

An experimental and theoretical study of molecular structure and vibrational spectra of 3- and 4-pyridineboronic acid molecules by density functional theory calculations

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Abstract

The experimental and theoretical vibrational spectra of 3- and 4-pyridineboronic acids (abbreviated as p3 and p4) were studied. The Fourier transform Raman and Fourier transform infrared spectra of p3 and p4 molecules were recorded in the solid phase. The structural and spectroscopic analysis of the p3 and p4 acids were made by using density functional harmonic calculations. Both p3 and p4 only one form was most stable using B3LYP level with the 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p) and 6-311++G(d,p) basis sets. Selected experimental bands were assigned based on the scaled theoretical wavenumbers. Finally, geometric parameters, infrared and Raman bands and intensities were compared with experimental data of the molecules.

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1. Introduction

The boronic acid ligands have been incorporated into various biologically important compounds. A wide variety of boronic acid derivatives of divergent biologically important compounds have been synthesized as anti-metabolites for a possible two-pronged attack on cancer [1–3]. In addition to inhibition of tumor growth, the use of boron-10 neutron capture therapy [4] would be possible owing to the preferential localization of boron compounds in tumor tissue. Boronic acid analogs have been synthesized as transition state analogs for acyl transfer reactions [5] and inhibitors of dihydrotase [6]. The boronic acid moiety has also been incorporated into amino acids and nucleosides as anti-tumor, anti-viral agents [7].

The crystal geometries of the p3 and p4 molecules are unknown. Otherwise, the phenylboronic acid molecule resembles to this molecule and we know crystal structure of phenylboronic acid [8] from literature. In addition, crystal geometry, the infrared and Raman spectra of pentafluorophenyl-

boronic acid were discussed in detail [9,10]. In order to study these biologically important types of molecules by density functional methods (DFT), the necessary parameters had to be developed.

Up to our knowledge no DFT calculations and detailed vibrational IR and Raman analysis have been performed on the p3 and p4 molecules. A detailed quantum chemical study will aid vibrational modes of the p3 and p4 and clarifying the experimental data available for this molecules. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity effects [11–16]. Recently, DFT is now accepted as a popular post-HF approach for the computation of molecular structure, vibrational frequencies and energies of molecules by ab-initio community [17].

In this work, by using B3LYP, method, we calculate the vibrational frequencies of p3 and p4 molecules in the ground state to distinguish the fundamentals from the many experimental vibrational frequencies and geometric parameters. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

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2. Experimental

The p3 and p4 samples were purchased from Acros Chemical Company with a stated purity of greater than 98% and it was used as such without further purification. The samples of p3 and p4 are in solid forms at room temperature. Infrared spectra of the samples were recorded between 4000 and 400 cm^{-1} on a Mattson 1000 FTIR spectrometer which was calibrated using polystyrene bands. The samples were prepared as a KBr disc. FT-Raman spectra of the samples were recorded on a Bruker RFS 100/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 4 cm^{-1} resolution using a laser power of 100 mW.

3. Calculations

The molecular structures of p3 and p4 in the ground state (in vacuo) are optimized by B3LYP with the several basis sets (6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p) and 6-311++G(d,p)). There are no significant difference geometric and vibrational frequencies by the selection of the different basis sets.

The Becke's three-parameter hybrid density functional, B3LYP [18,19], was used to calculate harmonic vibrational wavenumbers with the (6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p) and 6-311++G(d,p) basis sets. It is well known in the quantum chemical literature that among available functionals the B3LYP functional yields a good description of

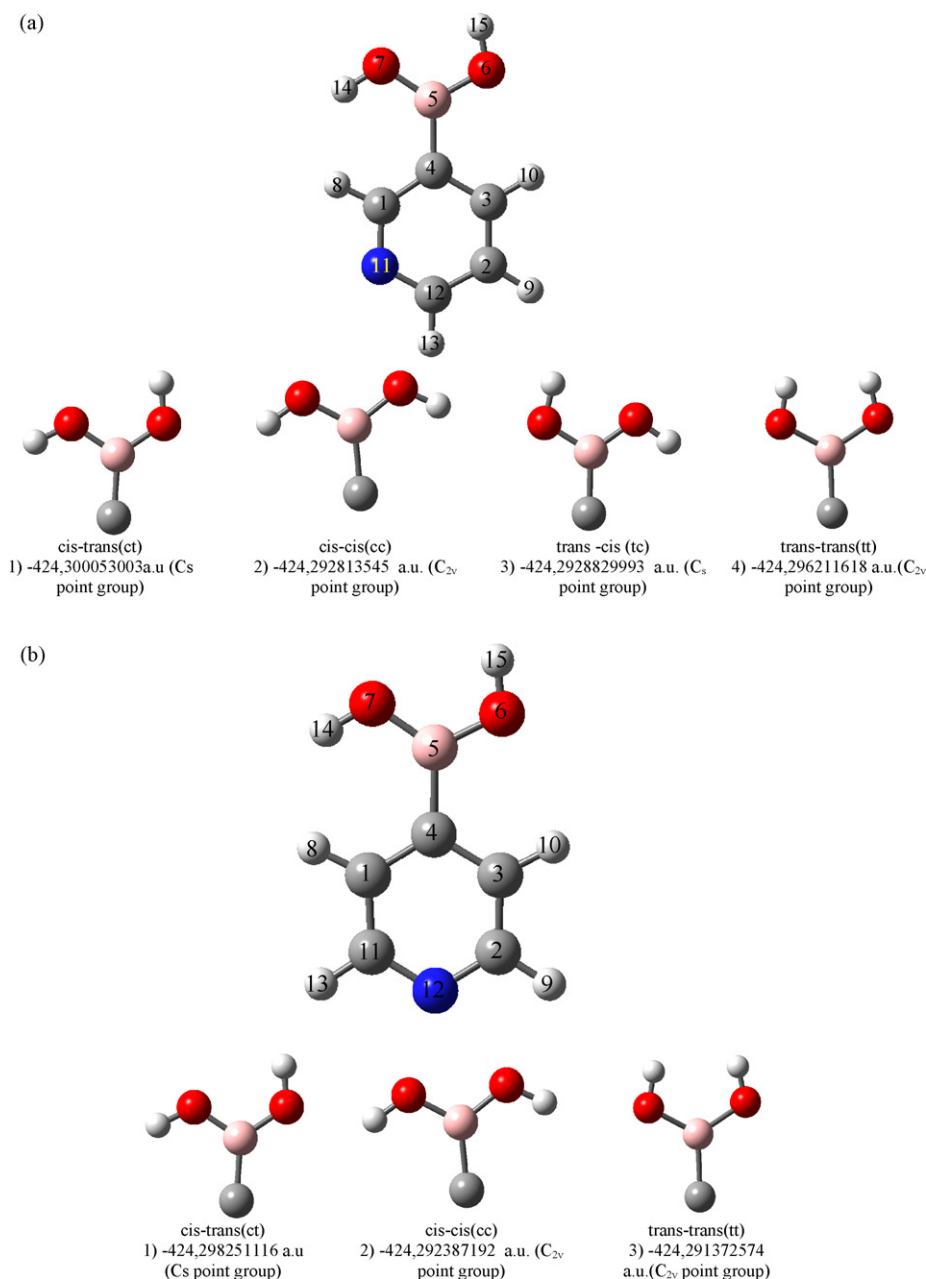


Fig. 1. (a) Structures of p3 relative conformations of boronic acid group and their energies (for 6-31G(d) basis set). (b) Structures of p4 relative conformations of boronic acid group and their energies (for 6-31G(d) basis set).

Table 1a
Geometric parameter set of p3 molecule for ct form

	P3	6-311++G(d,p)	6-311G(d,p)	6-311G(d)	6-31G(d,p)	6-31G(d)	Experiment [8]
R1	C1–C4	1.403	1.402	1.402	1.404	1.404	1.404
R2	C1–H8	1.090	1.090	1.091	1.092	1.093	1
R3	C1–H11	1.335	1.335	1.335	1.337	1.337	1.389
R4	C2–C3	1.390	1.389	1.389	1.392	1.392	1.390
R5	C2–H9	1.084	1.084	1.085	1.086	1.086	1
R6	C2–C12	1.394	1.394	1.394	1.396	1.396	–
R7	C3–C4	1.403	1.403	1.403	1.405	1.405	1.402
R8	C3–H10	1.084	1.084	1.085	1.086	1.086	1
R9	C4–B5	1.567	1.568	1.568	1.570	1.570	1.568
R10	B5–O6	1.366	1.364	1.363	1.366	1.367	1.362
R11	B5–O7	1.372	1.370	1.370	1.372	1.373	1.378
R12	O6–H15	0.964	0.963	0.964	0.966	0.970	0.75
R13	O7–H14	0.960	0.960	0.961	0.963	0.967	0.75
R14	N11–C12	1.337	1.337	1.336	1.340	1.339	–
R15	C12–C13	1.087	1.087	1.088	1.089	1.089	1
A1	C4–C1–H8	120.6	120.5	120.6	120.3	120.3	120
A2	C4–C1–N11	125.2	125.3	125.3	125.4	125.5	121.8
A3	H8–C1–N11	114.3	114.3	114.1	114.3	114.2	120
A4	C3–C2–H9	121.3	121.3	121.3	121.3	121.3	120
A5	C3–C2–C12	118.5	118.4	118.4	118.4	118.4	–
A6	H9–C2–C12	120.2	120.2	120.2	120.3	120.3	–
A7	C2–C3–C4	119.8	119.8	119.8	119.8	119.8	121.1
A8	C2–C3–H10	120.7	120.8	120.7	120.7	120.7	120
A9	C4–C3–H10	119.5	119.5	119.5	119.4	119.5	120
A10	C1–C4–C3	116.2	116.1	116.1	116.0	116.0	120
A11	C1–C4–B5	122.9	122.9	123.0	123.0	123.0	120.8
A12	C3–C4–B5	120.9	120.9	120.9	121.0	121.1	122
A13	C4–B5–O6	118.0	117.9	118.1	117.7	117.9	125
A14	C4–B5–O7	124.6	124.4	124.5	124.4	124.4	118.7
A15	O6–B5–O7	117.4	117.7	117.4	117.8	117.7	116.3
A16	B5–O6–H15	112.6	111.9	111.9	111.4	110.8	111
A17	B5–O7–H14	115.4	114.8	115.3	114.4	113.9	111
A18	C1–N11–C12	117.0	116.9	116.9	116.7	116.7	–
A19	C2–C12–N11	123.4	123.5	123.5	123.6	123.6	–
A20	C2–C12–C13	120.5	120.5	120.6	120.4	120.5	120
A21	N11–C12–C13	116.0	116.0	115.9	116.0	115.9	–

harmonic vibrational wavenumbers for small and medium sized molecules.

Five sets of vibrational frequencies for these species are calculated with hybrid method and then scaled by corresponding scaling factors.¹ In literature, there is no global scaling factor for B3LYP/6-311++G(d,p) basis set. Molecular geometry is restricted and all the calculations are performed by using Gauss View molecular visualisation program [20] and Gaussian 03 program package on the personal computer [21]. The programs allow one to examine, graphically, the G03 generated IR spectra. Then the spectral numerical data was copy to the Microsoft Excel™ Program XP version where the spectral ranges were edited.

4. Results and discussion

The molecules of p3 and p4 consist of 15 atoms, so it has 39 normal vibrational modes. Our first set of calculations involved

the investigation of the possible conformations of p3 and p4. There are four possible conformers for p3 and three possible conformers, illustrated in Fig. 1a and b, dependent on the positions of the hydrogen atoms bonded to oxygen, whether they are directed away from or toward the pyridine ring. Our calculations show that the four conformations for p3 and three conformations for p4, do not differ greatly in energy, but demonstrate that conformation *cis-trans* (abbreviated as ct) has the lowest energy. On the basis of a C_s symmetry the 39 fundamental vibrations ct and tc form of p3 and p4 can be distributed as 12A'' + 27A'. If we take into account C_{2v} symmetry cc and tt forms of p3 and p4 molecule, 39 normal vibrations can be distributed 14A₁ + 5A₂ + 7B₁ + 13B₂. In the cc, ct, tc and tt forms of molecule, boronic acid and benzene ring are in the same plane. The C_s structure is the lowest in energy at all levels. The molecular structure and numbering of the atoms of p3 and p4 are shown in Fig. 1a and b. We reported some geometric parameters and vibrational frequencies for p3 and p4 by using B3LYP comparing some observed bond lengths and bond angles for phenylboronic acid molecule. Vibrational assignment is based on solely on the B3LYP/6-31G(d) and B3LYP/6-311G(d,p) calculations.

¹ <http://srdata.nist.gov>.

Table 1b
Geometric parameter set of p4 molecule for ct form

	P4	6-311++G(d,p)	6-311G(d,p)	6-311G(d)	6-31G(d,p)	6-31G(d)	Experiment [8]
R1	C3–C4	1.402	1.401	1.401	1.404	1.404	1.404
R2	C3–H10	1.084	1.084	1.084	1.085	1.086	1
R3	C3–H13	1.393	1.392	1.392	1.394	1.395	1.389
R4	C11–C1	1.393	1.392	1.392	1.395	1.395	1.390
R5	C11–H13	1.087	1.087	1.088	1.089	1.089	1
R6	C11–N12	1.336	1.336	1.336	1.339	1.338	–
R7	C1–C4	1.401	1.401	1.401	1.403	1.403	1.402
R8	C1–H8	1.087	1.087	1.088	1.089	1.089	1
R9	C4–B5	1.573	1.574	1.573	1.576	1.575	1.568
R10	B5–O7	1.371	1.369	1.369	1.371	1.372	1.362
R11	B5–O6	1.364	1.362	1.361	1.364	1.365	1.378
R12	O7–H14	0.960	0.960	0.961	0.963	0.967	0.75
R13	O6–H15	0.963	0.963	0.964	0.966	0.970	0.75
R14	N12–C2	1.337	1.337	1.337	1.340	1.340	–
R15	C2–H9	1.1	1.1	1.1	1.1	1.089	1
A1	C4–C3–H10	120.1	120.0	120.1	120.0	120.1	120
A2	C4–C3–C2	119.7	119.7	119.7	119.8	119.8	121.8
A3	H10–C3–C2	120.1	120.2	120.2	120.2	120.2	120
A4	C1–C11–H13	120.4	120.4	120.5	120.3	120.4	120
A5	C1–C11–N12	123.4	123.5	123.5	123.5	123.5	–
A6	H13–C11–N12	116.2	116.1	116.0	116.1	116.1	–
A7	C11–C1–C4	120.0	120.0	120.0	120.0	120.0	121.1
A8	C11–C1–H8	118.3	118.4	118.3	118.4	118.4	120
A9	C4–C1–H8	121.7	121.7	121.8	121.6	121.6	120
A10	C3–C4–C1	116.2	116.2	116.2	116.1	116.1	120
A11	C3–C4–B5	120.5	120.6	120.5	120.6	120.7	120.8
A12	C1–C4–B5	123.3	123.2	123.3	123.3	123.2	122
A13	C4–B5–O7	124.2	124.0	124.1	124.1	124.1	125
A14	C4–B5–O6	118.1	118.0	118.1	117.8	117.9	118.7
A15	O7–B5–O6	117.8	118.0	117.8	118.1	118.0	116.3
A16	B5–O7–H14	115.3	114.6	115.0	114.1	113.7	111
A17	B5–O6–H15	112.9	112.2	112.1	111.6	110.9	111
A18	C11–N12–C2	117.1	117.0	116.9	116.8	116.8	–
A19	C3–C2–N12	123.6	123.7	123.7	123.8	123.8	–
A20	C3–C2–H9	120.4	120.4	120.5	120.3	120.3	120
A21	N12–C2–H9	116.0	115.9	115.8	116.0	115.9	–

5. Geometrical structures

The molecular structures of p3 and p4 have been not studied by X-ray diffraction. As the experimental values for p3 and p4 are not known so, theoretically calculated values may give an idea about the geometry of these molecules and also it gives the idea how geometry of these molecules changes from phenylboronic acid when we substitute N atom in place of C–H atoms. The phenylboronic acid molecule was studied by X-ray diffraction [8]. Total energies and geometry parameters of the molecule are given in Tables 1a and 1b, in accordance with the atom numbering scheme given in Fig. 1a and b. The p4 molecule can be all-*trans*, all-*cis* and mixed *trans–cis* or *cis–trans* relative to the B–C bond. The p3 molecule can also be all-*trans*, all-*cis* and mixed *trans–cis* relative to the B–C bond. According to theoretical results, the *cis–trans* (ct) conformation is the most stable for the p3 and p4 molecule. Both hydrogen are in the O–B–O plane. Most probably, the oxygen lone pairs have a resonance interaction with the empty p orbital of boron, which forces the hydrogen to be in the O–B–O plane. Thus, in the lowest-energy form of p3 and p4, the –B(OH)₂ groups are planar and at the

whole of computational levels, lie in the plane of the benzene ring. The calculated B–O and B–C bond lengths in p3 and p4 molecules are in good agreement with those found in the X-ray structure [8].

Theoretical calculations show that, C–H bonds for the phenylboronic acid are approximately equal to C–H bonds for p3 and p4. The similar treatments are valid between the C–C ring bond lengths and bond angles these molecules by using B3LYP/6-31G(d) level of theory. For example, in phenylboronic acid (=pba) molecule, ring C–C bond lengths vary from 1.386 to 1.394 range. In p3 and p4 molecules these bond lengths vary from ~1.360 to 1.400 ranges. In general, typical B–O distances are ~1.360 Å [9] consistent with relatively strong π -interactions. Conversely, the C–B bond length is slightly greater than that typically found in boroxines, indicating a weakening of this bond by the electron-withdrawing nature of the ring group. But by using HF/6-31G(d) levels of theory, for the few boronic acids including phenylboronic acid molecule, Chen et al. [7] found approximately same value of this bond length.

Bond angles at B and C are consistent sp² hybridization but with significant deviations from the expected 120° angles occur-

ring in close proximity the $-\text{B}(\text{OH})_2$ substituent on C_4 atoms for p3 and p4. In the phenylboronic acid, the experimental values of $\text{C}_1-\text{C}_4-\text{C}_3$, $\text{C}_5-\text{C}_6-\text{H}_9$ and $\text{C}_3-\text{C}_4-\text{H}_{11}$ angles are significantly smaller than the other $\text{C}-\text{C}-\text{C}$ and $\text{C}-\text{C}-\text{H}$ angles, respectively. Theoretical calculations are supported by these experimental results for p3 and p4 molecules (see Tables 1a and 1b).

As can be seen in Tables 1a and 1b, there is good agreement the bond angles at B and C_4 . In the pentafluorophenylboronic acid molecule [10], while $\text{C}_1-\text{C}_4-\text{B}$ bond angle is $\sim 122.6^\circ$, this bond angle varies from 122.9° to 123.3° for p3 and p4 formations. Experimental values of corresponding bond angle are 122.0° for pba [8], 121.9° for 1,4 phenylenediboronic acid [22]. There are excellent agreements between calculated and experimental bond angles by using B3LYP level of theory.

It is interesting that, there are no significant difference of $\text{C}_1-\text{C}_4-\text{H}_8$ bond angle between ct and cc forms, tc and tt of p3 molecules. In the case of p4, ct form of this bond angle is approximately equal to cc form. In the tt form, this bond angle is lower than $\sim 1^\circ$. The experimental results show that, the $-\text{B}(\text{OH})_2$ group is twisted by 21.4° , 35° , 38.14° , relative to the ring group for phenylboronic acid [8], 1,4-phenylenediboronic acid [22] and pentafluorophenylboronic acid [9], respectively. The corresponding calculated values are different from these values ($=0^\circ$), because both of ring and $\text{B}(\text{OH})_2$ groups lie in the same plane. Potential energy scan with the whole levels of theoretical approximation were performed along $\text{C}-\text{C}-\text{B}-\text{O}$ torsional angle of p3 and p4 molecules in order to localize the structures that correspond to the energy minima. All the geometrical parameters were simultaneously relaxed during the calculations while the $\text{C}-\text{C}-\text{B}-\text{O}$ torsional angle was varied in steps of 10° . The resulted potential energy curves depicted in Fig. 2 show ct forms for minimum energies.

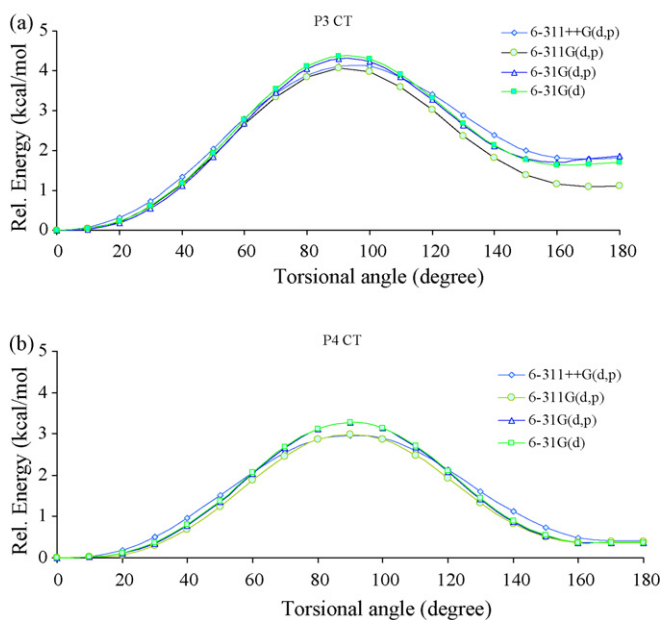


Fig. 2. (a) Torsion profile of $\text{C}-\text{C}-\text{B}-\text{O}$ in p3 ct form by B3LYP for selected basis sets. (b) Torsion profile of $\text{C}-\text{C}-\text{B}-\text{O}$ in p4 ct form by B3LYP for selected basis sets.

6. Vibrational spectra

In order to obtain the spectroscopic signature of the p3 and p4 molecules, studied in this work, we performed a frequency calculation analysis. Calculations were made for a free molecule in vacuum, while experiments were performed for solid samples, so there is disagreements between calculated and observed vibrational wavenumbers. Vibrational frequencies were calculated for p3 and p4 molecules using the B3LYP method and several basis sets. The theoretical frequencies obtained with the largest basis set (6-311G(d,p)) are in good agreement with their experimental ones. Tables 2a and 2b present the calculated vibrational frequencies and experimental values. According to the theoretical calculation, studied molecules have assumed to possess a planar structure of C_s point group symmetry. The 39 normal vibrations are distributed as $12A'' + 27A'$ considering C_s symmetry. All the 39 fundamental vibrations are active in both IR and Raman.

The C_s structure was the lowest in energy at all levels. Therefore we ignored the cc and tt conformations (both of them belong to C_{2v} symmetry) of the molecule. All of the calculated modes are numbered from the largest to the smallest frequency within each fundamental wave numbers, $\bar{\nu}$. On the basis of our calculations, and experimental infrared and Raman spectra, we made a reliable one-to-one correspondence between our fundamentals and any of our frequencies calculated by the B3LYP method.

Owing to lack of enough detailed experimental data for p3 and p4 molecules, the vibrational spectra were obtained by molecular orbital calculation using Gaussian 03. Because in the spectra, low infrared and Raman intensities of some modes make difficult their observation in the (Figs. 3 and 4) infrared and Raman spectra. Vibrational modes of p3 and p4 were investigated by harmonic frequency calculations performed at the corresponding energy optimised geometries. The assignment of the vibrational absorptions was made by the comparison with the related molecules and also with the results obtained from the theoretical calculations. The descriptions of the modes presented here are only approximate, being some of the vibration mixed together.

Except the mode at 3320 (vs.) cm^{-1} for p4 IR spectrum experimentally, there are no any peaks at the IR and Raman spectrum in OH stretching region for both p3 and p4. The calculated values of O–H stretching modes are overestimated

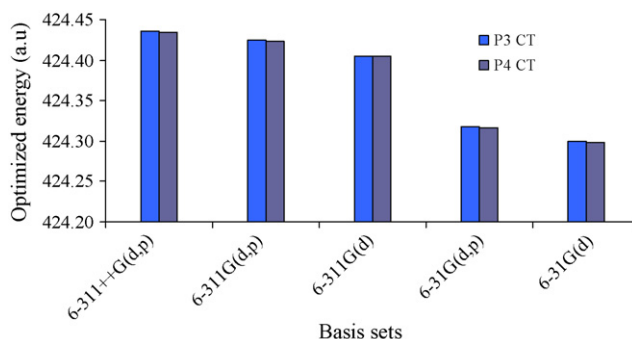


Fig. 3. Comparison of different basis sets for calculated energies (in a.u. units).

Table 2a

Experimental and calculated fundamental harmonic frequencies^a infrared intensities^b and scattering activities^c for p3 molecule (ct form for selected basis sets)

		6-31G(d)	Scaled	I_{Infrared}	I_{Raman}		6-311G(d,p)	Scaled	I_{Infrared}	I_{Raman}	p3 IR	p3 Raman	Approximate mode descriptions
1	A'	3808	3657	30.77	44.54	A'	3884	3755	42.63	44.51			OH str
2	A'	3769	3619	57.19	181.94	A'	3845	3717	75.41	174.19			OH str
3	A'	3216	3088	14.14	147.69	A'	3192	3086	13.31	164.97	3099 m	3082m	CH str
4	A'	3201	3073	12.02	83.42	A'	3177	3071	8.92	84.34	3032 m	3050m	CH str
5	A'	3171	3046	19.84	117.24	A'	3146	3042	16.39	127.57			CH str
6	A'	3121	2997	62.14	92.43	A'	3101	2998	52.93	100.75	1612 m	1607w	CH str
7	A'	1650	1584	78.28	42.77	A'	1631	1577	78.38	41.77	1593 m, 1574 m	1588w	ring CC, CN str
8	A'	1621	1557	29.79	4.42	A'	1603	1550	29.85	4.01	1484 m		ring CC, CN str
9	A'	1531	1470	9.98	0.66	A'	1512	1462	8.75	0.92	1426 vs	1308vw	ring CC, CN str
10	A'	1470	1412	109.93	2.42	A'	1454	1405	103.87	1.93	1368 vs		ring CCH, NCH bend.
11	A'	1418	1362	141.97	1.74	A'	1400	1353	149.70	2.14	1311 vs	1187vw	ring CCH, NCH bend.
12	A'	1391	1336	384.12	15.32	A'	1377	1331	391.77	13.61			BC str+ip BOH +BCC+CCH+NCH bend.
13	A'	1377	1322	40.93	3.04	A'	1358	1313	18.50	2.19	1228 m	1036vs	ip CCH bend.
14	A'	1303	1251	2.28	2.79	A'	1278	1236	1.77	2.38	1208 m		ip CC, NC str+CCH, NCH bend.
15	A'	1243	1194	18.74	8.00	A'	1229	1188	20.08	6.75	1157 s	994w	Íp CCH+NCH bend.+NC, CC str
16	A'	1154	1109	47.97	1.68	A'	1146	1108	50.52	1.64	1086 vs		Íp CCH+NCH+BOH bend.
17	A'	1140	1095	16.82	4.58	A'	1129	1092	10.09	4.33	1061 m	753vw	Íp CCH+NCH+BOH bend.
18	A'	1067	1025	7.03	24.89	A'	1059	1024	6.64	27.69	1003 m		Ring CC+CN str+BOH bend.
19	A'	1046	1005	22.05	6.93	A'	1044	1010	3.46	7.60		236m	ip CNC+CCC bend.+ BOH+CCH bend.
20	A'	1036	995	142.85	2.51	A'	1031	997	160.10	2.88	964 m	178vw	Íp BO str+BOH bend.
21	A''	1013	972	0.12	0.16	A''	1019	986	0.02	0.03			oop CH bend.
22	A''	1000	960	123.93	2.17	A''	995	962	123.14	1.58	868 m	82vs	Íp BO str+BOH bend.
23	A''	987	947	0.30	2.16	A''	989	956	0.10	0.32	817, 803 s		oop CH bend.
24	A''	950	912	0.02	2.74	A''	946	915	0.08	0.63	765 m, 746 m		oop CH bend.
25	A''	830	798	5.18	1.64	A''	832	804	5.64	0.38	715 vs		oop CH bend.
26	A'	758	728	6.92	8.92	A'	758	733	6.67	9.49	688 m		BC str+CCC +CCN bend.
27	A''	730	701	28.27	0.34	A''	732	708	44.20	0.08	643 m		oop ring CCH bend.
28	A''	662	636	66.98	0.30	A''	676	654	66.61	0.22	592 m		oop CBO +CCC+CCN bend.
29	A'	639	614	8.55	5.36	A'	640	619	8.35	5.59			Íp BCC+CCC+NCC+OBO bend.
30	A''	585	562	34.39	3.66	A''	579	560	35.05	2.56	476 w		oop OH+ CH bend.
31	A'	541	519	30.97	2.73	A'	542	524	32.15	2.69			Íp OBO+CCC+CNC bend.
32	A''	476	458	165.39	1.22	A''	471	455	145.94	1.12			oop OH bend.
33	A'	421	405	1.75	0.98	A'	421	407	1.65	0.87			Íp CCB+CBO bend.
34	A''	417	400	0.94	1.65	A''	416	402	1.08	1.23			CCH, NCH, BOH oop bend.
35	A''	379	364	2.30	0.08	A''	376	364	1.53	0.06			CCH, NCH out of plane bend.
36	A'	333	320	7.10	2.61	A'	332	321	6.92	2.79			OBO bend.+BC str
37	A'	170	163	5.50	0.25	A'	168	162	5.78	0.23			in plane OBC bend.
38	A''	142	136	0.02	4.02	A''	140	135	0.11	3.81			Out of plane bend.
39	A''	8	7	7.37	1.13	A''	18	17	6.73	0.98			OBCC torsion

m: middle, s: strong, vs: very strong, w: weak, vw: very weak, str: stretching, ip: in plane, bend.: bending, oop: out-of-plane.

^a Frequencies in cm^{-1} .^b Intensities in km/mol .^c Raman scattering activities.

Table 2b

Experimental and calculated fundamental harmonic frequencies^a infrared intensities^b and Raman scattering activities^c for p4 molecule (ct form for selected basis sets)

		6-31G(d)	Scaled	I_{infrared}	I_{Raman}		6-311G(d,p)	Scaled	I_{infrared}	I_{Raman}	P4 IR	P4 Raman	Approximate mode descriptions
1	A'	3807	3656	27.76	46.35	A'	3882	3753	39.41	46.53			OH str
2	A'	3769	3620	59.68	174.57	A'	3846	3718	78.76	165.32	3320 vs		OH str
3	A'	3217	3089	8.18	103.95	A'	3192	3086	7.04	113.38		3075m	CH str
4	A'	3177	3051	26.85	189.42	A'	3153	3048	28.17	211.87	3089 m		CH str
5	A'	3171	3045	46.67	88.67	A'	3145	3040	38.88	91.48	3051m	1621m	CH str
6	A'	3150	3025	21.87	63.54	A'	3130	3026	14.56	68.79	3013 w (sh)		CH str
7	A'	1657	1591	0.18	28.57	A'	1639	1585	0.15	26.18	1626 s	1239vw	ring CC, CN str
8	A'	1600	1536	2.99	1.54	A'	1583	1530	3.02	1.56	1542 vw	1210w	ring CC, CN str
9	A'	1545	1484	11.85	2.24	A'	1526	1475	10.80	2.82	1433 s	1158vw	ring CC, CN str
10	A'	1460	1402	157.04	1.41	A'	1443	1395	146.67	1.43			ring CCH, NCH bend.
11	A'	1431	1374	143.42	1.87	A'	1413	1366	155.60	2.13	1318 s	1067m	ring CCH, NCH bend.
12	A'	1386	1331	431.92	16.07	A'	1372	1327	419.34	14.30	1286 s	1046 m	BC str+ip BOH +BCC+CCH+NCH bend.
13	A'	1361	1307	3.28	4.32	A'	1346	1301	3.56	3.10	1240 m		ip CCH bend.
14	A'	1285	1234	4.85	3.61	A'	1260	1218	5.21	3.78	1215 m	770 vw	ip CC, NC str+CCH, NCH bend.
15	A'	1260	1210	1.33	11.01	A'	1247	1206	1.75	9.12	1157 s	740 m	ip CCH+NCH bend.+NC, CC str
16	A'	1148	1103	43.40	6.91	A'	1138	1100	40.48	8.90		662m	ip CCH+NCH+BOH bend.
17	A'	1122	1077	1.68	0.93	A'	1110	1073	0.72	0.92	1073 m	602 vw	ip CCH+NCH+BOH bend.
18	A'	1102	1059	4.83	7.44	A'	1096	1060	3.83	5.80	1054 m-sh		Ring CC+CN str+BOH bend.
19	A'	1039	997	141.42	2.55	A'	1031	997	137.16	2.90		363 s	ip CNC+CCC bend.+ BOH+CCH bend.
20	A'	1013	972	11.30	18.82	A''	1013	979	0.05	0.26	957 vs	284 vw	ip BO str+BOH bend.
21	A''	1002	962	0.16	1.12	A'	1011	977	8.61	23.76	874 w	116 s	oop CH bend.
22	A'	997	958	123.54	4.43	A'	992	960	124.23	2.59	848 w	93 vs	ip BO str+BOH bend.
23	A''	980	941	0.13	1.71	A''	985	953	0.01	0.34		66 s	oop CH bend.
24	A''	906	870	0.20	4.46	A''	904	874	0.49	0.93	784 vs		oop CH bend.
25	A''	830	797	12.12	0.24	A''	830	802	14.32	0.14	746 vs		oop CH bend.
26	A''	766	735	1.25	0.16	A''	769	744	5.26	0.09	675 vs		BC str+CCC +CCN bend.
27	A'	735	706	9.35	8.49	A'	736	712	8.90	8.79	573 w		oop ring CCH bend.
28	A'	686	658	0.69	6.38	A'	685	662	0.75	6.42	508 w		oop CBO +CCC+CCN bend.
29	A''	659	633	107.19	0.01	A''	671	648	112.62	0.01	463 vw		ip BCC+CCC+NCC+OBO bend.
30	A''	592	569	12.62	5.42	A''	586	566	12.92	3.80			oop OH+ CH bend.
31	A'	530	509	43.65	2.04	A'	532	514	45.26	2.06			ip OBO+CCC+CNC bend.
32	A''	481	462	166.55	0.97	A''	478	462	150.86	0.91			oop OH bend.
33	A''	428	411	2.70	0.14	A''	426	412	4.29	0.11			ip CCB+CBO bend.
34	A'	421	405	4.46	0.85	A'	421	407	4.31	0.75			CCH, NCH, BOH oop bend.
35	A''	379	364	4.35	0.07	A''	377	365	3.65	0.03			CCH, NCH out of plane bend.
36	A'	327	314	6.28	2.28	A'	326	315	6.03	2.43			OBO bend.+BC str
37	A'	168	162	3.18	0.05	A'	166	160	3.48	0.05			in plane OBC bend.
38	A''	139	134	0.77	2.27	A''	138	133	0.48	2.11			Out of plane bend.
39	A''	-17	-16	3.02	1.75	A''	-10	-9	2.61	1.60			OBCC torsion

m: middle, s: strong, vs: very strong, w: weak, vw: very weak, str: stretching, ip: in plane, bend.: bending, oop: out-of-plane.

^a Frequencies in cm^{-1} .^b Intensities in km/mol .^c Raman scattering activities.

about 300 cm^{-1} for 6-31G(d), 398 cm^{-1} for 6-311G(d,p) for p4 molecule. Best reliable value is 3620 cm^{-1} harmonic calculation for the B3LYP method. In the high frequency region, calculated 6-31G(d) values are more reliable than 6-311G(d,p) basis set.

Empirical assignments of vibrational modes for peaks in the fingerprint region are difficult. In the wavenumber region of $600\text{--}1660\text{ cm}^{-1}$, the spectrum observed in the experiments closely resembles the calculated spectrum, except for differences in details.

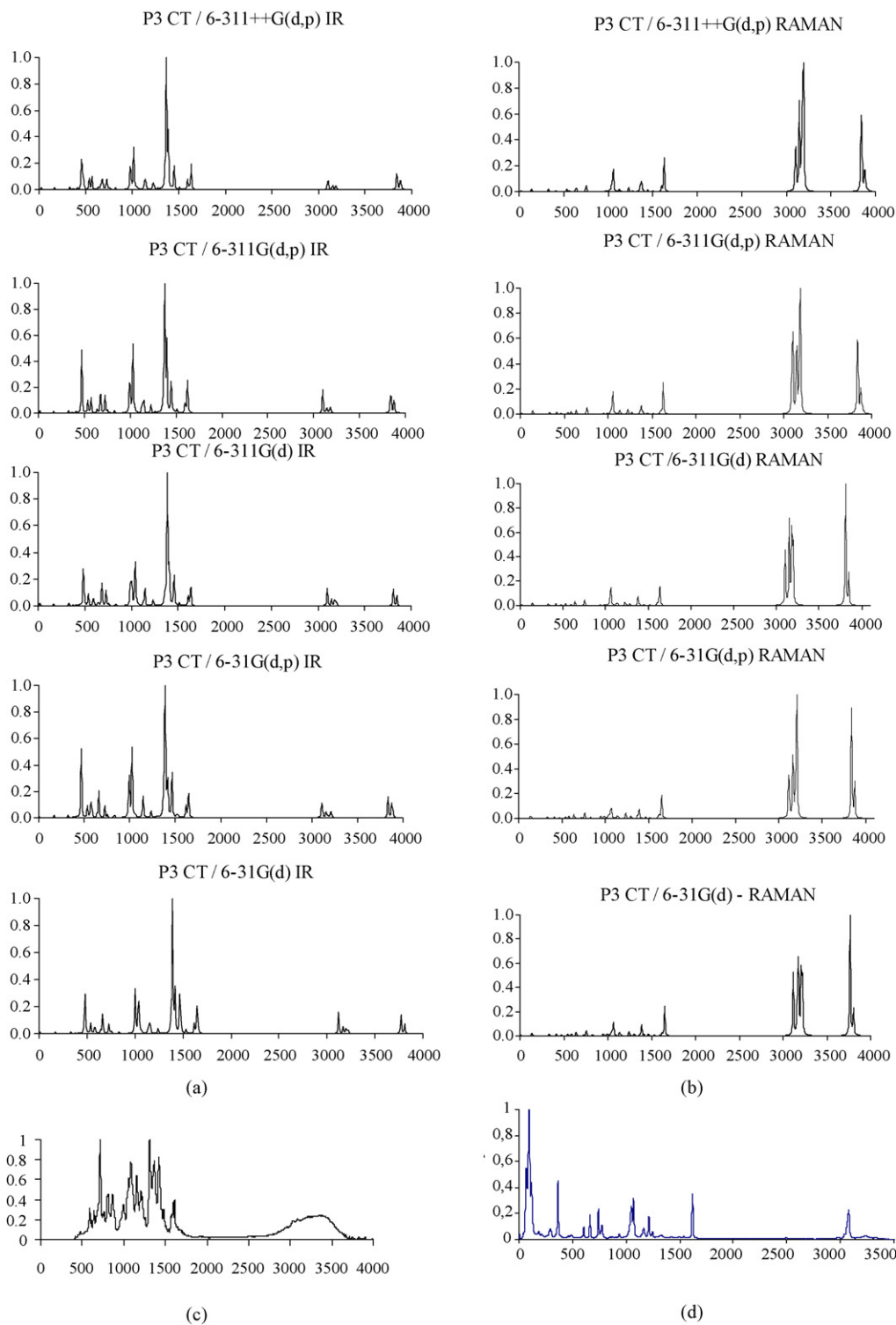


Fig. 4. (A) Comparison of connected frequencies in cm^{-1} for p3 ct form and normalized IR intensity and Raman scattering activities at each level of calculations considered. (a) Calculated IR spectrum, (b) calculated Raman spectrum, for studied basis sets, (c) experimental IR spectrum and (d) experimental Raman spectrum. (B) Comparison of connected frequencies in cm^{-1} for p4 ct form and normalized IR intensities and Raman scattering activities at each level of calculations considered. (a) Calculated IR spectrum, (b) calculated Raman spectrum for studied basic sets, (c) experimental IR spectrum and (d) experimental Raman spectrum.

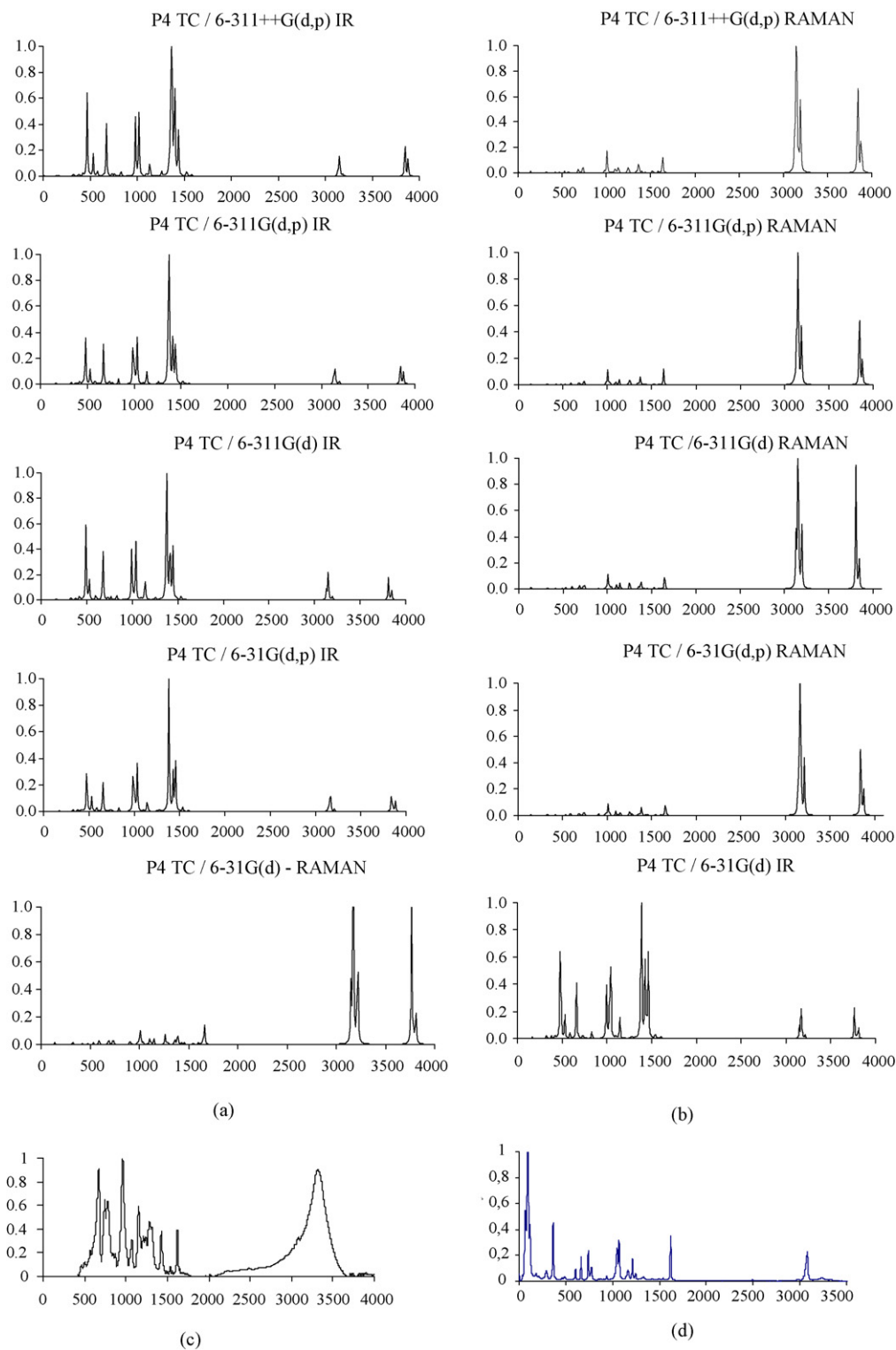


Fig. 4. (Continued).

The experimental sharp and strong bands at $\sim 1600\text{ cm}^{-1}$ may come from the absorption due to the stretching vibration of the C–C bond, and bending vibration of the C–C–C in the ring part. These bands observed at 1649 cm^{-1} (IR), 1657 cm^{-1} (IR), 1634 (IR)– 1633 (Ra), for the pentafluorobenzene, alfa-bromopentafluoro-toluene [23] and $\text{C}_6\text{F}_5\text{I}$ [24] molecules, respectively.

With the $\text{B}(\text{OH})_2$ coordination these modes are not changing significantly. Therefore the modes at $\sim 1600\text{ cm}^{-1}$ are insensitive with the $\text{B}(\text{OH})_2$ coordination. If we consider phenylboronic acid case, the band at 1607 cm^{-1} shifted to 1657 cm^{-1} for pentafluorophenylboronic acid. Similar comparative analysis has been made for the other selected strong or medium bands.

As seen in Tables 2a and 2b, calculated modes mixed with, C–H, pyridine C–N, C–C and boronic acid group modes in different proportions.

7. Conclusion

Attempts have been made in the present work for the molecular conformational parameters and frequency assignments for the compound p3 and p4 from the FTIR and FT-Raman spectra. With regard to the C–B bonds, we considered the conformations *cis–cis*, *trans–trans*, *cis–trans* and *trans–cis*. We found a preference for *cis–trans* conformation for both p3 and p4. With the equilibrium geometries, harmonic frequencies of p3 and p4 were determined and analyzed at DFT level of theory utilizing 6-31G(d), 6-31G(d,p), 6-311G(d), 6-311G(d,p) and 6-311++G(d,p) basis sets. There is a great mixing of the ring vibrational modes and also between the ring and substituent modes. The descriptions of the C–H, pyridine C–N, C–C and boronic acid group modes are very difficult due to low symmetry of the molecules. Because there is not regularity in the change of wavenumbers of the analysed band along with the position of the substituted B(OH)₂ group in the aromatic ring.

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