

# The Quantum Mechanical Computations of the Conformational, Structural, Electronic and Spectroscopic Properties of 3-Cyanophenylboronic Acid

Guventurk Ugurlu\*

Department of Physics, Kafkas University, 36100 Kars, Turkey

## ABSTRACT

In the present study, Conformational analysis of 3-cyanophenylboronic Acid(3-CyBA) molecule have been carried by calculating Potential Energy Surface (PES) as a function of two dihedral angles, C1-B-O1-H and C1-B-O2-H, using DFT/B3LYP/6-31G (d) level of theory. As a result of PES, molecular conformers corresponding to low energy of title molecule, anti-syn, syn-anti, syn-syn, anti-anti, respectively, have been determined according to the orientations of the hydroxyl groups attached to the boron atom. The geometries of anti-syn, syn-anti, syn-syn, anti-anti, conformers of studied molecule were fully optimized at the Hartree-Fock (HF) and DFT/B3LYP levels of the theory with 6-311++G (d,p) basis set and compared with its crystal structure in the literature. The vibrational frequencies, infrared (FT-IR) intensities Raman (FT-Raman) scattering activities of all the conformers of the title molecule were calculated both methods and vibrational assignments were performed by means of Potential Energy Distribution (PED). Also, frontier molecular orbitals, the linear and nonlinear optics parameters, such as the polarizability ( $\alpha$ ) ground state dipole moment ( $\mu$ ) and the first-order hyperpolarizability ( $\beta$ ) of 3-CyBA molecule, were calculated the same methods. The anti-syn conformer is found to be more stable than the syn-anti, syn-syn and anti-anti-conformers by 0.227, 1.078 and 4.577 kcal/mol in HF/6-311++G(d,p) and 0.248, 1.465 and 3.855 kcal/mol in DFT/B3LYP/6-311++G(d,p) level of theory, respectively. UV-visible absorption spectra such as excitation energies, absorption wavelengths ( $\lambda$ ) and oscillator power (f) and stimulation contributions of all examined conformers were examined using TD-DFT/B3LYP and TD-HF methods and transitions were determined.

**Keywords:** Conformational analysis; 3-cyanophenylboronic acid; Polarizability; Hyperpolarizability; Vibrational frequencies; UV-visible

## INTRODUCTION

Boronic acids show soft Lewis acids due to the empty orbital of the boron atom. This property makes boronic acids receptor, organic solar cells, protecting group and biologically attractive [1-4]. Boronic acids have many use areas in medicine, chemistry, biology and materials science. Boronic acids do not cause any environmental damage as they decompose to ortho boric acid and do not harm human health since they are non-toxic. In the systems that using liquid membrane system and allowing fructose to separate from other sugar mixtures have been tested many new many new anions, cations, borates and boronic acid derivatives that can form complexes with sugars [5]. Boronic acids have a special place in the design of chemical sensors used to detect the glucose molecule [6,7]. Boronic acid-containing polymers are also used in many biomedical applications such as HIV treatment to obesity, diabetes and cancer treatment [8]. In the literature,

boronic acid and its derivatives have a special place in the definition and separation of carbohydrates [9]. Boronic acids play an active role in the identification of many biomolecules such as enzymes, proteins and antibodies, especially glucose for analytical and medical purposes and in the detection of diseases, as they can form stable and reversible diol complexes [10]. Boronic acids are molecules that can selectively bind carbohydrates using molecular suppression techniques [11]. Also, due to ability baryonic acid to form hydrogen bonding in the molecular complexes and coordination in metal complexes, these compounds continue to be of increasing interest and research. It has been known since 1953 that phenylboronic acids can be condensed with polyols and form boranate esters [12,13].

Theoretical chemistry provides convenience to those dealing with chemistry. With these programs, molecules can be observed from different angles by rotating them on the computer screen, their isomers and geometric structures can be understood, and their

**Correspondence to:** Guventurk Ugurlu, Department of Physics, Kafkas University, 36100 Kars, Turkey, E-mail: gugurlu@kafkas.edu.tr

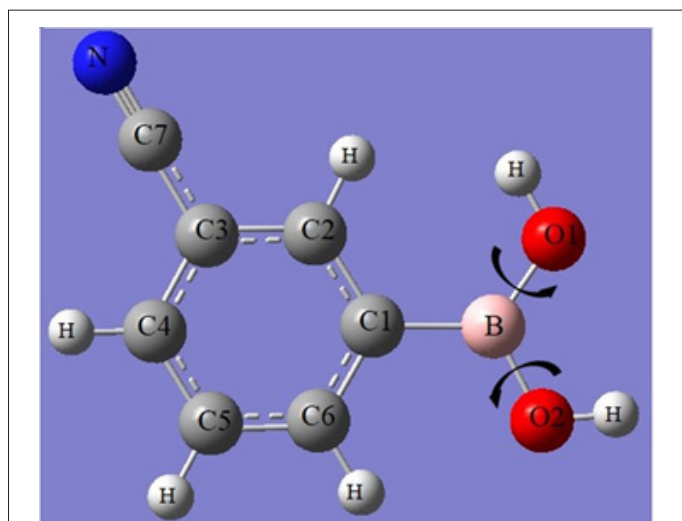
**Received:** 30-May-2023, Manuscript No. JCCLM-23-24596; **Editor assigned:** 01-Jun-2023, Pre QC No. JCCLM-23-24596 (PQ); **Reviewed:** 15-Jun-2023, QC No. JCCLM-23-24596; **Revised:** 22-Jun-2023, Manuscript No. JCCLM-23-24596 (R); **Published:** 29-Jun-2023, DOI: 10.35248/JCCLM.23.6.268

**Citation:** Ugurlu G (2023) The Quantum Mechanical Computations of the Conformational, Structural, Electronic and Spectroscopic Properties of 3-Cyanophenylboronic Acid. J Clin Chem Lab Med.6:268

**Copyright:** © 2023 Ugurlu G. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

energies can be calculated. Ultraviolet (UV), Infrared Radiation (IR), Nuclear Magnetic Resonance (NMR) spectra can be drawn and even Molecular Orbital (MO) diagrams can be accessed [14-18]. In addition to experimental methods, computational chemistry methods are also used in the determination of corrosion inhibitors. The activity of an inhibitor, several quantum chemical parameters, can be calculated theoretically without the need for experimentation. The quantum chemical parameters generally used in theoretical studies on corrosion are atomic charges and molecular orbital energies [19-23].

The several studies have been carried out experimentally and computationally on the substituted phenylboronic acid derivatives. The studies about crystal and molecular structure of phenylboronic acid and its ortho-, meta-, para-halogen or alkoxy groups and 3-amino-, and 3-cyano derivatives [24-30]. The investigation on supramolecular synthesis of phenylboronic derivatives were studied [17,21-23]. The study on conformational analysis of phenylboronic derivatives was reported. In this study, 3-cyanophenylboronic acid molecule, having the B(OH)<sub>2</sub> and C≡N groups is modeled theoretical and molecular properties such as structural and electronic properties have been investigated using Hartree-Fock (HF) and Density Functional Theory (DFT) with B3LYP (Becke 3 Parameter Lee-Yang-Parr) model using the 6-311++(d,p) basis set in gas phase [14,31,32]. The search of literature on 3-CyBA revealed that its crystal and molecular structure of reported, but conformational analysis, electronic, linear and nonlinear properties of this molecule has not been calculated experimentally and theoretically. The potential energy surface of studied compound has been carried out by calculating 3D conformation analysis. Also, electron affinity A and ionization energy IP were defined as A=-ELUMO and IP=-EHOMO and by using these values have obtained global chemical reactivity like chemical hardness ( $\eta$ ), softness ( $\sigma$ ), electronegativity ( $\chi$ ), electronic chemical potential ( $\mu$ ), and electrophilicity Index ( $\omega$ ). The molecular structure using numbering scheme of 3-CyBA is given in Figure 1.



**Figure 1:** The theoretical geometric structure of 3-cyanophenylboronic acid.

## MATERIALS AND METHODS

### Computational details

Firstly, quantum mechanical methods on the 3-CyBA molecule

was performed by the aid of Gaussian 09W program package and Gauss view 5.0 molecular visualization programs in the gas phase. The conformational analysis of 3-CyBA molecule has been carried by calculating potential energy surface as a function of two dihedral angles, C1-B-O1-H and C1-B-O2-H, using DF/B3LYP/6-31G level of theory. As a result of PES, molecular conformers corresponding to low energy of title molecule, anti-syn, syn-anti, syn-syn, anti-anti, respectively, have been determined according to the orientations of the hydroxyl groups attached to the boron atom [34]. The geometries of anti-syn, syn-anti, syn-syn, anti-anti, conformers of studied molecule were fully optimized at the Hartree-Fock (HF) and Density Functional Theory (DFT) with B3LYP with 6-311++G(d,p) basis set. After optimization, structural parameters, vibrational frequency, the electronic energy, the dipole moment ( $\mu$ ), the Highest Occupied Molecular Orbital (HOMO) energy, the Lowest Unoccupied Molecular Orbital (LUMO) energy, the polarizability ( $\alpha$ ) and hyperpolarizability ( $\beta$ ) of all the conformer of studied molecule were calculated at HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) level of theory in gas phase. The obtained vibrational wave numbers were scaled with appropriate scale factors and the assigning of these vibrational wavenumbers was made according to the potential energy distribution using the VEDA 4f program.

## RESULTS AND DISCUSSION

### Conformational analysis

Conformation analysis of title molecule has been carried out by calculating three Dimensional (3D) potential energies of studied molecule. The Potential Energy Surface (PES) scan has been carried out as a function of two dihedral angles, C1-B-O1-H and C1-B-O2-H, varied between 0 and 360°C with increments of 10°C at B3LYP/6-31G (d) level of theory. By using data obtained from PES scan calculation, PES and potential energy contour format of 3-CyBA molecule have been plotted and are given Figures 2a and 2b. As seen in the Figure 2a, the potential energy changes of the different spatial orientations of the hydroxyl groups attached to the boron atom have been shown on the potential energy surface and potential energy contour format. It is seen that there is more than one conformation with maximum and minimum energy on the PES and potential energy contour. The points corresponding to the maximum and minimum energy conformations are numbered 1 to 13. The number 1 conformation has the lowest energy and corresponds to the anti-syn conformer. Conformations 2, 3, 4 and 5 correspond to the syn-anti conformer. Conformations 6 and 7 correspond to the syn-syn conformer. Conformations 8 and 9 correspond to the anti-anti conformer. The conformations 11, 12, 13 and 14 correspond to the maximum energy conformations. As a result of conformational analysis, molecular conformers corresponding to low energy of title molecule, anti-syn, four syn-anti, two syn-syn and two anti-anti have been determined according to the orientations of the hydroxyl groups attached to the boron atom, respectively. According to results of conformational analysis, for conformers with low energy such as anti-syn, syn-anti, syn-syn, anti-anti, both hydrogen atoms bonded oxygen are almost in the O1-B-O2 plane but in the conformation 11, 12, 13 and 14 corresponding to the maximum energy, these hydrogens are out of O1-B-O2 plane.

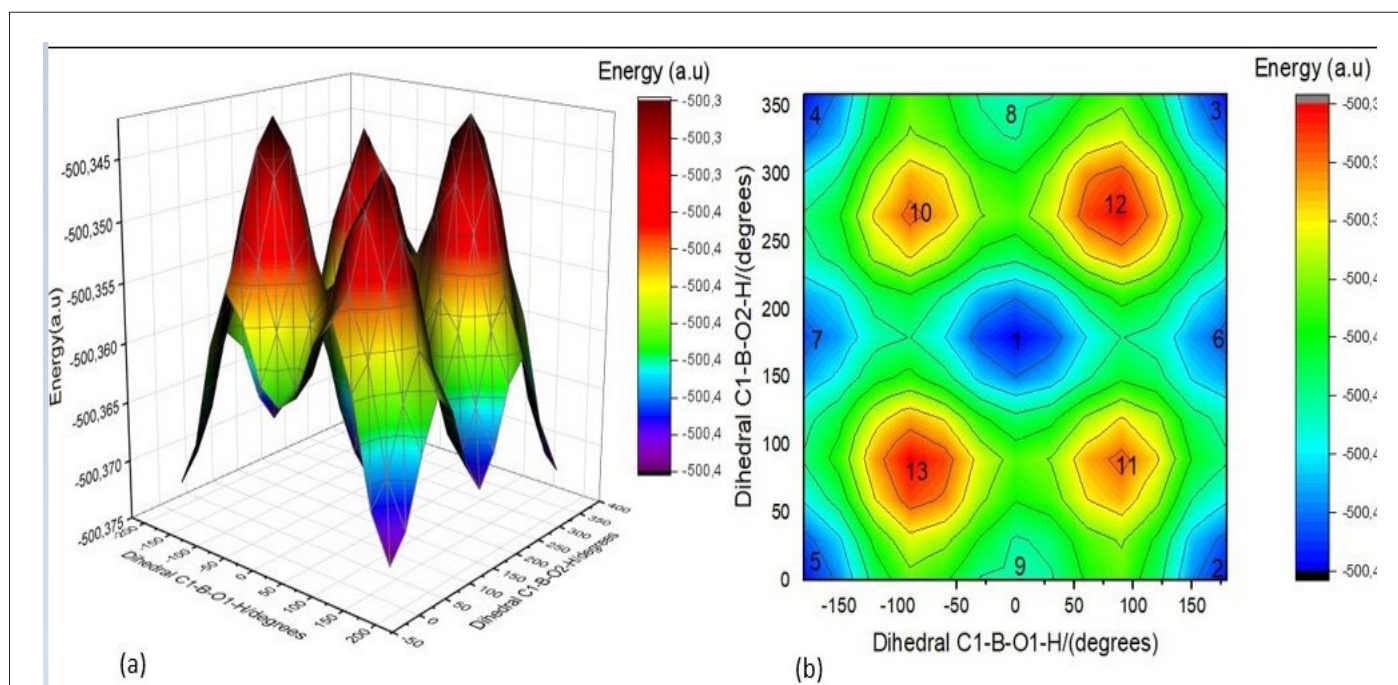
## Geometrical structure

3-CyBA molecule, C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>BN, is substituted benzene with two different functional groups a nitrile (–C≡N) and boronic acid (–B(OH)<sub>2</sub>). The all metastable conformations, an anti-syn, four syn-anti, two syn-syn, two anti-anti, on the PES of studied molecule were optimized at the HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) levels of the theory. It has been observed that when more than one metastable conformation with the same name is optimized, these conformations convert to a stable conformer with the same name and the stable conformers determined as a result of optimization, anti-syn, syn-anti, syn-syn and anti-anti is given in Figure 2b. The stability of the optimized structures of all the conformers has been affirmed by vibration modes calculation, which gave positive values for entire vibration modes (Figure 3).

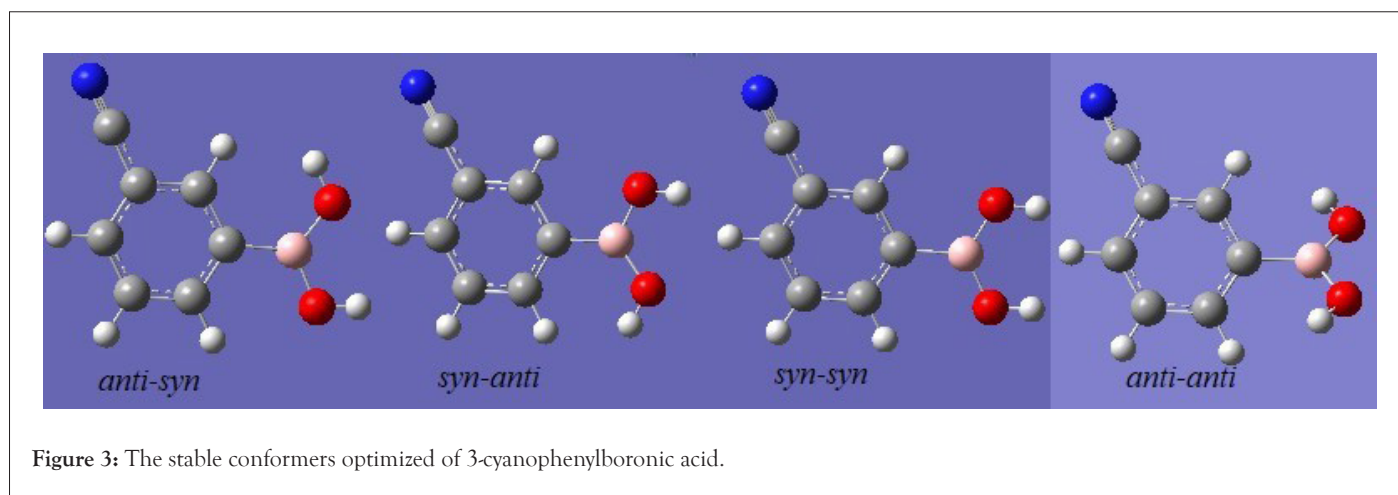
Afterward, structure parameter of stable conformers as an initial geometry utilized to compute polarizability, hyperpolarizability, HOMO, LUMO energies calculated HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) levels are given Table 1. The energy

band gap was obtained using HOMO and LUMO energies ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ , where  $E_{\text{LUMO}}$  and  $E_{\text{HOMO}}$  are HOMO and LUMO energies). While the band gap values of the three conformers calculated DFT/B3LYP/6-311++G(d,p) levels of the theory have the same value (5.66 eV), that of the anti-anti is close to this value. This result shows that the energy of the molecule is not affected by conformers. The calculated energy band gap on phenylboronic acid derivatives in the literature have been determined as 5.39 eV for 4-(methoxycarbonyl)-phenylboronic acid and 4.97-5.96 eV.

The importance of polarizability and initial hyperpolarizability in molecular systems is associated with electronic communication between donor and acceptor groups due to intramolecular charge transfer [35]. The molecular electronic dipole moment, molecular polarizability, polarizability anisotropy and molecular initial hyperpolarizability of conformers (anti-syn, syn-anti, syn-syn and anti-anti) were calculated using the same methods and the results are given in Table 1.



**Figure 2:** Potential energy surface scan of 3-cyanophenylboronic acid molecule as a function of its two flexible torsional angles in (a) a surface format and (b) a contour format.



**Figure 3:** The stable conformers optimized of 3-cyanophenylboronic acid.

**Table 1:** HOMO, LUMO energy, dipole moment, polarizability, hyperpolarizability, and energy gap ( $\Delta E$ ) of the compound ( $\Delta E/\text{kcal mol}^{-1}$ ).

B3LYP/6-311++G(d,p)								
	Electronic energy	$\Delta E$	$\mu$	$\alpha$	$\beta$	EHOMO	ELUMO	Eg
	(a.u)	(kcal/mol)	(D)	(a.u)	(a.u)	(a.u)	(a.u)	(eV)
a-s	-500.661669	0	3.55	105.75	52.44	-0.281065	-0.073087	5.66
s-a	-500.661275	0.248	5.69	105.78	60.73	-0.281785	-0.073719	5.66
s-s	-500.659334	1.465	6.5	106.37	125.89	-0.27053	-0.062582	5.66
a-a	-500.655525	3.855	4.07	105.61	63.1	-0.288744	-0.079446	5.7
HF/6-311++G(d,p)								
a-s	-497.687644	0	3.63	95.6	23.59	-0.362239	0.033789	10.78
s-a	-497.687282	0.227	5.94	95.64	46.96	-0.363826	0.028076	10.66
s-s	-497.685925	1.078	6.7	96.07	39.22	-0.353329	0.026112	10.32
a-a	-497.680349	4.577	4.24	95.55	41.7	-0.371474	0.027715	10.86

The optimized structural parameters of these stable conformers along with the experimental parameters in the literature are listed in Table 1 [30]. As can be seen from Table 1, according to results of conformational analysis, for conformers with low energy such as anti-syn, syn-anti, syn-syn, anti-anti, both hydrogen atoms bonded oxygen are almost in the O1-B-O2 plane and anti-syn, syn-anti, syn-syn conformers are planar but anti-anti conformers are not planar that is, conformational preference of dihedral angle of four possible conformers between the boronic acid group and benzene ring have varied between  $0^\circ$  at the both methods and  $-35.61^\circ$ . For anti-syn, syn-anti and syn-syn conformers, this angle has been calculated as  $0^\circ$  but anti-anti-conformer is  $-35.61^\circ$  (B3LYP) and  $-35.05^\circ$  (HF). As can be seen from Table 2, B-C bond lengths are in the range of 1.5651-1581 Å (B3LYP) and 1.570-1.589 Å (HF). For phenylboronic acids with the type and position of the substituents on phenyl ring, these values are 1.562 Å, 1.5747 Å and 1.5675 Å experimentally, 1.572-1586 Å, 1.565-1598 Å and 1.177 Å theoretically [9,24,30,36-38]. In general, B-O bond length in the unsubstituted phenyl boronic acids can change according to orientation of the hydrogen atoms attached the oxygen atoms to phenyl ring. B-O1/2 bond length is in the range of 1.5651-1581 Å (B3LYP) and 1.570-1.589 Å (HF). According to published articles, experimentally B-O1/2 bond length have been reported as 1.3455/1.3661 Å, 1.354/1.369 Å these values have been calculated theoretically as 1.363/1.367, 1.363/1.373 Å (B3LYP) and 1.5324/1.3661 Å (HF) [15].

When evaluated energetically in possible conformers anti-syn conformer is most stable than other conformers. The energy difference value ( $\Delta E = E_i - E_{\text{anti-syn}}$ ,  $i = \text{syn-anti, syn-syn and anti-anti}$ , respectively) between conformers increase in the order anti-syn < syn-anti (up to 0.248) < syn-syn (1.465) < anti-anti (3.855 kcal/mol) for B3LYP/6-311++G(d,p) levels of the theory and in the order anti-syn < syn-anti (up to 0.227) < syn-syn (1.0785) < anti-anti (4.577 kcal/mol) for HF/6-311++G(d,p) method. In other words, anti-syn conformer is approximal up to 0.248 kcal/mol more stable than syn-anti up to 1.465 kcal/mol more stable than syn-syn, up to 3.855 kcal/mol more stable than anti-anti and up to 0.227 kcal/mol more stable than syn-anti up to 1.0785 kcal/mol more stable than syn-syn up to 3.577 kcal/mol more stable than anti-anti, respectively. Also, relative energy shows that anti-syn conformer is the most stable, the remaining syn-anti, syn-syn and anti-anti conformers are in range of 0.248-3.855 kcal/mol (HF) and in range of 0.227-3.577 kcal/mol (B3LYP). For molecule, these values are only in range of 14 kcal/mol [32]. It shows that

the relative energy values obtained in this study are compatible with the values in the literature.

### Molecular electrostatic potential and frontier molecular orbitals

Molecular Electrostatic Potential (MEP) describes information about the net electrostatic impact generated at that point by total charge distribution (electron+proton) of around a molecular system. The Molecular Electrostatic Potential (MEP) surface gives information on the reactive sites. The color scheme is as follows, red demonstrates areas of most electro negative EP, blue demonstrates areas of most positive EP and green demonstrates areas of zero potential. The EP increases in the order red < orange < yellow < green < blue. MEP surfaces are plotted over equilibrium geometries of all the conformers at B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) level of theory. From Figure 4 shows that the MEP contours map of conformers. As can be seen Figure 4, in syn-syn conformer has an electrophilic area (red color) around nitrile group ( $-\text{C}\equiv\text{N}$ ) and a nucleophilic area (blue color) around two hydroxyl groups, anti-anti conformer has an electrophilic area around both nitrile group ( $-\text{C}\equiv\text{N}$ ) and two oxygens atoms in boronic acid and other conformers have an electrophilic domain around both the nitrile group ( $-\text{C}\equiv\text{N}$ ) and the oxygen atom attached to the hydrogen atom in the anti-state, while about the oxygen atom attached to the hydrogen atom in the syn-state compose the nucleophilic site.

Frontier molecular orbitals and their features like energy are important in the physicists and chemists. The HOMO represents electron donor and LUMO represents electron acceptor. The HOMO and LUMO plots of all the conformers are shown in Figure 5. As seen in the Figure 5, the frontier molecular orbital HOMO of all the conformers calculated in both methods have exhibited similar behavior and the charge density have localized nitrile group and phenyl ring. The frontier molecular orbital LUMO of all the conformers calculated in both methods have not exhibited similar behavior but LUMO calculated at B3LYP/6-311++G(d,p) method have not exhibited similar behavior.

### Vibrational analysis

3-CyBA molecule consists of 17 atoms, with 45 normal vibrational modes. The stability of the optimized structures of all the conformers has been affirmed by vibration modes calculation, which gave positive values for entire vibration modes. While three

conformers, syn-ant, syn-syn and anti-anti, of 3-CyBA molecule belong to C1 symmetry, anti-syn a conformer belongs to Cs symmetry. The obtained theoretically vibrational frequencies are generally higher than the corresponding experimental quantities owing to the combination of electron correlation effects and basis sets deficiencies. So, calculated vibrational frequencies were scaled suitable scale factors. For B3LYP/6-311++G(d,p), scaling factors are used as 0.958 for greater and 0.983 smaller than 1800 cm<sup>-1</sup> and for HF/6-311++G(d,p) as 0.906, respectively. The selected wavenumbers data of all the conformer were summarized in Table 3. Additionally, the theoretical IR and Raman spectra are displayed in Figures 6 and 7 respectively. The assignments of vibrational numbers are calculated by employing The VEDA 4f program based on potential energy distribution. OH, CH and CN vibration analyzes of all conformers were performed and characterized. OH, CH and CN vibrations in the functional group region were observed to be compatible with the literature. In particular, when the CN vibration was examined, it was calculated that the CN vibration, which was determined as 2232 cm<sup>-1</sup> [40] in the literature, was in the range of 2232-2235 cm<sup>-1</sup> in the study. It was determined that the vibrations in the fingerprint region were the same in all four conformations examined and it was observed that they were not affected by the conformation. It was concluded that all the values calculated in the study were consistent with the values in the literature.

The selected wavenumbers data of all the conformer were summarized in Table 3. Additionally, the theoretical IR and Raman spectra are displayed in Figures 6-9. The assignments of

vibrational numbers are calculated by employing The VEDA 4f program based on potential energy distribution.

### UV-vis spectral properties

The UV-vis absorption spectra of the 4 conformer of 3-CyanophenylBoronic Acid (3-CyBA) were investigated (Figures 8 and 9). Calculations were made according to TD-HF and TD-DFT/B3LYP methods using optimized structure.

The 4 conformers of 3-CyBA revealed three absorption bands at the theoretically derived electronic spectra (Figures 8 and 9). Absorption bands in the 300-200 nm range represent  $\pi \rightarrow \pi^*$  electronic transitions in the benzene ring [41]. As a result, according to these units, All conformers of 3-CyBA have a longer UV-vis absorption wavelength.  $\pi \rightarrow \pi^*$  transitions are observed in the range of 254.83-202.93 nm originating from the benzene ring in its structure in its 4 conformer. GaussSum 3.0 software was used to determine the stimulation contributions to the UV-visible transitions (Table 4) [42]. For TD-DFT and TD-HF calculations, the primary transition contribution from HOMO-1 to LUMO (56-40%) was calculated as  $\pi \rightarrow \pi^*$  transitions at 255.11-252.02/221.30-220.89 nm, the primary transition contribution from HOMO to LUMO (68-50%) was calculated as  $\pi \rightarrow \pi^*$  transitions at 229.73-229.24/177.81-176.07 nm and the primary transition contribution from HOMO-2 to LUMO (98-91%) was identified as  $\pi \rightarrow \pi^*$  transitions at 214.85-202.93/370.37 nm for anti-syn, syn-anti, syn-syn and anti-anti conformers. Table 4 displays the predicted excitation energies, absorption wavelengths ( $\lambda$ ) and oscillator power (f) of the all conformers.

**Table 2:** The selected structural parameter of the stable conformers.

Bond length (Å)									
Atoms	B3LYP/6-311++G(d,p)					HF/6-311++G(d,p)			
	Expa	a-s	s-a	s-s	a-a	a-s	s-a	s-s	a-a
C1-C2	1.3917(17)	1.3987	1.4012	1.3998	1.4005	1.3901	1.3935	1.3915	1.3918
C1-C6	1.3987(18)	1.4056	1.4031	1.4038	1.4052	1.3965	1.3933	1.3941	1.3955
C1-B	1.5747(18)	1.5718	1.5718	1.5651	1.5812	1.5786	1.5787	1.5704	1.5892
C2-C3	1.3948(17)	1.4015	1.4002	1.4008	1.4017	1.389	1.3872	1.3881	1.3888
C3-C4	1.3882(19)	1.4019	1.4029	1.4031	1.4018	1.3886	1.3904	1.3904	1.3887
C3-C7	1.4401(18)	1.4316	1.4324	1.4321	1.432	1.4429	1.4436	1.4433	1.4434
C4-C5	1.3825(19)	1.3905	1.3894	1.3901	1.3899	1.3827	1.3811	1.382	1.3823
C5-C6	1.3834(91)	1.3927	1.3936	1.3935	1.3935	1.3847	1.3861	1.386	1.3852
C7-N	1.1416(18)	1.1557	1.1555	1.1558	1.1555	1.1311	1.1309	1.1313	1.1308
B-O1	1.3661(18)	1.3704	1.3642	1.3708	1.3646	1.3575	1.3512	1.3578	1.3507
B-O2	1.3455(17)	1.3653	1.3712	1.3717	1.3654	1.3522	1.3579	1.3585	1.3514
Bond angle (°)									
C2-C1-C6	117.51(11)	117.78	117.8	118.32	117.62	117.7	117.71	118.24	117.58
C2-C1-B	122.70(11)	122.47	119.36	120.64	121.05	122.74	119.18	120.65	121.09
C6-C1-B	119.79(11)	119.75	122.85	121.05	121.32	119.56	123.1	121.11	121.33
C2-C3-C4	121.02(12)	119.87	120.1	120.03	120.02	121.07	120.81	120.61	121
C2-C3-C7	119.00(21)	119.95	120.1	120.09	119.97	120.28	120.47	120.37	120.43
C4-C3-C7	119.98(11)	120.17	119.8	119.88	120.01	119.75	119.93	119.93	119.76
C1-B-O1	123.75(11)	124.7	117.93	117.93	122.43	119.98	119.6	119.69	119.8
C1-B-O2	117.10(12)	117.79	124.43	117.86	122.18	124.46	117.88	118.19	122.01
O1-B-O2	119.15(12)	117.51	117.64	124.21	115.38	117.84	124.27	118.22	121.78
B-O1-H		115.98	112.87	116.77	114.32	117.7	117.85	123.59	116.22

		112.65	115.67	116.59	114.16	117.37	113.82	117.77	115.81
Dihedral angle (°)									
C2-C1-B-O1	21.3	0	0	0	-35.61	0	0	0	-35.05
C2-C1-B-O2	-159.4	180	-179.98	180	144.54	-180	-180	180	145.03
C6-C1-B-O1	-158.2	180	-180	-180	144.33	-180	-179.98	-180	144.97
C6-C1-B-O2	21.14	0	0.03	0	-35.53	0	0.02	0	-34.94

Note: anti-syn: a-s, syn-anti: s-a, syn-syn: s-s, anti-anti: a-a.

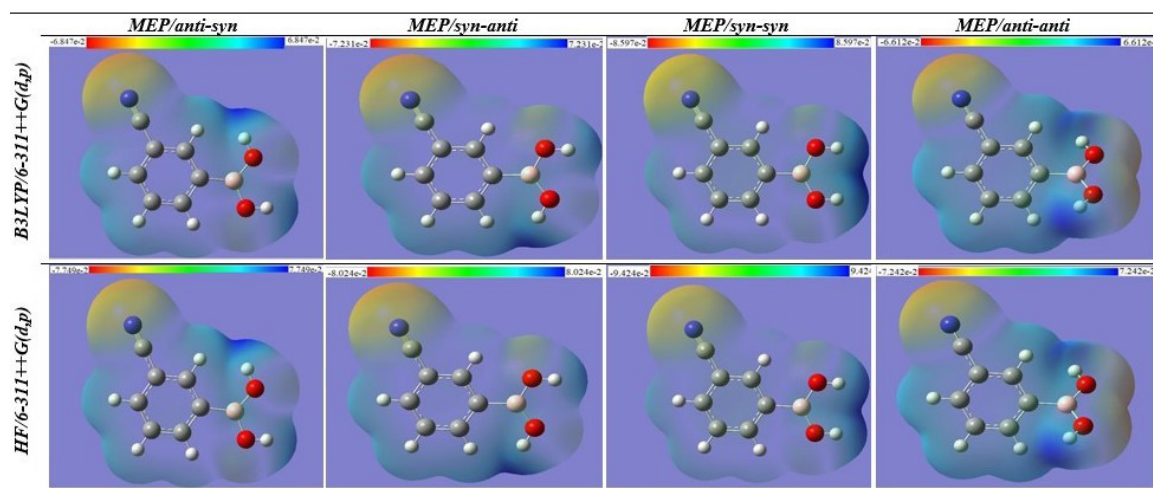


Figure 4: The shapes of molecular electrostatic potential of the stable conformers.

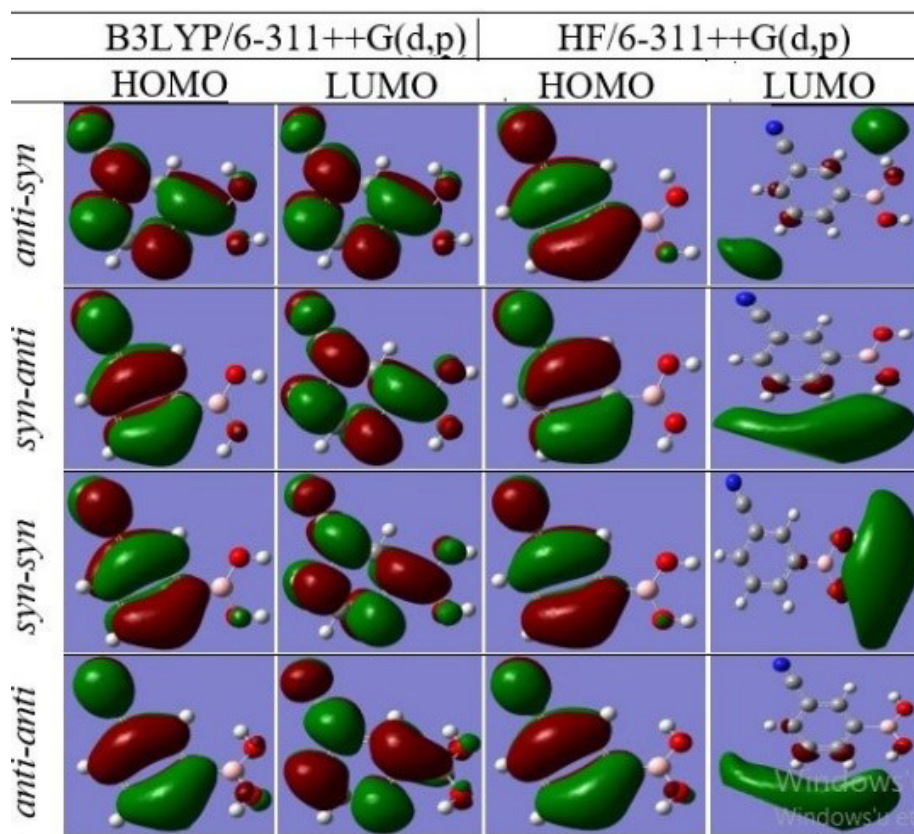


Figure 5: The shapes of HOMO and LUMO of the stable conformers.

Table 3: The selected structural parameter of the stable conformers.

Anti-syn				
Unscaled	Scaled	IR Raman	Raman-Raman	Selected vibration types
3888	3725	43.7	44.9	$\nu$ O2H(51) $\nu$ O1H(48)
3848	3686	97.2	183.4	$\nu$ O2H(48) $\nu$ O1H(52)
3200	3066	5.7	189.9	$\nu$ C2H(24) $\nu$ C4H(01) $\nu$ C5H(19) $\nu$ C6H(46)
3199	3065	1.7	71.7	$\nu$ C4H(56) $\nu$ C5H(12) $\nu$ C6H(31)
3182	3048	2.4	63.5	$\nu$ C2H(60) $\nu$ C5H(32)
3140	3008	11	55	$\nu$ C2H(15) $\nu$ C4H(33) $\nu$ C5H(36) $\nu$ C6H(16)
2333	2235	41.2	467.5	$\nu$ NC7(89) $\nu$ C7C3(11)
Syn-anti				
3888	3725	45	50.6	$\nu$ O2H(51) $\nu$ O1H(48)
3848	3686	97	173.7	$\nu$ O2H(48) $\nu$ O1H(52)
3200	3066	1.2	99.8	$\nu$ C2H(24) $\nu$ C4H(01) $\nu$ C5H(19) $\nu$ C6H(46)
3199	3065	3.8	110	$\nu$ C4H(56) $\nu$ C5H(12) $\nu$ C6H(31)
3182	3048	7.3	87.6	$\nu$ C2H(60) $\nu$ C5H(32)
3140	3008	20.9	86.1	$\nu$ C2H(15) $\nu$ C4H(33) $\nu$ C5H(36) $\nu$ C6H(16)
2333	2235	35.2	467	$\nu$ NC7(89) $\nu$ C7C3(11)
Syn-syn				
3871	3709	110.8	365.8	$\nu$ O2H(98)
3867	3705	16.6	34.6	$\nu$ O1H(98)
3198	3063	6.8	211.6	$\nu$ C4H(14) $\nu$ C6H(82)
3196	3062	0.8	25.2	$\nu$ C2H(19) $\nu$ C4H(39) $\nu$ C5H(32) $\nu$ C6H(10)
3188	3054	4.6	80.5	$\nu$ C2H(72) $\nu$ C4H(21)
3173	3040	1.9	56.5	$\nu$ C4H(26) $\nu$ C5H(66)
2331	2233	44.5	471	$\nu$ NC7(89) $\nu$ C7C3(11)
Anti-anti				
3892	3728	3.4	87.5	$\nu$ O2H(98)
3891	3727	111	2.4	$\nu$ O1H(98)
3200	3066	3.4	152.7	$\nu$ C4H(38) $\nu$ C6H(51)
3182	3049	6.4	108.5	$\nu$ C2H(58) $\nu$ C5H(29) $\nu$ C6H(12)
3169	3036	3.2	49.1	$\nu$ C2H(28) $\nu$ C4H(27) $\nu$ C5H(22) $\nu$ C6H(23)
3155	3022	6.6	72.9	$\nu$ C2H(10) $\nu$ C4H(34) $\nu$ C5H(42) $\nu$ C6H(13)
2334	2236	33	468	$\nu$ NC7(89) $\nu$ C7C3(11)

Note:  $\nu$ : Upsilon used to represent vibrational energy.

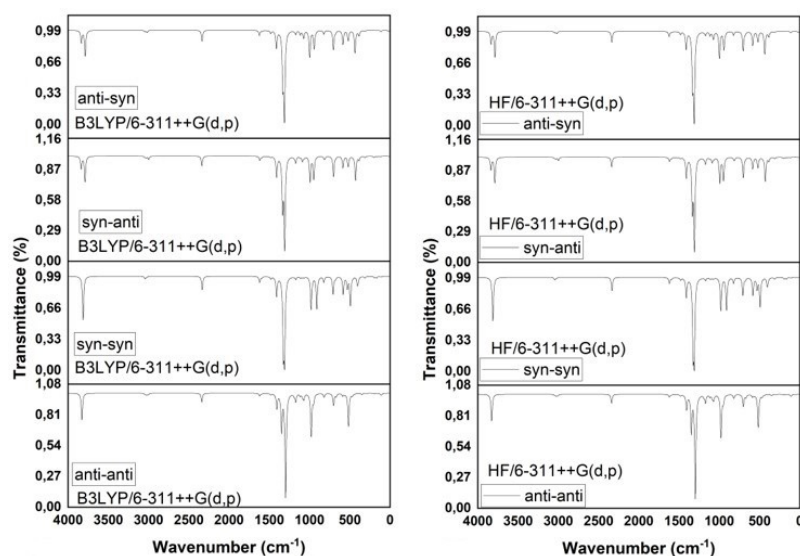


Figure 6: The shapes of the HOMO-LUMO orbitals of complexes 1-3 and HL at the B3LYP/MIX.

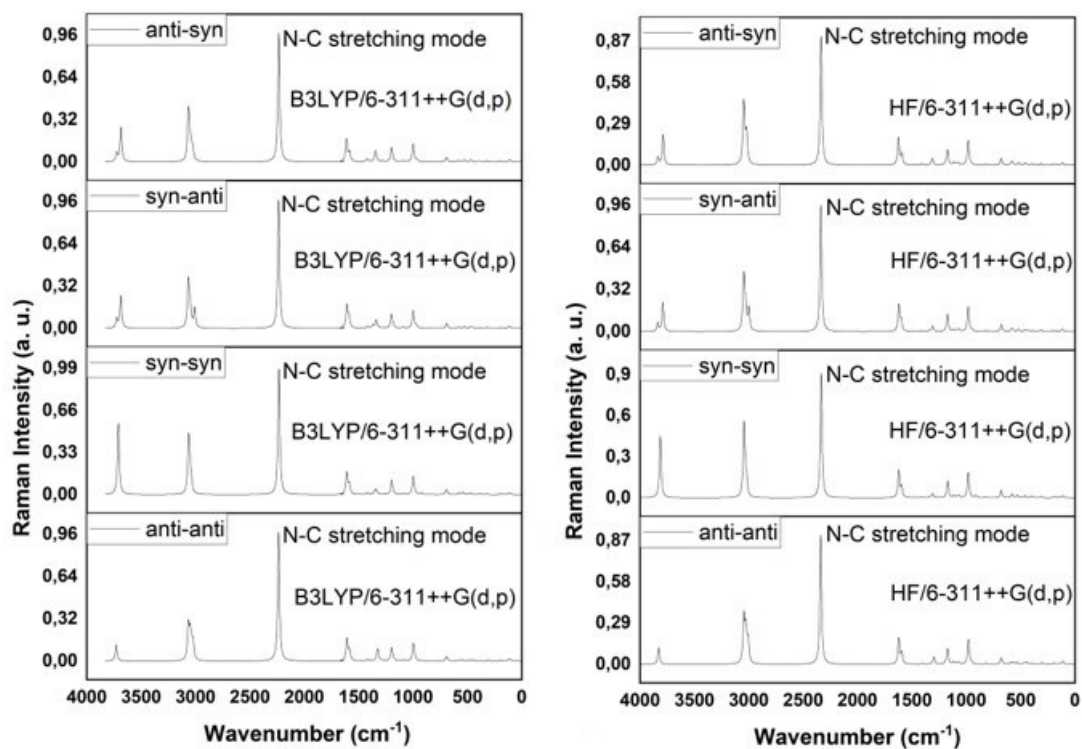


Figure 7: The shapes of the HOMO-LUMO orbitals of complexes 1-3 and HL at the B3LYP/MIX.

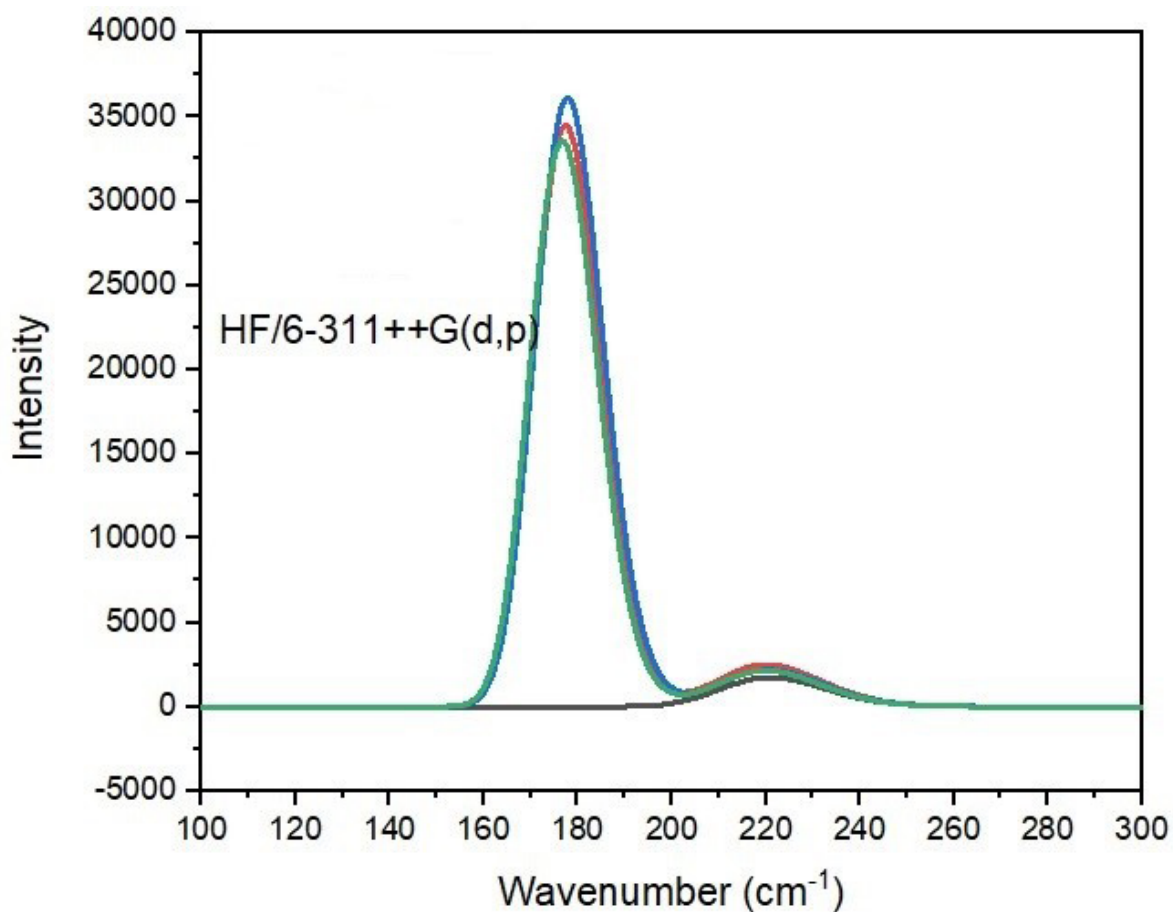
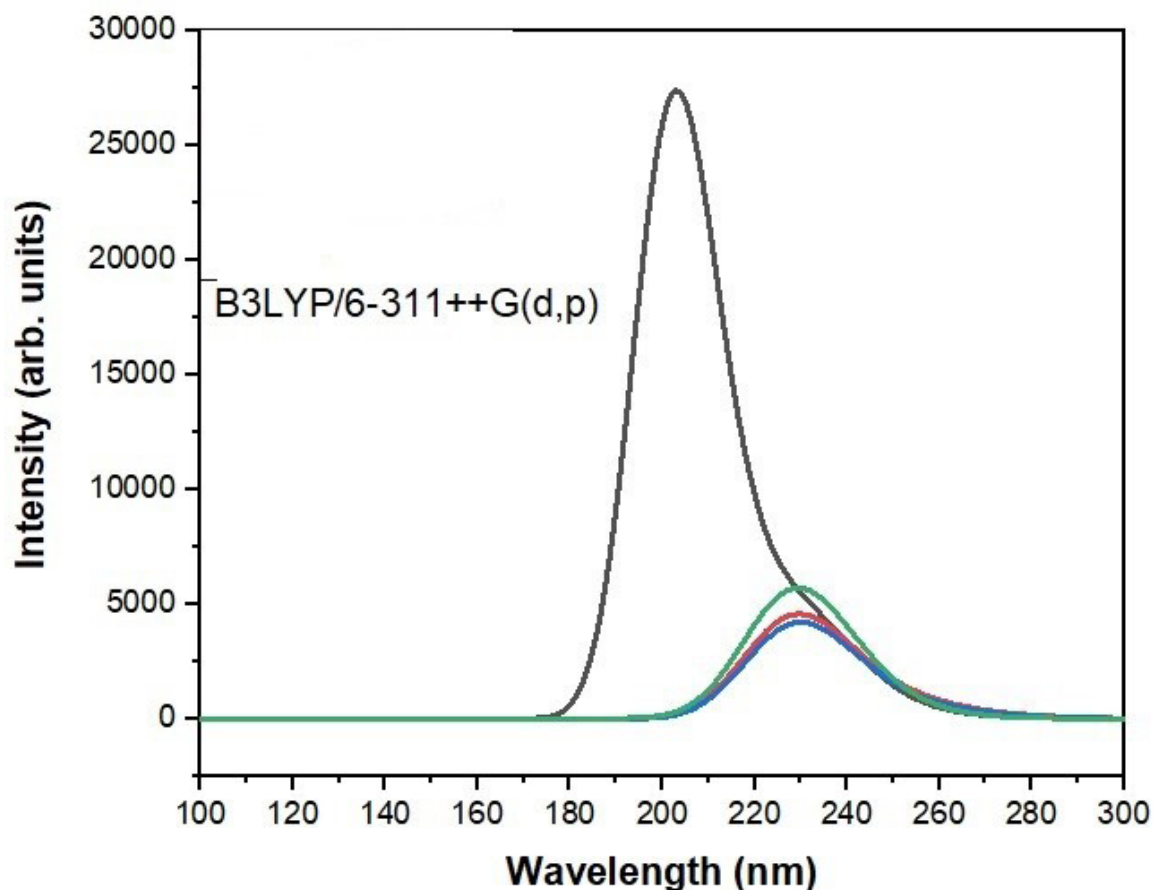


Figure 8: The generated UV-vis spectra graphic for all conformers for (HF/6-311++G(d,p)). Note: anti-anti (—), syn-anti (—), syn-syn (—), anti-anti (—).





**Figure 9:** The generated UV-vis spectra graphic for all conformers for (DFT/B3LYP/6-311++G(d,p)). Note: anti-anti (—), syn-anti (—), syn-syn (—), anti-anti (—)

**Table 4:** The experimental-theoretical UV-vis, oscillator power and the primary transition contribution values with TD-DFT/B3LYP and TD-HF levels of all conformers.

	$\lambda$ (nm)	Excitation energy (cm <sup>-1</sup> )	Oscillator power (f)	Main transition
	B3LYP/HF	B3LYP/HF	B3LYP/HF	B3LYP/HF
Anti-syn	254.07/221.30	4.8799/5.6026	0.0033/0.0387	H-1>L (42%), H->L+1 (39%)/H->L+4 (56%)
	229.73/218.45	5.3971/5.6757	0.1084/0.0044	H->L (68%)/H-1>L+4(50%)
	202.93/176.07	6.1097/7.0417	0.6720/0.0001	H-1>L (44%), H->L+1 (50%)
Syn-anti	254.83/220.89	4.8653/5.6129	0.0122/0.0376	H-1>L (39%), H->L+1 (30%) / H->L+3 (40%)
	229.24/219.12	5.4085/5.6583	0.1107/0.0241	H->L (58%)/H-1>L+3 (40%)
	203.14/177.39	6.1035/6.9895	0.0001/0.8516	H-2>L (92%), H->L+7 (48%)
Syn-syn	255.51/221.21	4.8523/5.6049	0.0093/0.0398	H-1>L (36%), H->L+1 (30%)/H->L+6 (51%)
	229.66/219.03	5.3986/5.6605	0.1023/0.0144	H->L (56%)/H-1>L+6 (48%)
	214.85/177.81	5.7707/6.9727	0.0001/0.8921	H->L+2 (98%)/H-1>L+8 (33%)
Anti-anti	252.02/220.54	4.9197/5.6218	0.0035/0.0424	H-1>L (54%), H->L+1 (43%)/H->L+3 (56%)
	229.34/217.93	5.4062/5.6891	0.1396/0.0106	H->L (81%)/H-1>L+3 (54%)
	208.00/176.72	5.9607/7.0158	0.0016/0.8291	H-2>L (91%)/H-1>L+6 (46%)

Note: H: HOMO AND L: LUMO.

## CONCLUSION

In this work, the Lowest Unoccupied Molecular Orbital (LUMO) and the Highest Occupied Molecular Orbital (HOMO), structural parameters, dipole moments and nonlinear optical properties of all the conformers of 3-CyBA were calculated by both HF/6-311++(d,p) and B3LYP/6-311++(d,p) level of theory. The relative stability of four conformers, anti-syn, syn-anti, syn-syn, anti-anti is 0.00, 0.227, 1.078, 4.577 kcal/mol (HF) and 0.00, 0.248, 1.465, 3.855 kcal/mol (B3LYP), respectively. In both methods, relative energy values of conformers increase in the order: syn-anti<syn-syn<anti-anti. For phenylboronic acid derivative, the values in literature are 1-4 kcal/mol, nearly. The relative energy results show that relative energy values of all the conformers obtained at both methods are in agreement with values in literature. OH, CH and CN vibration analyzes of all conformers were performed and characterized. OH, CH and CN vibrations in the functional group region were observed to be compatible with the literature. It was determined that the vibrations in the fingerprint region were the same in all four conformations examined and it was observed that they were not affected by the conformation. It was concluded that all the values calculated in the study were consistent with the values in the literature.

## DATA AVAILABILITY

X-ray crystallography data for the title compound (CCDC 1825335) have been deposited with the Cambridge Crystallographic Data Center.

## REFERENCES

- Dehghani B, Hosseini MS, Salami-Kalajahi M. Neutral pH monosaccharide receptor based on boronic acid decorated poly (2-hydroxyethyl methacrylate): Spectral Methods for determination of glucose-binding and ionization constants. *Microchem J.* 2020;157:105112.
- Kurukavak CK, Yılmaz T, Buyukbekar A, Kus M. Effect of different terminal groups of phenyl boronic acid self-assembled monolayers on the photovoltaic performance of organic solar cells. *Opt Mater.* 2021;112:110783.
- Yan J, Jin S, Wang B. A novel redox-sensitive protecting group for boronic acids, MPMP-diol. *Tetrahedron Lett.* 2005;46(49):8503-8505.
- Cruz CD, Wrigstedt P, Moslova K, Iashin V, Makkyla H, Ghemtio L, et al. Installation of an aryl boronic acid function into the external section of N-aryl-oxazolidinones: Synthesis and antimicrobial evaluation. *Eur J Med Chem.* 2021;211:113002.
- Di Luccio M, Smith BD, Kida T, Borges CP, Alves TL. Separation of fructose from a mixture of sugars using supported liquid membranes. *J Membr. Sci.* 2000;174(2):217-224.
- Fang H, Kaur G, Wang B. Progress in boronic acid-based fluorescent glucose sensors. *J Fluoresc.* 2004;14:481-489.
- Worsley GJ, Tourniaire GA, Medlock KE, Sartain FK, Harmer HE, Thatcher M, et al. Measurement of glucose in blood with a phenylboronic acid optical sensor. *J Diabetes Sci Technol.* 2008;2(2):213-220.
- Cambre JN, Sumerlin BS. Biomedical applications of boronic acid polymers. *Polymer.* 2011;52(21):4631-4643.
- Bhavya NR, Mahendra M, Doreswamy BH, Kumar S, Gilandoust M, El-khatatneh NA. Computational and spectroscopic investigations on boronic acid based fluorescent carbohydrate sensor in aqueous solution at physiological pH 7.5. *J Mol Struct.* 2019;1194:305-319.
- Baluchova S, Danhel A, Dejmekova H, Ostatna V, Fojta M, Schwarzova-Peckova K. Recent progress in the applications of boron doped diamond electrodes in electroanalysis of organic compounds and biomolecules—A review. *Anal Chim Acta.* 2019;1077:30-66.
- Piest M, Ankoné M, Engbersen JF. Carbohydrate-interactive pDNA and siRNA gene vectors based on boronic acid functionalized poly (amido amine) s. *J Control Release.* 2013;169(3):266-275.
- Halo TL, Appelbaum J, Hobert EM, Balkin DM, Schepartz A. Selective recognition of protein tetraserine motifs with a cell-permeable, pro-fluorescent bis-boronic acid. *J Am Chem Soc.* 2009;131(2):438-439.
- Debiais M, Vasseur JJ, Smietana M. Applications of the Reversible Boronic Acids/Boronate Switch to Nucleic Acids. *Chem Rec.* 2022;22(8):e202200085.
- BEYTUR M, UĞURLU G. Theoretical studies on the structural, vibrational, conformational analysis and nonlinear optic (NLO) property of 4-(Methoxycarbonyl) phenylboronic acid. *J Chem Sec.* 2020;59(10):1504-1512.
- Beytur M, Irak ZT, Manap S, Yüksek H. Synthesis, characterization and theoretical determination of corrosion inhibitor activities of some new 4, 5-dihydro-1H-1, 2, 4-Triazol-5-one derivatives. *Heliyon.* 2019;5(6):e01809.
- Beytur M, Avinca I. Molecular, electronic, nonlinear optical and spectroscopic analysis of heterocyclic 3-substituted-4-(3-methyl-2-thienylmethyleneamino)-4, 5-dihydro-1H-1, 2, 4-triazol-5-ones: experiment and DFT calculations. *Indian J Heterocycl Chem.* 2021;27(1):1-6.
- Rai NS, Kalluraya B, Lingappa B, Shenoy S, Puranic VG. Convenient access to 1, 3, 4-trisubstituted pyrazoles carrying 5-nitrothiophene moiety via 1, 3-dipolar cycloaddition of sydnone with acetylenic ketones and their antimicrobial evaluation. *Eur J Med Chem.* 2008;43(8):1715-1720.
- Tamer O, Avcı D, Arıoğlu Ç, Basoğlu A, Atalay Y. A theoretical study on structural, spectroscopic, electronic and electric properties of 4-chloro 4-nitrostilbene. *Indian J Phys.* 2015;89:1-1.
- Karelson M, Lobanov VS, Katritzky AR. Quantum-chemical descriptors in QSAR/QSPR studies. *Chem Rev.* 1996;96(3):1027-1044.
- Atalay Y, Basoğlu A, Avcı D. Molecular structure, IR and NMR spectra of 2, 6 distyrylpyridine by density functional theory and ab initio Hartree-Fock calculations. *Spectrochim Acta A Mol Biomol Spectrosc.* 2008;69(2):460-466.
- Suvitha A, Periandy S, Boomadevi S, Govindarajan M. Vibrational frequency analysis, FT-IR, FT-Raman, ab

- initio, HF and DFT studies, NBO, HOMO-LUMO and electronic structure calculations on pycolinaldehyde oxime. *Spectrochim Acta A Mol Biomol Spectrosc.* 2014;117:216-224.
22. Parlak AE, Omar RA, Koparir P, Salih MI. Experimental, DFT and Theoretical Corrosion Study for 4-(((4-ethyl-5-(thiophen-2-yl)4H-1, 2, 4-triazole-3-yl) thio) methyl)-7, 8-dimethyl-2H-chromen-2-one. *Arab J Chem.* 2022;15(9):104088.
23. Srikanth E, Ramaia K, Rao KJ, Rao DP, Naik KL, Veeraiah A. et al. Experimental and theoretical analyses on structural (monomer and dimeric form), spectroscopic and electronic properties of an organic semiconductor 2, 6-dimethoxyanthracene. *Indian J Phys,* 2020;94:1153-1167.
24. Rettig SJ, Trotter J. Crystal and molecular structure of phenylboronic acid, C<sub>6</sub>H<sub>5</sub>B(OH)<sub>2</sub>. *Can J Chem.* 1977;55(17):3071-5.
25. Cyranski MK, Klimentowska P, Rydzewska A, Serwatowski J, Sporzynski A, Stepien DK. Towards a monomeric structure of phenylboronic acid: The influence of ortho-alkoxy substituents on the crystal structure. *Cryst Eng Comm.* 2012;14(19):6282-94.
26. Wu YM, Dong CC, Liu S, Zhu HJ, Wu YZ. 3-Fluorophenylboronic acid. *Acta Crystallogr Sect E Struct Rep Online* 2006;62(10):o4236-7.
27. SeethaLekshmi N, Pedireddi VR. Solid-state structures of 4-carboxyphenylboronic acid and its hydrates. *Cryst Growth Des.* 2007;7(5):944-9.
28. Flanagan KJ, Senge MO. Crystal structure of 4-(methoxycarbonyl) phenylboronic acid. *Acta Crystallogr E Crystallogr Commun.* 2015;71(10):1151-4.
29. Vega A, Zarate M, Tlahuext H, Höpfl H. 3-Aminophenylboronic acid monohydrate. *Acta Crystallogr Sect E* 2010;66(6):o1260.
30. Cárdenas-Valenzuela AJ, González-García G, Zárraga-Núñez R, Höpfl H, Campos-Gaxiola JJ, Cruz-Enríquez A. Crystal structure and Hirshfeld surface analysis of 3-cyanophenylboronic acid. *Acta Crystallogr E Crystallogr Commun.* 2018;74(4):441-4.
31. Pedireddi VR, SeethaLekshmi N. Boronic acids in the design and synthesis of supramolecular assemblies. *Tetrahedron Lett.* 2004;45(9):1903-6.S
32. Ajami D, Dube H, Rebek J. Boronic acid hydrogen bonding in encapsulation complexes. *J Am Chem Soc.* 2011;133(25):9689-91.
33. Madura ID, Czerwinska K, Soldanilska D. Hydrogen-bonded dimeric synthon of fluoro-substituted phenylboronic acids versus supramolecular organization in crystals. *Cryst Growth Des.* 2014;14(11):5912-21.
34. Sert YU, Uzun F, Büyükata MU. Vibrational spectroscopic studies of 3-hydroxyphenylboronic acid: molecular structure. *Indian J Phys Proc Indian Assoc Cultiv Sci.* 2013;87:113-9.
35. Prasad O, Sinha L, Misra N, Narayan V, Kumar N, Pathak J. Molecular structure and vibrational study on 2, 3-dihydro-1H-indene and its derivative 1H-indene-1, 3 (2H)-dione by density functional theory calculations. *J Mol Struct.* 2010;940(1-3):82-6.
36. Çöpçü B, Sayin K, Karakaş D. Investigations substituent effect on structural, spectral and optical properties of phenylboronic acids. *J Mol Struct.* 2021;1227:129550.
37. Piergies N, Proniewicz E, Ozaki Y, Kim Y, Proniewicz LM. Influence of substituent type and position on the adsorption mechanism of phenylboronic acids: infrared, Raman, and surface-enhanced Raman spectroscopy studies. *J Phys Chem A.* 2013;117(27):5693-705.
38. Sert Y, El-Emam AA, Al-Abdullah ES, Al-Tamimi AM, Çırak Ç, Uzun F. Use of vibrational spectroscopy to study 4-benzyl-3-(thiophen-2-yl)-4, 5-dihydro-1H-1, 2, 4-triazole-5-thione: A combined theoretical and experimental approach. *Spectrochim. Acta A: Mol Biomol Spectrosc.* 2014;126:280-90.
39. Sas EB, Kose E, Kurt M, Karabacak M. FT-IR, FT-Raman, NMR and UV-Vis spectra and DFT calculations of 5-bromo-2-ethoxyphenylboronic acid (monomer and dimer structures). *Spectrochim Acta A Mol Biomol Spectrosc.* 2015;137:1315-33.
40. Mfuh AM, Doyle JD, Chhetri B, Arman HD, Larionov OV. Scalable, metal-and additive-free, photoinduced borylation of haloarenes and quaternary arylammonium salts. *J Am Chem Soc.* 2016;138(9):2985-8.
41. Zhenming D, Heping S, Yufang L, Diansheng L, Bo L. Experimental and theoretical study of 10-methoxy-2-phenylbenzo [h] quinoline. *Spectrochim Acta A Mol Biomol Spectrosc.* 2011;78(3):1143-8.
42. Tanak H. DFT computational modeling studies on 4-(2, 3-Dihydroxybenzylideneamino)-3-methyl-1H-1, 2, 4-triazol-5 (4H)-one. *Comput Theor Chem.* 2011;967(1):93-101.