RESEARCH ARTICLE

VIBRATIONAL STUDIES OF MONOMER, DIMER AND TRIMER STRUCTURES OF 4-CARBOXY PHENYLBORONIC ACID

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ABSTRACT

4-carboxyphenylboronic acid (4-cpba) was investigated theoretically and experimentally by spectroscopic methods such as FT-IR and Raman. The molecular structure and spectroscopic parameters were determined by computational methods. The molecular dimer1, dimer2 and trimer structures were investigated for possible intermolecular hydrogen bonding interactions. Moreover, minimum conformational energy search was carried out by potential energy surface (PES) analysis. Potential energy distribution analysis of normal modes was performed to identify characteristic frequencies. The findings of this research work should be useful to experimentalists in their quests for functionalized 4-cpba derivatives.

Keywords: 4-carboxyphenylboronic acid, Vibrational analysis, DFT calculations, PES analysis

1. INTRODUCTION

Boronic acids have been used in drug discovery studies. Especially they have been used for the treatment of fungal, bacterial, and parasitic infections. Moreover, boronic acids and their derivatives have been used as diagnostic tools and for radiation treatment, bioconjugation, and catalysis applications. Boronic acids are used for drug discovery studies because of their enhancing effect on drug activity and pharmacokinetic properties. The discovery process of boronic acids also relies on the approach. For instance, substrate mimicry or peptidomimetics design, rational design via computational methods, or use as bioisosteres to substitute for certain functional groups can be given as examples [1-8].

Characterization studies about phenylboronic acid and its derivatives can be considered as an ongoing process since these molecules can easily become dimer form and some of them also be present in the anhydrite structure. On the other hand, since the energy difference between the conformational states of these molecules is quite low, these molecules might contain more than one conformational state in solid form. In this case, it is difficult to characterize such molecules [9–15]. Phenylboronic acid and its derivatives have been used in organic synthesis, biosensors and nanoparticular systems. In the literature, 4-cpba has wide applications, but there is no detailed information about vibrational properties of 4-cpba and its dimer and trimer forms.

In present work, the vibrational properties of 4-cpba monomer, dimers and trimer structures were studied using computational means. These structures of 4-cpba molecule was characterized by FT-IR and Raman approaches. Lastly, in order to gain a deeper insight, monomer, dimers and trimer structures were investigated using density functional theory (DFT) method to examine vibrational properties of 4-cpba. The results of these experimental and theoretical studies were also reported in this study.

2. MATERIALS AND METHODS

2.1. Experimental

4-cpba was bought from Aldrich (95%). FT-IR spectrum of 4-cpba were collected with KBr pellets between 4000–400 cm^{-1} with Perkin Elmer Spectrum Two FT-IR spectrometer. Raman spectrum was recorded by Renishaw Invia Raman spectrometer in the spectral region of 4000–400 cm^{-1}.

2.2. Computational Details

All the calculations were performed using Gaussian 09 program package [17] and GaussView 5.0.8 [18] was used for indication of chemical structure of 4-cpba and indication of IR and Raman spectra of 4-cpba. PES SCAN analysis was carried out by two C3–B11–O13–H18 and C3-B11-O12-H19 torsion angles for examine conformational isomers and 4-cpba scanned from 0 to 180 degree, with 10º increments. According to orientations of hydrogen atoms bonded to oxygen atom, title compound has four different conformational states and these conformational states can be identified as trans-cis (tc), cis-trans (ct), trans-trans (tt) and cis-cis (cc) (Figure 1). Moreover, two different dimer structures were identified as dimer1 and dimer2 (Figure 1). Trimer structure (anhydrite) was given in Figure 2. tc isomer form has lower energy value than other isomer forms and so monomer structure of 4-cpba was calculated according to ct isomer form. All of the chemical forms were optimized using DFT method and B3LYP/ 6-31+G(3df,d) level of theory in the gas phase. Geometric parameters and vibrational frequencies of 4-cpba were calculated with 6-31+G(3df,d) basis set in the gas phase. Theoretically obtained scaled vibrational frequencies and total energy distribution (TED) calculations were performed with SQM program [19, 20].
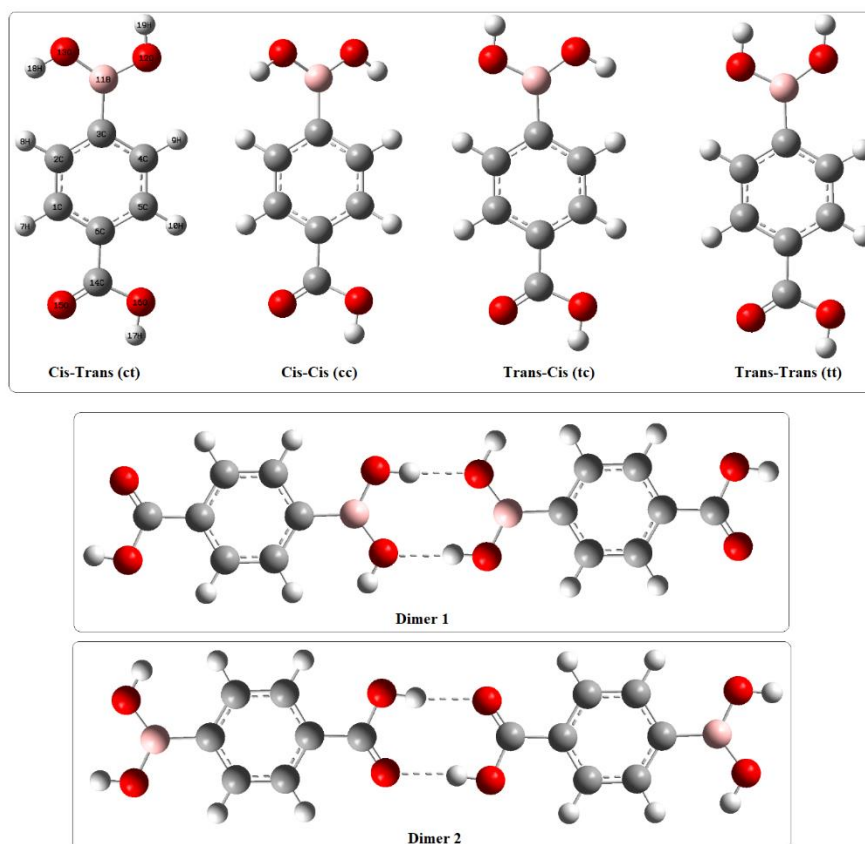
Figure 1. Optimized structures of 4-cpba monomers and dimers [9]
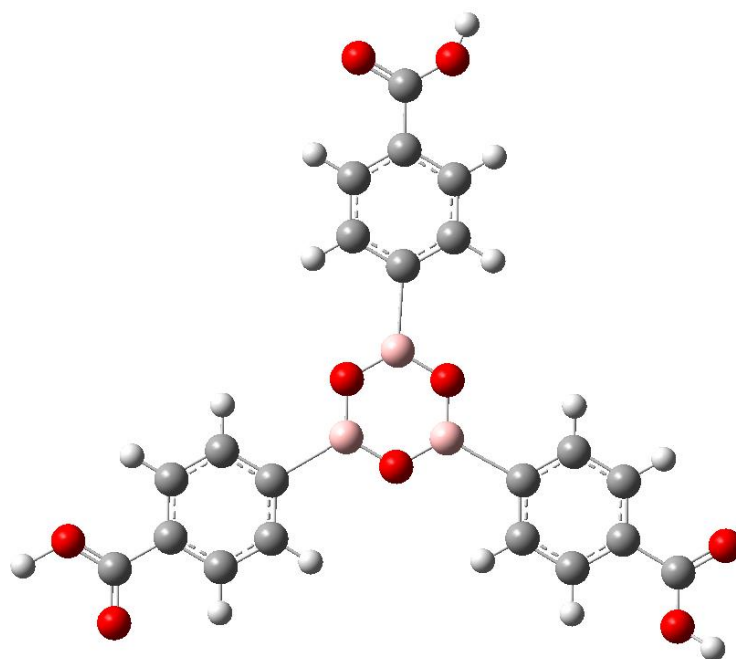
Figure 2. Optimized structure of 4-cpba trimer (anhydrite) structure

3. RESULTS AND DISCUSSION

The results of conformational states and vibrational modes of 4-cpba molecule for monomer, dimers and trimer structures have been reported and discussed.

3.1. Geometrical Structure

Conformational analysis was carried out using PES scan to determine most stable isomer in the ground state of 4-cpba molecule (Figure 3). Energy values, imaginary frequencies and dipole moment of four conformational isomers of 4-cpba monomer in the C1 point group were given in Table 1 and energy values, dipole moments of dimers and trimer structure were given in Table 2. The most stable form was determined as ct isomer. So, vibrational analysis, geometrical parameters and dimer structure were carried out using ct isomer. Relative stability among tt, tc and cc conformers were calculated as 1.861, 0.092 and 3.357 kcal/mol, respectively. PES SCAN analysis was performed by rotating the boronic acid group [dihedral angle of atom According to PES scan, rotational energy differences between isomers were calculated as 1.092, 2.162 kcal/mol.
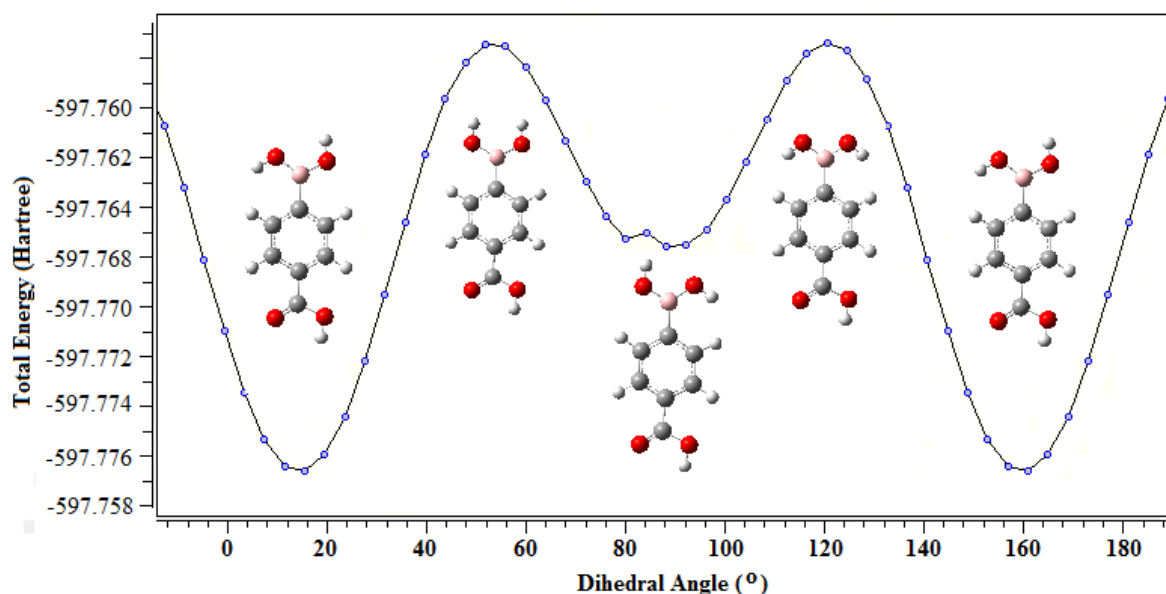
Figure 3. PES diagram of 4-cpba

The minimum energy of most stable conformers of 4-cpba monomer, dimer and trimer structures were calculated using B3LYP/6-31+G(3df,d). Four different conformers were calculated and ct isomer found as the most stable conformers for monomer structures. Energy value of dimer structure is lower than cc and tt conformers. The optimized structures of monomer, dimer and trimer structures were given in Figures 1 and 2.

Table 1. Energy values of 4-cpba monomer conformers

Parameters	Cis-Trans	Cis-Cis	Trans-Cis	Trans-Trans
ΔG (Hartree)	-597.03171409	-597.02636458	-597.03156779	-597.02874893
Relative stability (kcal/mol)	0	3.357	0092	1.861
Imaginary frequency	0	1	0	0
Mole fraction (%)	56.2	0.0	41.9	1.9
Dipole Moment (Debye)	1.1931	2.0758	2.8358	4.3642

Table 2. Energy values of 4-cpba dimers and trimer structures

Parameters	Dimer 1	Dimer 2	Trimer
ΔG (Hartree)	-1193.27091369	-1194.08918346	-1561.69971911
Imaginary frequency	1	0	0
Dipole Moment (Debye)	3.1212	0.0046	0.0019
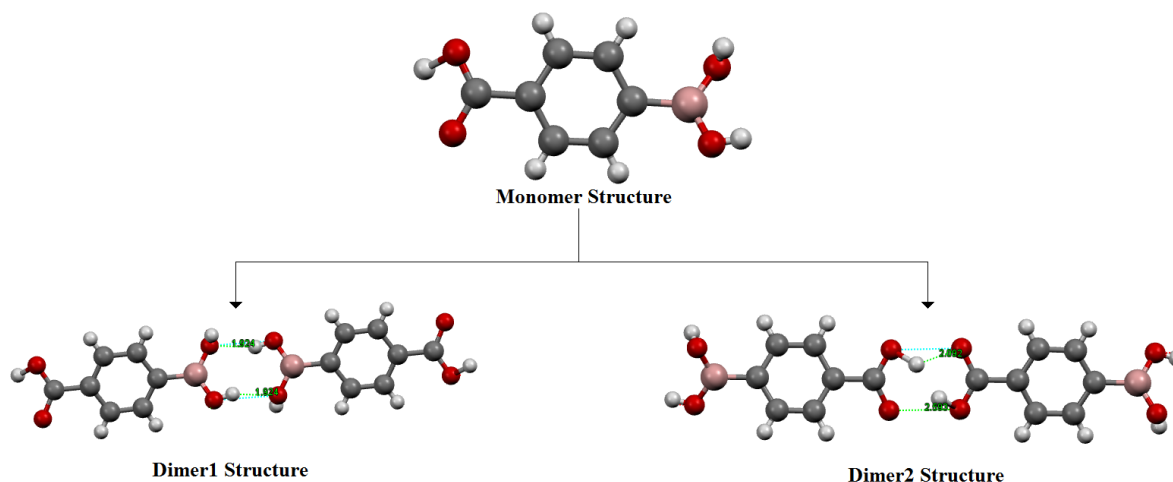
Figure 4. Experimental monomer and dimers structure of 4-cpba [9]

3.2. Vibrational Studies

Theoretically and experimentally obtained vibrational frequencies and assignments and of 4-cpba are given in Tables 4 and 5. For 4-cpba, corresponding vibrational frequencies were presented in this manuscript.

3.2.1. OH vibrations

The OH stretching band appears as a very broad band and it was observed in the range from 3600 to 3400 cm^{-1}. The OH stretching band shows intra-inter molecular hydrogen bonding interactions. Moreover, it can be due to moisture residue [15, 21, 22]. In the IR spectrum of monomer structure of 4-cpba, OH stretching band was observed at 3392 cm^{-1}, 3157 cm^{-1} and this band was calculated as 3757 cm^{-1}, 3684 cm^{-1}, respectively. Differences were come across between theoretical and experimental OH stretching values since intermolecular hydrogen bondings were built up between boronic acid groups of 4-cpba.

After then, OH modes were considered for dimer structure. Theoretical vibrational modes for dimer structures and trimer structure were collected in Table 5. According to dimer structures, boronic acids exhibit free and hydrogen bonded OH stretching modes. As shown in Table 5. OH stretching modes were calculated at 3724 and 3211 cm^{-1} for dimer1 structure, calculated at 3757 and 3312 cm^{-1} for dimer2 structure and only peak calculated at 3702 cm^{-1} belongs to COOH functional group was observed in trimer structure.

For monomer structure of 4-cpba in the gas phase, in general OH stretching was observed range from 3700-3500 cm^{-1}. However, in dimer structure these vibrations changed and observed at 3400-3150 cm^{-1} since there is a strong intermolecular O-H···O interaction in the dimer structure. Moreover, hydrogen bonding between carboxylic acid groups in dimer structure caused a broad band referred to OH stretching. Moreover, below 2950 cm^{-1} there are a lot of subtle submaxima. These bands indicate hydrogen bonds. In trimer structure spectrum, band of B(OH)$_2$ group was not calculated.

3.2.2. C=O vibrations

C=O stretching band of 4-cpba was observed in IR spectrum at 1687 cm^{-1} and 1682 cm^{-1} in Raman spectrum and this band calculated as 1744 cm^{-1}. It is nearly appeared as a pure mode (81%, TED). C=O stretching band was observed as an intense band in infrared spectrum, whereas it was observed as a smaller band in Raman spectrum. Because, this vibration is in symmetric stretching mode in Raman

spectrum, while is anti-symmetric stretching in infrared spectrum. In plane COH bending vibrations were calculated at 1355 and 1098 cm^{-1} for monomer, 1371 and 1075 cm^{-1} dimer1, 1356 and 1089 cm^{-1} for dimer 2 and 1352 and 1077 cm^{-1} for trimer structures. These vibrations were observed experimentally at 1352 and 1042 cm^{-1} in the infrared spectrum and 1048 cm^{-1} in the Raman spectrum.

Out of plane COH vibration was seen in infrared spectrum at 524 cm^{-1} and in Raman spectrum at 531 cm^{-1}. It suggests that 4-cpba in the solid phase exists in dimer structure. Calculated peak for out of plane COH mode was computed at 570, 603, 567 and 569 cm^{-1} for monomer, dimer1, dimer2 and trimer structures, respectively and this band was contaminated by the other vibrations. In plane and out of plane COH wavenumbers increased in dimer structure compared to monomer structure.

3.2.3. C-H and C-C vibrations

Aromatic CH stretching modes generally appear as a weak band since negative charge on the carbon atoms decrease and so dipole moment decreases, as well. In the literature, corresponding bands were observed in the range of 3100-3040 cm^{-1} in infrared spectrum for phenylboronic acid derivatives [23-25]. In present work, CH stretching modes of 4-cpba were observed at 3095(IR)/3078(R), 302(IR)/3065(R) and 2935(IR)/3016(R) cm^{-1} in the infrared and Raman spectra and these modes were calculated as 3134, 3067 cm^{-1} for monomer, 3128, 2986 and 2981 cm^{-1} for dimer 1, 3133, 3129 and 3123 cm^{-1} for dimer 2 and 2984 for trimer structures with a TED contribution of 100%. In plane CH vibrations occur range from 1520 to 1000 cm^{-1} [26-27]. In plane and out plane CH stretching modes were mentioned in Tables 4 and 5. All results for CH stretching of 4-cpba agree with the literature [20]. Out of plane CH vibrations are observed in the range 1000-700 cm^{-1}. [26-27]. For 4-cpba, out of plane CH vibrations were observed at 968, 847, 808 and 771 cm^{-1} in infrared spectrum, 863, 802 and 776 cm^{-1} in Raman spectrum.

Aromatic C-C stretching modes are observed between 1620 and 1320 cm^{-1} of phenyl boronic acids [28-29]. The experimental and theoretical spectra for monomer, dimer and trimer infrared spectra of 4-cpba are shown in Figure 5 and theoretical and experimental Raman spectra of 4-cpba are shown in Figure 6. In this study, C-C stretching modes were observed between 1614 and 1427 cm^{-1} as seen in Table 4 and 5. These modes show good compliance with experimental data after scaling using SQM. C-C stretching modes indicated pure modes whereas CCC bending modes overlapped with other modes. Theoretical wavenumber calculated at 1073 cm^{-1} band belongs to ring breathing. This band is the strongest peak in the Raman spectrum, however it was appeared as s weak band in the infrared spectrum. However, there is hardly any differences between theoretical CC wavenumbers and experimental CC wavenumbers.

3.2.4. B-O and B-C vibrations

Boronic acids and its derivates particularly are defined by strong B–O stretching modes between 1380–1310 cm^{-1} [30-31]. In the literature, B–O modes were reported at 1368 cm^{-1} and 1365 cm^{-1} in FT-IR and Raman spectra, respectively. This band was calculated at 1374 cm^{-1} for derivatives of the phenyl boronic acid molecule [27]. This band for the present study for the 4-cpba, B–O stretching vibrations were seen at 1368 cm^{-1} is a contaminated type of B-O, C-C, C-B cm^{-1} in FT-IR and 1365 cm^{-1} in FT-Raman. Moreover, in present molecule, the CBO out-of-plane bending vibrations were calculated for monomer structure at 642 cm^{-1} using B3LYP method and observed at 671 cm^{-1} (IR) and 643cm^{-1} (R).

3.2.5. C–B modes

The modes of C–B stretching are inherent for boronic acids and its derivatives of their [32, 33]. In this study, as indicated in the B-O stretching vibrations, the C–B stretching vibrations also imply combinations of several vibrations and it is observed at 1368 cm^{-1} and 665 cm^{-1} in FT-IR and Raman, respectively. The predicted C–B stretching values were computed at 1374 and 653 cm^{-1} in well agreement in their experimental values and literature [32-33].

Table 4. The observed FTIR, FT-Raman and calculated wavenumbers of 4-cpba for ct monomer structure

	Assignments	Experimental		Monomer- 6-31+G(3df,p)			
	TED(≥10%)	IR	Raman	Unscaled	Scaled	I_{IR}	I_R
υ_1	υ(O-H) (100)	3392	-	3846	3757	35.3	-
υ_2	υ(O-H) (100)	3157	-	3771	3684	36.7	-
υ_3	$\upsilon(C_{ar}$-H) (94)	3095	3078	3287	3211	14.9	110.5
υ_4	$\upsilon(C_{ar}$-H) (93)	3021	3065	3208	3134	10.3	124.1
υ_5	$\upsilon(C_{ar}$-H) (94)	2935	3016	3140	3067	17.5	114.7
υ_6	υ(C=O) (81)	1687	1682	1785	1744	100.0	150.5
υ_7	υ (C_{ar}-C)(60) + υ (C_{ar}-B)(21)	1614	1613	1650	1612	11.3	201.8
υ_8	υ (C_{ar}-C_{ar})(60)+$\beta(C_{ar}$-H)(25)+α(CCC)(10)	1562	1561	1596	1559	24.1	0.4
υ_9	υ (C_{ar}-C_{ar})(60)+$\beta(C_{ar}$-H)(21)+α(CCC)(10)	1512	1511	1539	1504	15.7	2.6
υ_{10}	υ (C_{ar}-C_{ar})(49)+ υ (B-O)(17)+ υ (B-C)(10)	1427	1428	1432	1399	45.6	5.2
υ_{11}	υ (B-O)(61)+ β(C-O-H)(15)+ β(O=C-O)(12)+ $\beta(C_{ar}$-H)(10)	1352	-	1387	1355	48.6	-
υ_{12}	$\beta(C_{ar}$-H)(82)+ υ (C_{ar}-C_{ar})(11)	1308	-	1342	1311	0.8	-
υ_{13}	υ (C_{ar}-C_{ar})(76)	1268	1266	1312	1282	18.2	4.0
υ_{14}	$\beta(C_{ar}$-H)(85)	1191	1189	1222	1194	15. 6	1.9
υ_{15}	β(C-H)(52)+ β(O-H)(12)	1120	1124	1135	1109	4. 8	12.7
υ_{16}	β(COH)(64)+ υ(CC)(28)	1042	1048	1098	1073	19.8	0.5
υ_{17}	β(CC)(48)+ β(OH)(34)+ α(CCC)(27)	1013	1016	1037	1013	1.0	1.2
υ_{18}	β (OH)(38)+ υ(BO)(18)+γ(CH)(10)	968	-	984	961	11.3	-
υ_{19}	γ(CH)(24)+ υ(C-COOH)(12)	847	863	879	859	3.0	0.3
υ_{20}	γ(CH)(27)	808	802	855	835	1.8	36.5
υ_{21}	γ(CH)(41)+ γ(OH)(26)+ α(CCC)(13)+τ(COOH)(10)	771	776	801	783	0.3	0.4
υ_{22}	γ (BC)(36)+φ(CCC)(19)	709	724	725	708	14.7	0.8
υ_{23}	γ(CC)(52)+ γ(BO)(11)	671	643	657	642	28.2	7.7
υ_{24}	α(CCC)(81)	616	612	648	633	0.4	0.7
υ_{25}	α(CCC)(22)+ β(O=C-O)(14)+ γ(COH)(10)	524	531	583	570	0.5	0.6
υ_{26}	γ(OH)(52)+ γ(CC)(31)+φ(CCC)(12)	468	-	465	454	28.1	-
υ_{27}	β(BO)(17)+β(BC)(12)+β(CCO)(10)	426	414	434	424	9.6	0.5

Table 5. The observed FTIR, FT-Raman and calculated wavenumbers of 4-cpba for Dimer2 and Trimer structure

|	Assignments	Experimental		Dimer2-6-31+G(3df,p)				Trimer-6-31+G(3df,p)			
	TED($\geq$10%)	IR	Raman	Unscaled	Scaled	I_{IR}	I_R	Unscaled	Scaled	I_{IR}	I_R
ν_1	υ(O-H) (100)	3392	-	3846	3757	40.26	-	-	-	-	-
ν_2	υ(O-H) (100)	3157	-	3390	3312	35.70	-	3790	3702	6.5	-
ν_3	υ(C_{ar}-H) (94)	3095	3078	3207	3133	14.85	162.85	-	-	-	-
ν_4	υ(C_{ar}-H) (93)	3021	3065	3203	3129	0.13	0.03	3055	2984	1.7	105.5
ν_5	υ(C_{ar}-H) (94)	2935	3016	3196	3123	0.24	0.10	3054	2983	1.7	-
ν_6	υ(C=O) (81)	1687	1682	1733	1693	100	0.03	1688	1649	0.3	20.5
ν_7	υ (C_{ar}-C)(60) + υ (C_{ar}-B)(21)	1614	1613	1650	1612	0.89	10.10	1622	1585	17.6	24.0
ν_8	υ (C_{ar}-C_{ar})(60)+β(C_{ar}-H)(25)+α(CCC)(10)	1562	1561	1594	1557	11.27	10.20	1597	1560	65.0	46.0
ν_9	υ (C_{ar}-C_{ar})(60)+β(C_{ar}-H)(21)+α(CCC)(10)	1512	1511	1540	1505	24.07	0.03	1591	1554	100.0	0.5
ν_{10}	υ (C_{ar}-C_{ar})(49)+ υ (B-O)(17)+ υ (B-C)(10)	1427	1428	1430	1397	45.70	0.27	1439	1406	46.0	101.8
ν_{11}	υ (B-O)(41)+ β(C-O-H)(25)+ β(O=C-O)(12)+ β(C_{ar}-H)(10)	1352	-	1388	1356	65.58	-	1384	1352	6.9	5.3
ν_{12}	β(C_{ar}-H)(82)+ υ (C_{ar}-C_{ar})(11)	1308	-	1344	1313	88.58	-	1341	1310	22.3	4.7
ν_{13}	υ (C_{ar}-C_{ar})(76)	1268	1266	1309	1279	0.77	56.61	1304	1274	90.6	232.0
ν_{14}	β(C_{ar}-H)(85)	1191	1189	1213	1185	84.24	0.4	1225	1197	22.9	10.7
ν_{15}	β(C-H)(52)+ β(O-H)(12)	1120	1124	1132	1106	15.56	0.03	1134	1108	20.0	30.7
ν_{16}	β(COH)(64)+ υ(CC)(28)	1042	1048	1115	1089	4.78	0.02	1102	1077	2.0	33.3
ν_{17}	β(CC)(48)+ β(OH)(27)+ α(CCC)(10)	1013	1016	1038	1014	19.77	58.01	1039	1015	13.5	13.0
ν_{18}	β (OH)(38)+ υ(BO)(18)+γ(CH)(10)	968	-	985	962	1.03	-	987	964	24.8	472.5
ν_{19}	γ(CH)(24)+ υ(C-COOH)(12)	847	863	887	867	11.34	10.21	899	878	0.5	0.6
ν_{20}	γ(CH)(27)	808	802	855	835	3.96	10.01	890	870	13.2	0.5
ν_{21}	γ(CH)(47)+ γ(OH)(21)+ α(CCC)(18)+τ(COOH)(13)	771	776	819	800	1.80	0.56	800	782	8.8	0.1
ν_{22}	γ (BC)(36)+φ(CCC)(19)	709	724	730	713	0.30	79.78	730	713	12.0	2.3
ν_{23}	γ(CC)(52)+ γ(BO)(11)	671	643	657	642	14.73	8.01	664	649	60.9	35.7
ν_{24}	α(CCC)(81)	616	612	648	633	28.19	7.01	645	630	1.2	10.3
ν_{25}	α(CCC)(22)+ β(O=C-O)(14)+ γ(COH)(10)	524	531	580	567	0.43	0.62	582	569	0.5	1.7
ν_{26}	γ(OH)(57)+ γ(CC)(23)+φ(CCC)(10)	468	-	470	459	5.47	-	470	459	2.9	1.0
ν_{27}	β(BO)(17)+β(BC)(12)+β(CCO)(10)	426	414	437	427	28.14	1.20	431	421	2.4	4.5
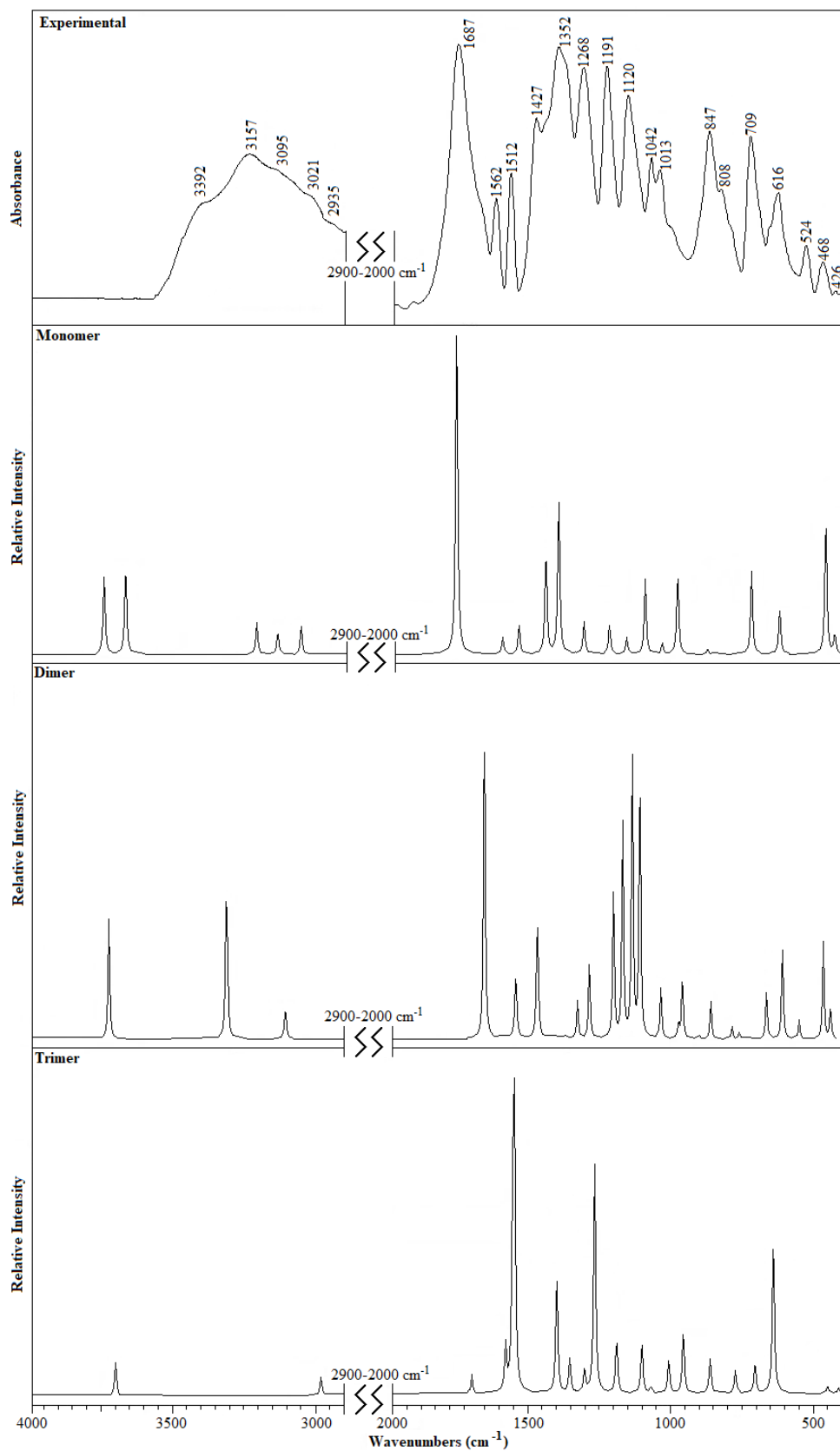
Figure 5. Infrared spectra of 4-cpba
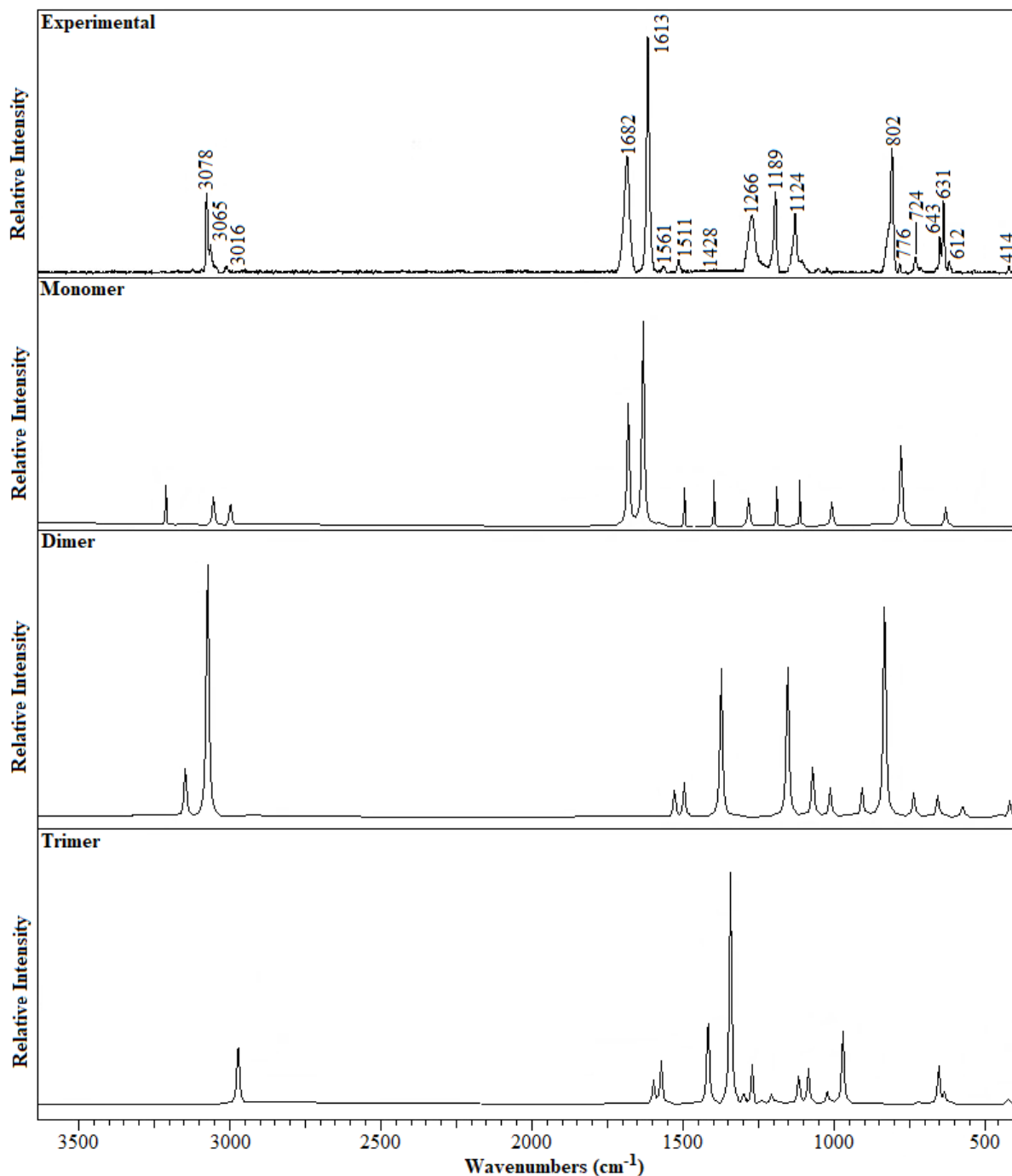
Figure 6. Raman spectra of 4-cpba

3.4. Frontier Molecular Orbital Analysis

Frontier Molecular Orbitals give information about electric properties and chemical reactivity of molecules. FMOs are highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). HOMO and LUMO are related to abilities of electron giving and electron accepting of a molecule, respectively. HOMO nodes delocalized to the ring and oxygen atoms. However, LUMO

nodes located all over the 4-cpba (Fig. 7). Furthermore, HOMO and LUMO show the π bonding character and π anti bonding character, respectively [28-29]. Energy gap determines charge transfer from HOMO to LUMO and charge transfer interactions in the molecule. FMOs were computed with B3LYP/6-31+G(3df,p) method for gas phase. The energy gap shows the final charge transfer interactions occurring in the molecule.

E_{LUMO}= -1.90536 eV
(First exited state)

E_{Gap} = 5.30327 eV

E_{HOMO}= -7.20863 eV
(Ground state)
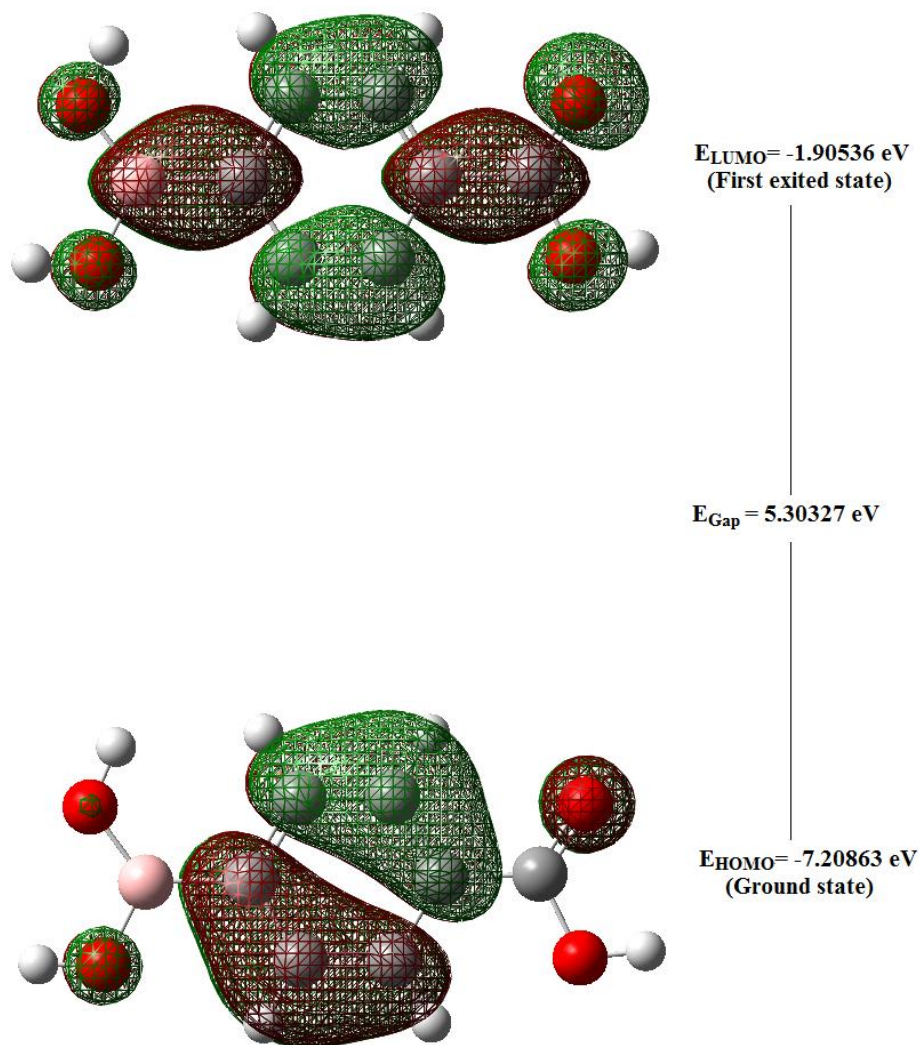
Figure 7. Atomic orbital compositions of the frontier molecular orbital for 4-cpba

4. CONCLUSIONS

The structural and vibrational analyses of 4-cpba molecule were performed using FT-IR, Raman and quantum chemical computations. Vibrational properties of monomer, dimer 1, dimer 2 and trimer chemical structures of 4-cpba were examined. The B3LYP functional is reliable for describing the wavenumbers of 4-cpba. As a result, it has been observed that the 4cpba molecule is present in solid form in different dimer structures as well as in the trimer structure. Since the OH groups bound to the boron atom are not in the trimer structure, they were not observed in the IR spectrum. The observed imaginary frequencies of the optimized structures indicate certain transition states but they are lower in energy in magnitude when compared to the rest of the optimized structures.

CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

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