	4.30 (16)		-	-
C2-C3-B-O1		-179.7	179.8	-175.21 (12)		-	-
C2-C3-B-O2		0.3	-0.2	3.78 (17)		-	-
C4-C3-B-O1		0.4	-0.2	3.3 (2)		-	-
C4-C3-B-O2		-179.6	179.8	-177.72 (12)		-	-
O3-C5-C6-C7		-35.2	-19.0	-8.77 (17)		-	-
O3-C5-C6-C11		147.5	162.9	173.27 (10)		-	-
N1-C1-O3-C5		-178.2	-178.5	-175.72 (10)		-	

([a] ref Durka et al. 2014)

The pictures of HOMO and LUMO obtained at the B3LYP/6-311++G (d, p) of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule at the B3LYP/6-311++G (d, p) is given in Figure 4.

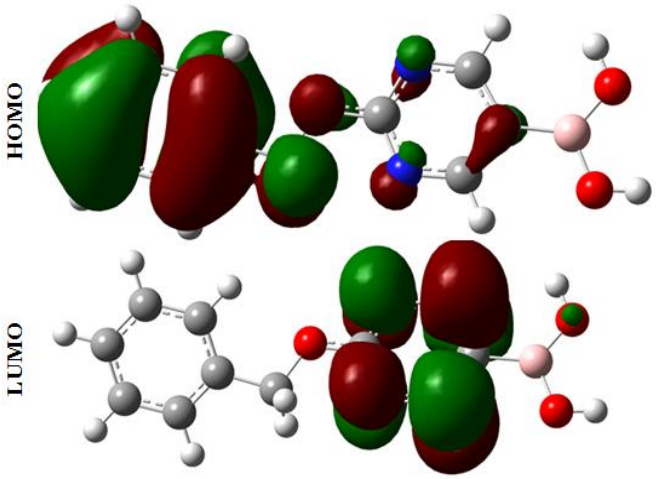

Figure 4. The pictures of HOMO and LUMO of (2-Benzyloxy-Pyrimidin-5-yl Boronic Acid molecule

^{1}H and ^{13}C NMR values of of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule has been calculated and given in Tables 3.

Table 3. NMR chemical shifts of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule

B3LYP/6-311++(2d,p)				HF/6-31(d)			
Atoms	Gas	Atoms	Gas	Atoms	Gas	Atom	Gas
C1	174.	H4	9.38	C4	169.13	H4	9.33
C4	172.	H3	8.82	C2	164.98	H3	8.60
C2	168.	H7	8.12	C1	159.71	H7	7.97
C6	143.	H8	7.65	C6	133.28	H8	7.42
C8	133.	H10	7.61	C8	125.64	H10	7.32
C10	132.	H9	7.54	C10	124.59	H9	7.22
C9	132.	H11	7.52	C9	123.07	H11	7.12
C7	131.	H5	5.73	C7	122.69	H5	4.93
C11	130.	H6	5.26	C11	121.34	H6	4.90
C3	118.	H2	4.19	C3	103.44	H2	3.44
C5	74.3	H1	3.50	C5	59.21	H1	3.02

Conclusion

The ground state geometrical parameter, energy, dipole moment, polarizability, hyperpolarizability, $E_{HOMO,}$ $E_{LUMO,}$ ΔEg of (2-Benzyloxy-Pyrimidin-5-yl) Boronic Acid molecule are examined both HF/6-311++G (d,p) and B3LYP/6-311++G(d,p) level of the theory. The 1H and 13C NMR chemical shifts were calculated by GIAO approach by using B3LYP/6-311+G (2d, p) and HF/6-31G (d) level of theory. The potential energy surface of title molecule has been investigated as a function dihedral angles (C3-B-O1-H1 and C3-B-O2-H2). The dipole moment title molecule are calculated at 1.20 Debye at DFT/B3LYP/6-311++G (d, p) and 1.58 Debye at HF/6-311++G (d, p), respectively. Structural parameters of title molecules compared with the experimental data in the literature. The structural parameters of title molecules indicates that results of HF/6-311++G (d, p), and B3LYP/6-311++G (d,p) level of the theory are in a good agreement with experimental data for (2-Benzyloxy-Pyrimidin-5-yl) Boronic acid molecule.

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