Hindawi Publishing Corporation
Journal of Spectroscopy
Volume 2014, Article ID 247237, 8 pages
http://dx.doi.org/10.1155/2014/247237

Research Article

Structure Characterization of [*N*-Phenylamino(2-boronphenyl)-*R*-methyl]phosphonic Acid by Vibrational Spectroscopy and Density Functional Theory Calculations

Natalia Piergies[1] and Edyta Proniewicz[2]

[1] *Faculty of Chemistry, Jagiellonian University, Ulice Ingardena 3, 30-060 Krakow, Poland*
[2] *Faculty of Foundry Engineering, AGH University of Science and Technology, Ulice Reymonta 23, 30-059 Krakow, Poland*

Correspondence should be addressed to Edyta Proniewicz; proniewi@agh.edu.pl

Received 2 September 2013; Accepted 23 November 2013; Published 23 January 2014

Academic Editor: Yizhuang Xu

We present the first Fourier-transform infrared absorption (FT-IR) and Fourier-transform Raman (FT-Raman) analysis of vibrational structure of [*N*-phenylamino(2-boronphenyl)-*R*-methyl]phosphonic acid ([PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2). Assignments of experimental wavenumbers are based on performed theoretical calculations using density functional theory (DFT). Theoretical calculations show that the most stable structure of the investigated molecule is dimer in *cis-trans* conformation created by a pair of intermolecular hydrogen bonds between the boron hydroxyl groups of two monomers.

1. Introduction

In recent years aminophosphonic acids gain the attention and interest of the researchers because of their diverse and interesting biological activities [1–4]. These compounds are defined as amino acid derivatives, in which the carboxylic acid group [–C(=O)OH] is replaced by the phosphonic acid moiety [–P(=O)$(OH)_2$] [5]. Such modification inhibits the activity of certain enzymes by effective competition for the active site of the enzyme and by forming strong electrostatic binding [6]. Thus, the aminophosphonic acids found application as enzyme inhibitors [6–8] and medical [9, 10] and herbicidal agents [5]. α-Amino boronic acids also demonstrate high potential in medical chemistry [11, 12], especially as anticancer therapy agents [13], antibiotics [14], and enzymes inhibitors [15]. This is due to the boronic acid moiety ability to create hydrogen bonds and stable covalent bonds in the enzyme active side [12, 16].

The unique properties of the phosphonic and boronic acid groups cause that the amino acids analogues containing these functional groups become very attractive molecular systems. Therefore, we present the first vibrational characteristic of [*N*-phenylamino(2-boronphenyl)-*R*-methyl]phosphonic acid ([PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2) (see Figure 1 for molecular structure) considered as potential protease and kinase inhibitor. We used Fourier-transform Raman spectroscopy to investigate the vibrations and structure of the abovementioned compound. Because the absorption infrared method gives complementary information to the Raman method, supports the Raman analysis, and helps to solve ambiguities during this analysis, the absorption infrared spectra are also examined. Both these methods are commonly employed in both experimental investigations [17–20] and theoretical calculations [21–23] to analyze and compare structures for a large number of conformers of the investigated compounds. Interpreting the Raman and absorption infrared spectra involves explaining spectral regions and wavenumbers based on likely vibrational modes. Such an understanding of a molecule's vibrational spectrum is essential for explaining the relation between the molecular

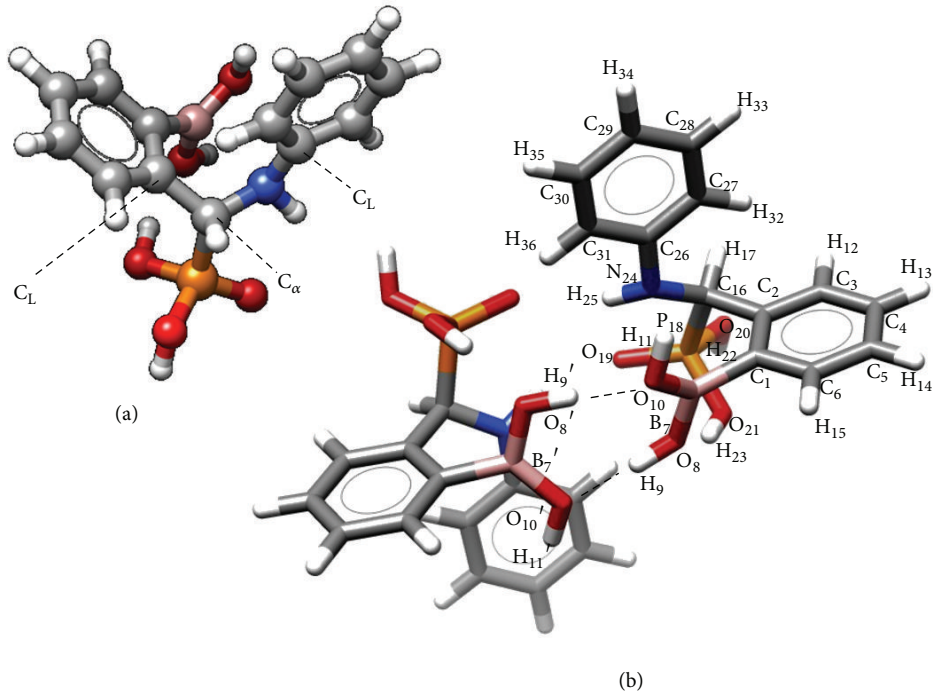

FIGURE 1: The molecular structure of [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$ monomer (a) and dimer structure (b) (where C_L denotes carbon atom of the aromatic ring connected to the aliphatic chain).

structure and spectral response. To provide the definitive band assignments needed to generate vibrational spectra useful for structural analysis, we performed vibrational analysis using Density Functional Theory (DFT) calculations at the B3LYP/6-311G(d,p) level of theory. Our aim is to produce an extensive look-up table of infrared and Raman spectra that can make structure determination a fast and accurate process.

2. Materials and Methods

2.1. [N-phenylamino(2-boronphenyl)-R-methyl]phosphonic Acid Synthesis. The investigated compound was synthesized according to the previous published procedure [24]. Its purity and chemical structure were checked using ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectroscopy (Bruker Avance DRX 300 MHz spectrometer, Bruker Polska, Poznań) and ESI-MS (Bruker MicrOTOF-Q spectrometer, Bruker Polska, Poznań).

2.2. FT-Raman Measurements. A Nicolet spectrometer (model NXR 9650) equipped with a liquid-nitrogen-cooled germanium detector was used for the FT-Raman measurements of [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$ on a glass plate. The 1064 nm line from a continuous-wave Nd^{3+}:YAG laser was used as an excitation source with a power output of 500 mW. During the measurements, 1000 scans were collected with a resolution of 4 cm^{-1}.

2.3. FT-IR Measurements. FT-IR spectra were obtained for thin pellets containing about 1 mg of [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$ dispersed in 200 mg KBr at room temperature. These measurements were carried out using a Bruker spectrometer (EQUINOX 55) equipped with a DT-GS detector in the range of 400–4000 cm^{-1} with a Nernst rod as an excitation source.

2.4. Theoretical Analysis. To optimize the ground-state geometry of [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$ and to calculate their FT-Raman and FT-IR spectra, the Gaussian 03 suite was used [25]. Our earlier analysis of various types of *N*-benzylamino(boronphenyl) methylphosphonic acids [26] and a literature study for similar compounds [27, 28] noted that the most stable structure of the boronic acid derivatives is a cyclic dimer formed by a pair of intermolecular hydrogen bonds between the boron hydroxyl groups of two monomers. Based on previous experience, here we present the theoretical calculations for the most stable structure of the substituted phenylboronic acid dimer (Figure 1). We also performed calculations for the monomer (not shown) and compare its energy with the energy of the corresponding dimer. The calculated stabilization of the energy indicates that dimer is more stable than monomer ($E_{\text{dimer}} = -1634029$ kcal/mol, $E_{\text{monomer}} = -817006$ kcal/mol).

A DFT method with the B3LYP level of theory was employed to optimize the molecular structure of [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$. The triple-split valence basis with a polarization function on heavy atoms and hydrogens (6-311G(d,p)) was applied as the basis set [29]. This type of basis was applied for the calculations of similar phenylboronic acid derivatives and provides reliable results [27, 28]. No imaginary wavenumbers were observed during optimization, which demonstrates that the calculated structure correspond

to energy minima on the potential energy surface for nuclear motion.

Theoretical Raman intensities were calculated by the Raint program, which uses the following relationship [30]:

$$I_i^R = 10^{-12}(\nu_0 - \nu_i)^4 \nu_i^{-1} S_i \quad (1)$$

in which I_i is given in arbitrary units, ν_0 is the laser excitation wavenumber [cm^{-1}] (9398.5 cm^{-1} for a Nd:YAG laser), ν_i is the frequency of the normal mode obtained from the DFT calculation, and S_i is the Raman scattering activity of the normal mode.

The theoretical vibrational spectra were generated by the free GaussSum 0.8 software package [31]. The calculated wavenumbers were scaled by a scaling factor of 0.987, and the theoretical spectra were plotted by setting the full width at half maximum (FWHM) at 11 cm^{-1} (the average value of a typical FWHM for these compounds in the condensed phase with a 50%/50% Gaussian/Lorentzian band shape). This scaling factor and FWHM were fitted based on the comparison between the wavenumbers and shape of bands of theoretical and experimental spectra. This procedure was used in order to better reproduce the experimental results.

To obtain normal mode assignments for the calculated vibrational bands, the potential energy distribution (PED) for the optimized structures was determined with the freeware Gar2ped program [32] in conjunction with a visualization script.

3. Results and Discussion

3.1. Geometric Structures. The most stable structure of [PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2 is a cyclic dimer formed by a pair of intermolecular hydrogen bonds between the boron hydroxyl groups of two monomers. Thus, the theoretical spectra presented are calculated for dimer. For this dimer specie, there are two possible conformers (*cis-trans* and *trans-cis*) depending on the positions of the hydrogen atoms bonded to the oxygen atom of the boronic group, whether they are directed away from (*trans*) or toward (*cis*) the phenylboronic ring. Our calculations show that the *cis-trans* conformation has the lowest energy; thus, it is the most stable. The molecular structure and numbering scheme of the atoms of the investigated compounds are given in Figure 1, while Table 1 lists some geometric parameters for this molecule.

The O_8–B_7–O_{10} and O_8'–B_7'–O_{10}' moieties in the presented dimer are almost perpendicular to the ring. This structure is promoted by possible interaction between nitrogen and boron atoms [33]. The hydrogen atoms of both boronic groups in the dimers (H_9, H_{10}, H_9', and H_{10}') lie in the O–B–O plane (Figure 1). This could be explained on the basis of the oxygen lone-electron pairs having a resonance interaction with the empty p-orbital of the boron atom, forcing the hydrogen atoms to be in the O–B–O plane [34]. The calculated B–O and C–B bond lengths (Table 1) for [PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2 are in good agreement with those present in the X-ray structure of phenylboronic (B–O: 1.362 Å—*cis* H (atom H directed toward the phenylboronic ring), 1.378 Å—*trans* H (atom H directed toward the phenylboronic ring); C–B: 1.568 Å) [33] and pentafluorophenylboronic (B–O: 1.362 Å—*cis* H, 1.355 Å—*trans* H; C–B: 1.579 Å) acids [34]. The calculated B_7–O_8 and B_7–O_{10} (Table 1) bonds distance (~1.371 Å) for the investigated compound indicates typical B–O length of phenylboronic acid derivatives which lie in the range of 1.35–1.38 Å [33].

Table 1: Select calculated bond lengths and angles of the [PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2 dimer.

Bond	Bond length [Å]	Bond	Bond length [Å]	Angle	[°]
C_1–C_2	1.406	P_{18}–O_{19}	1.485	C_1–B_7–O_8	117.1
C_2–C_3	1.394	P_{18}–O_{20}	1.613	B_7–O_8–H_9	116.5
C_3–C_4	1.392	P_{18}–O_{21}	1.605	O_8–B_7–O_{10}	117.2
C_4–C_5	1.391	O_{20}–H_{22}	0.964	C_1–B_7–O_{10}	124.9
C_5–C_6	1.393	O_{21}–H_{23}	0.982	B_7–O_{10}–H_{11}	112.7
C_6–C_1	1.401	C_{16}–N_{24}	1.458	B_7–O_{10}–H_9'	114.4
C_1–B_7	1.575	N_{24}–H_{25}	1.020	B_7'–O_{10}'–H_9	114.4
B_7–O_8	1.371	N_{24}–C_{26}	1.410		
O_8–H_9	0.979	C_{26}–C_{27}	1.407		
H_9–O_{10}'	1.826	C_{27}–C_{28}	1.387		
B_7–O_{10}	1.382	C_{28}–C_{29}	1.396		
O_{10}–H_{11}	0.963	C_{29}–C_{30}	1.389		
O_{10}–H_9'	1.826	C_{30}–C_{31}	1.395		
C_2–C_{16}	1.524	C_{31}–C_{26}	1.402		
C_{16}–P_{18}	1.863				

3.2. FT-Raman, FT-IR, and DFT Studies. Figure 2 shows the experimental (black traces) and theoretical (red traces) FT-Raman and FT-IR spectra of [PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2 in the spectral range between 3650 and 400 cm^{-1}, whereas Table 2 summarizes the experimental and theoretical band wavenumbers with the calculated (DFT, B3LYP/6-311 G(d,p)) potential energy distribution (PED, in %) (the whole PED information is provided in Table S1 in Supplementary Material available online at http://dx.doi.org/10.1155/2014/247237). The given vibrational analysis is also based on our earlier investigations of [*N*-benzylamino(boronphenyl)methyl] [26], fluoro- and formyl [35], and phenyl [36–38] analogues of phosphonic acids.

Aromatic Vibrations. The 3069/3056, 1606, 1588, 1188, 1161, 1031, 1008/999, 775, 617, and 490 cm^{-1} spectral features due to the characteristic phenyl ring vibrations (see Table 2 for precise bands assignment) dominate the [PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2 Raman spectrum (Figure 2, the top black trace). The noticeable spectral shift to lower wavenumbers for the ν_2, ν_{8a}, and ν_{12} modes of the phenylboronic ring compared to that of phenyl reflects some redistribution of the π-electrons caused by the electron donor character of the boronic acid group (acceptor). Some of the ring bands are also observed in the corresponding FT-IR spectrum (at 3058, 1604, 1590, 1177, 998/983, and 777 cm^{-1}). These bands are associated with the ν_2, ν_{8a}, ν_{8b}, ν_{9a}/ν_{15}, ν_{12}, and ν_{11}

Table 2: The calculated wavenumbers and potential energy distribution (PED, %) for the FT-Raman and FT-IR spectra of [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$[a].

Wavenumbers/cm^{-1}			Assignment
Calc.	Exp.		
	FT-Raman	FT-IR	B3LYP/6-311G(d,p) (PED %; >5%)
449	432	430	$\gamma_{as}(\phi)_B(31)$, $\delta_{oop}(CC_L(C_\alpha)C)_{\phi B}$, $\delta_s(C_\alpha PO_3)$, $\delta_{p(bridge)}$
451	474		$\gamma_{as}(\phi)_B(29)$, $\delta_{oop}(CC_L(C_\alpha)C)_{\phi B}$, $\delta_s(C_\alpha PO_3)$, $\gamma_{as(bridge)}$
499	490	491	$\boldsymbol{\delta_{p(bridge)}}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$, $\boldsymbol{\delta_{oop}(CC_L(C_\alpha)C)_{\phi B}}$
531		533	$\delta_{p(bridge)}$, $\gamma_{s(bridge)}$, $\gamma_{as(bridge)}$
553	543		$\boldsymbol{\delta_{p(bridge)}(48)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$
581	591	591	$\boldsymbol{\delta_{p(bridge)}(36)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$
627	617	617	$\boldsymbol{\delta_{as}(\phi)(34)}$, $\boldsymbol{\delta_{oop}(CBO_2)}$, $\boldsymbol{\gamma_{as(bridge)}}$, $\boldsymbol{\gamma_{s(bridge)}}$
659	635	636	$\delta_{p(bridge)}(25)$, $\gamma_{as(bridge)}$, $\gamma_{s(bridge)}$
696		688	$\boldsymbol{\delta_{p(bridge)}(46)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$
717		710	$\boldsymbol{\gamma_{as(bridge)}(32)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\delta_{p(bridge)}}$
720	722		$\boldsymbol{\delta_{p(bridge)}(49)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$
746	**745**	**742**	$\boldsymbol{\delta_{p(bridge)}(18)}$, $\boldsymbol{\delta_p(\phi)_B}$, $\boldsymbol{\gamma_{s(bridge)}}$
793	775	777	$\delta_{oop}(CC_L(C_\alpha)C)_{\phi B}(36)$, $\delta_p(\phi)_B$, $\delta_{oop}(C_L C_{B(OH)_2}(B)C)_{\phi B}$
822	808	809	$\delta_{p(bridge)}(43)$, $\gamma_{s(bridge)}$, $\gamma_{as(bridge)}$
823	826	827	$\nu(PO)(12)$, $\gamma_{as(bridge)}$
886	884	882	$\boldsymbol{\delta_{p(bridge)}(35)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$
919	899	903	$\boldsymbol{\nu(PO)(30)}$, $\boldsymbol{\delta_{oop}(CC_L(C_\alpha)C)_{\phi B}}$
924		924	$\boldsymbol{\nu(PO)(22)}$, $\boldsymbol{\delta_{p(bridge)}}$
952	934		$\delta_{oop}(C_{B(OH)_2}C(H)C)_{\phi B}(27)$, $\delta_{oop}(C_L C(H)C)_{\phi B}$, $\delta_{oop}(CC(H)C)_{\phi B}$, $\gamma_{as}(\phi)_B$
987	999	983	$\delta_{oop}(CC(H)C)_{\phi B}(48)$, $\delta_p(\phi)_B$
999	1008	998	$\boldsymbol{\delta_{trig}(\phi)(40)}$, $\boldsymbol{\delta_{p(bridge)}}$, $\boldsymbol{\rho_b(POH)}$, $\boldsymbol{\gamma_{s(bridge)}}$
1036	1031	1021	$\boldsymbol{\nu(CC)_\phi(51)}$
1045		1042	$\boldsymbol{\delta_{p(bridge)}(31)}$, $\boldsymbol{\nu(CC)_{\phi B}}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$
1084	1074	1073	$\nu(C_\alpha N)(14)$, $\delta_{p(bridge)}$
1106		1090	$\gamma_{as(bridge)}(48)$, $\gamma_{s(bridge)}$, $\delta_{p(bridge)}$
1165	1161	1162	$\boldsymbol{\rho_r(CC(H)C)_\phi(58)}$, $\boldsymbol{\delta_{p(bridge)}}$, $\boldsymbol{\gamma_{s(bridge)}}$
1171	1181	1177	$\boldsymbol{\rho_r(CC(H)C)_{\phi B}(60)}$, $\boldsymbol{\rho_r(C_L C(H)C)_{\phi B}}$
1194	1188	1189	$\boldsymbol{\rho_r(C_L C(H)C)_\phi(34)}$, $\boldsymbol{\rho_r(CC(H)C)_\phi}$
1216		1206	$\boldsymbol{\nu(P{=}O)(16)}$, $\boldsymbol{\rho_r(C_L C_\alpha(H)P)}$, $\boldsymbol{\rho_r(C_\alpha(H,P)N)}$, $\boldsymbol{\rho_r(C_L C_\alpha(H,P)N)}$
1234		1227	$\boldsymbol{\nu(P{=}O)(46)}$, $\boldsymbol{\rho_r(C_L C_\alpha(H)P)}$, $\boldsymbol{\rho_r(C_\alpha(H,P)N)}$, $\boldsymbol{\rho_r(C_L C_\alpha(H,P)N)}$
1244	1242		$\boldsymbol{\delta_{p(bridge)}(36)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\nu(P{=}O)}$, $\boldsymbol{\gamma_{as(bridge)}}$
1271		1264	$\boldsymbol{\delta_{p(bridge)}(42)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\gamma_{as(bridge)}}$
1286		1285	$\delta_{p(bridge)}(39)$, $\gamma_{s(bridge)}$, $\gamma_{as(bridge)}$
1346	1330	1330	$\boldsymbol{\delta_{p(bridge)}(26)}$, $\boldsymbol{\gamma_{s(bridge)}}$, $\boldsymbol{\rho_r(C_L C(H)C)_\phi}$, $\boldsymbol{\gamma_{as(bridge)}}$
1349		1363	$\gamma_{as(bridge)}(38)$, $\gamma_{s(bridge)}$, $\nu(BO)$, $\delta_{p(bridge)}$
1446	1428	1428	$\boldsymbol{\rho_r(CC(H)C)_\phi(36)}$, $\boldsymbol{\nu(CC)_\phi}$, $\boldsymbol{\rho_r(C_\alpha N(H)C_L)}$
1450		1450	$\rho_r(CC(H)C)_{\phi B}(43)$, $\nu(CC)_{\phi B}$, $\nu(C_L C)_{\phi B}$
1510		1495	$\boldsymbol{\rho_r(CC(H)C)_\phi(28)}$, $\boldsymbol{\rho_r(C_L C(H)C)_\phi}$, $\boldsymbol{\nu}(CC)_\phi$
1519	1509		$\boldsymbol{\rho_r(C_\alpha N(H)C_L)(50)}$
1587	1588	1590	$\boldsymbol{\nu(CC)_{\phi B}(40)}$, $\boldsymbol{\nu(C_L C_{B(OH)_2})_{\phi B}}$, $\boldsymbol{\rho_r(CC(H)C)_{\phi B}}$
1620	1606	1604	$\boldsymbol{\nu(CC)_{\phi B}(30)}$, $\boldsymbol{\nu(C_L C)_{\phi B}}$
1625		1635	$\boldsymbol{\nu(CC)_\phi(42)}$, $\boldsymbol{\delta_{as}(\phi)}$
2938	2922	2924	$\boldsymbol{\nu(C_\alpha H)(99)}$
2938		2957	$\boldsymbol{\nu(C_\alpha H)(99)}$
3107	3059	3058	$\boldsymbol{\nu(CH)_{\phi B}(91)}$

Table 2: Continued.

Calc.	Wavenumbers/cm^{-1} Exp.		Assignment
	FT-Raman	FT-IR	B3LYP/6-311G(d,p) (PED %; >5%)
3145	3069		**ν(CH)$_{\phi}$(67), ν(CH)$_{\phi B}$**
3405	3482		**ν(NH)(96)**
3500	3503		ν(OH)$_{BOHbrigde}$(83), ν(OH)$_{POH}$

[a]Abbreviations: ν: stretching; ρ_r: rocking; δ: deformation; γ: torsion; p: puckering; δ_{trig}: trigonal deformation; s: symmetric; as: antisymmetric; oop: out-of-plane vibrations; ϕ: aromatic ring; ϕB: phenylboronic acid ring; bridge: hydrogen bonds [(HOBO)$_2$]; C$_L$: carbon atom of the aromatic ring connected to the aliphatic chain; C$_\alpha$: tetrahedral carbon atom; bold: vibrations related to band with Raman Intensity > 0.4 (%).

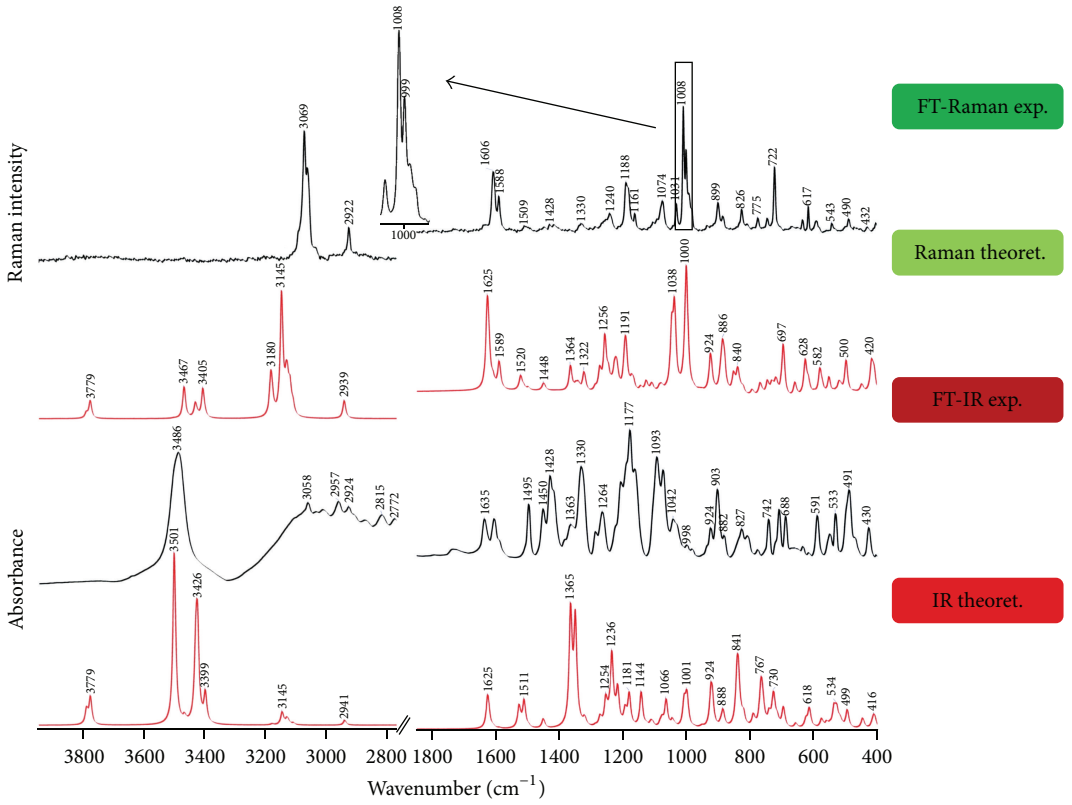

Figure 2: The experimental and theoretical FT-Raman and FT-IR spectra of [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$ in the spectral range of 3650–400 cm^{-1}.

modes (according to the Wilson numbering scheme) [39], respectively. The other ring vibrations appear in the FT-IR spectrum as two medium absorbencies at 1495 [ν_{19a}] and 1450 cm^{-1} [ν_{19b}].

Boronic Acid Group Vibrations. In the [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$ vibrational spectra, several moderate and weak bands due to the boronic acid group vibrations appear. From these, according to Erdogdu and Coworkers [40] and Ayyappan and Coworkers [41], the B–O stretching vibrations [ν(BO)] are expected to be enhanced near 1453–1450, 1384, and 1369–1361 cm^{-1}. Our calculations for dimer placed these vibrations at 1363–1349 cm^{-1}. The bands allocated to the –BOH deformation vibrations [δ(BOH)] appear in the spectral range of 1100–1000 cm^{-1} [40, 41]. Our calculations indicated that bands observed in these ranges are due to the deformation and torsion vibrations of the HOBO$\cdots$H bridge coupled with the ν(C$_\alpha$N) mode [$\delta/\gamma_{(bridge)}$] + ν(NC/C$_\alpha$N). Ayyappan and coworkers also suggested that bands assignable to the coupling of the B–C and B–O stretching vibrations [ν(BC/BO)] are seen at 809–797 cm^{-1}. However, the calculations performed for the [PhN-(2-PhB(OH)$_2$)-*R*-Me]PO$_3$H$_2$ dimer indicate that this band can be assigned to the $\delta/\gamma_{(bridge)}$ modes. Erdogdu and coworkers indicated that the γ(OBCC) and γ(HOBC/OBCC) vibrations appear in the range 740–580 cm^{-1}. Our theoretical calculations provide evidence that the bands occurring in this spectral ranges are connected with torsion and deformation vibrations of the HOBO$\cdots$H fragment. Additionally, the 540 cm^{-1} band may be assigned to the torsion of the –HOBC–, –HOBH–, and –HOBO–

fragments [γ(HOBC)/(HOBH)/(HOBO)] [37, 38], whereas our calculations pointed out that the 543 cm^{-1} bands are due to the to the torsion vibrations of HOBO$\cdots$H [$\delta_{(bridge)}$] and the deformation of HOBO$\cdots$H [$\gamma_{(bridge)}$]. The above discrepancies in the band assignments may be due to the fact that Erdogdu and coworkers and Ayyappan and coworkers presented results for phenylboronic acid derivative monomer, while we performed theoretical calculations for dimer.

Bearing in mind that the most stable structure of [PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2 is a dimer formed by two hydrogen bonds between the boron hydroxyl groups of two monomers, the deformation and torsion vibrations of the HOBO$\cdots$H bridge are expected in the vibrational spectra. These vibrations are manifested by the 1363–1330, 1286–1242, 1106–1090, 1074–1042, 886–882, 822–808, 746–732, 722–710, 659–635, 574–543, 533–522, and 499–490 cm^{-1} spectral features.

Phosphonate Group Vibrations. The $-PO_3H_2$ group gives rise to several vibrational bands. These appear in the 1242–1206, 1008–998, 924–903, 827–823, and 496–430 cm^{-1} spectral ranges. The 1242 and 1206 cm^{-1} spectral features are primarily due to the P=O stretching vibrations [ν(P=O)], whereas the 924–903 and 827–823 cm^{-1} bands are assigned to the P–O stretching mode [ν(P–O)]. The two other bands mentioned above, located at 1010–990 and 496–430 cm^{-1}, are mainly due to the ρ_b(POH) and $\delta_s(C_\alpha PO_3)$ vibrations, respectively.

Imine and Methine Groups Vibrations. In the [PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2 FT-IR spectrum, the broad, strong band due to the imine group vibrations is observed at 3482 cm^{-1} [31]. This band is associated with the N–H stretching mode [ν(NH)]. The broadness of this spectral feature can be explained by the formation of intermolecular and/or intramolecular hydrogen bonds between the $-PO_3H_2$, –NH–, and –BOH groups. The C–N stretching vibrations [$\nu(C_\alpha N)$] are observed at around 1074 cm^{-1}. The deformation modes of the $C_\alpha N(H)C$ fragment are enhanced at 1519–1509 and 1446–1428 cm^{-1}. In contrast, the rocking vibrations of the C_α(H,P)NH fragment contribute to the bands at 1509, 1428, and 1227–1206 cm^{-1}. The >CH– group's stretching vibrations exhibit also moderate spectral features in the high wavenumber range of the vibrational spectra (Table 2).

4. Conclusions

In this work, the [*N*-phenylamino(2-boronphenyl)-*R*-methyl] phosphonic acid ([PhN-(2-PhB$(OH)_2$)-*R*-Me]PO_3H_2) was investigated using Fourier-transform infrared and Fourier-transform Raman methods. We briefly discussed the characteristic FT-Raman and absorption infrared bands that are crucial for understanding vibrational structures of the tilted compound.

In order to better understand the correlation between obtained spectral feature and the vibrational structure, the DFT calculations at the B3LYP; 6-311G(d,p) level using Gaussian'03, GaussSum 0.8, and GAR2PED softwares were performed.

Our theoretical and experimental considerations provide the description of the most stable structure of the investigated molecules which is a cyclic dimer, in the *cis-trans* conformation, formed by a pair of intermolecular hydrogen bonds between the boron hydroxyl groups of two monomers. Moreover, the spectral range of FT-IR and FT-Raman bands associated with the aromatic and aliphatic functional group vibrations of the molecule was characterized.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

Acknowledgments

The authors are grateful to Professor P. Kafarski and Dr. A. Rydzewska for donation of samples. This work was supported by the National Science Center of the Polish Ministry of Science and Higher Education (Grants no. N N204 544339 to Edyta Proniewicz and no. 2011/03/N/ST4/00777 to Natalia Piergies and Edyta Proniewicz). Natalia Piergies gratefully acknowledges the Marian Smoluchowski Krakow Research Consortium: "Matter-Energy-Future" (KNOW) for financial support in the form of a scholarship. The authors kindly acknowledgethe Academic Computer Center "Cyfronet" in Krakow for computational facilities and Dr. M. Andrzejak (Jagiellonian University) for the use of the visualization script.

References

[1] P. Kafarski, B. Lejczak, R. Tyka, L. Koba, E. Pliszczak, and P. Wieczorek, "Herbicidal activity of phosphonic, phosphinic, and phosphonous acid analogues of phenylglycine and phenylalanine," *Journal of Plant Growth Regulation*, vol. 14, no. 4, pp. 199–203, 1995.

[2] E. Naydenova, M. Topashka-Ancheva, P. Todorov, T. Yordanova, and K. Troev, "Novel α-aminophosphonic acids. Design, characterization, and biological activity," *Bioorganic and Medicinal Chemistry*, vol. 14, no. 7, pp. 2190–2196, 2006.

[3] E. D. Naydenova, P. T. Todorov, and K. D. Troev, "Recent synthesis of aminophosphonic acids as potential biological importance," *Amino Acids*, vol. 38, no. 1, pp. 23–30, 2010.

[4] A. Kraszewski and J. Stawinski, "*H*-phosphonates: versatile synthetic precursors to biologically active phosphorus compounds," *Pure and Applied Chemistry*, vol. 79, no. 12, pp. 2217–2227, 2007.

[5] B. Lejczak and P. Kafarski, "Biological activity of aminophosphonic acids and their short peptides," *Topics in Heterocyclic Chemistry*, vol. 20, pp. 31–63, 2009.

[6] M. Pawelczak, K. Nowak, and P. Kafarski, "Synthesis of phosphono dipeptides, inhibitors of cathepsin C," *Phosphorus, Sulfur and Silicon and Related Elements*, vol. 132, pp. 65–71, 1998.

[7] M. E. Tanner, S. Vaganay, J. van Heijenoort, and D. Blanot, "Phosphinate inhibitors of the D-glutamic acid-adding enzyme of peptidoglycan biosynthesis," *Journal of Organic Chemistry*, vol. 61, no. 5, pp. 1756–1760, 1996.

[8] M. Bubenik, R. Rej, N. Nguyen-Ba, G. Attardo, F. Ouellet, and L. Chan, "Novel nucleotide phosphonate analogues with potent

antitumor activity," *Bioorganic and Medicinal Chemistry Letters*, vol. 12, no. 21, pp. 3063–3066, 2002.

[9] J. Grembecka, A. Mucha, T. Cierpicki, and P. Kafarski, "The most potent organophosphorus inhibitors of leucine aminopeptidase. Structure-based design, chemistry, and activity," *Journal of Medicinal Chemistry*, vol. 46, no. 13, pp. 2641–2655, 2003.

[10] R. Snoeck, A. Holý, C. Dewolf-Peeters, J. van den Oord, E. de Clercq, and G. Andrei, "Antivaccinia activities of acyclic nucleoside phosphonate derivatives in epithelial cells and organotypic cultures," *Antimicrobial Agents and Chemotherapy*, vol. 46, no. 11, pp. 3356–3361, 2002.

[11] D. S. Matteson, "α-amido boronic acids: a synthetic challenge and their properties as serine protease inhibitors," *Medicinal Research Reviews*, vol. 28, no. 2, pp. 233–246, 2008.

[12] P. C. Trippier and C. McGuigan, "Boronic acids in medicinal chemistry: anticancer, antibacterial and antiviral applications," *MedChemComm*, vol. 1, no. 3, pp. 183–198, 2010.

[13] D. Chen, M. Frezza, S. Schmitt, J. Kanwar, and Q. P. Dou, "Bortezomib as the first proteasome inhibitor anticancer drug: current status and future perspectives," *Current Cancer Drug Targets*, vol. 11, no. 3, pp. 239–253, 2011.

[14] A. M. Irving, C. M. Vogels, L. G. Nikolcheva et al., "Synthesis and antifungal and antibacterial bioactivity of cyclic diamines containing boronate esters," *New Journal of Chemistry*, vol. 27, no. 10, pp. 1419–1426, 2003.

[15] W. Yang, X. Gao, and B. Wang, "Boronic acid compounds as potential pharmaceutical agents," *Medicinal Research Reviews*, vol. 23, no. 3, pp. 346–368, 2003.

[16] T. Asano, H. Nakamura, Y. Uehara, and Y. Yamamoto, "Design, synthesis, and biological evaluation of aminoboronic acids as growth-factor receptor inhibitors of EGFR and VEGFR-1 tyrosine kinases," *ChemBioChem*, vol. 5, no. 4, pp. 483–490, 2004.

[17] E. Podstawka-Proniewicz, M. Kosior, Y. Kim, K. Rolka, and L. M. Proniewicz, "Nociceptin and its natural and specifically-modified fragments: structural studies," *Biopolymers*, vol. 93, no. 12, pp. 1039–1054, 2010.

[18] E. Podstawka-Proniewicz, D. Sobolewski, A. Prahl, Y. Kim, and L. M. Proniewicz, "Structure and conformation of Arg8 vasopressin modified analogs," *Journal of Raman Spectroscopy*, vol. 43, no. 1, pp. 51–60, 2012.

[19] E. Podstawka-Proniewicz, A. Kudelski, Y. Kim, and L. M. Proniewicz, "Adsorption of neurotensin-family peptides on SERS-active Ag substrates," *Journal of Raman Spectroscopy*, vol. 43, no. 9, pp. 1196–1203, 2012.

[20] E. Proniewicz, D. Skołuba, A. Kudelski et al., "B2 bradykinin receptor antagonists: adsorption mechanism on electrochemically roughened Ag substrate," *Journal of Raman Spectroscopy*, vol. 44, no. 2, pp. 205–211, 2013.

[21] E. Podstawka-Proniewicz, M. Andrzejak, P. Kafarski, Y. Kim, and L. M. Proniewicz, "Vibrational characterization of L -valine phosphonate dipeptides: FT-IR, FT-RS, and SERS spectroscopy studies and DFT calculations," *Journal of Raman Spectroscopy*, vol. 42, no. 5, pp. 958–979, 2011.

[22] E. Podstawka-Proniewicz, N. Piergies, D. Skołuba, P. Kafarski, Y. Kim, and L. M. Proniewicz, "Vibrational characterization of l-leucine phosphonate analogues: FT-IR, FT-Raman, and SERS spectroscopy studies and DFT calculations," *The Journal of Physical Chemistry A*, vol. 115, no. 40, pp. 11067–11078, 2011.

[23] E. Proniewicz, E. Pięta, A. Kudelski et al., "Vibrational and theoretical studies of the structure and adsorption mode of *m*-nitrophenyl α-guanidinomethylphosphonic acid analogues on silver surfaces," *The Journal of Physical Chemistry A*, vol. 117, no. 23, pp. 4963–4972, 2013.

[24] P. Młynarz, A. Rydzewska, and Z. Pokładek, "Preparation of a novel group of hybrid compounds N-benzyl aminoboronbenzylphosphonic and N,N′-ethylenedi(aminoboronbenzylphosphonic) acids," *Journal of Organometallic Chemistry*, vol. 696, no. 2, pp. 457–460, 2011.

[25] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., *Aussian03, Revision A. 1*, Gaussian Inc, Pittsburgh, Pa, USA, 2003.

[26] N. Piergies, E. Proniewicz, A. Kudelski et al., "Fourier transform infrared and Raman and surface-enhanced Raman spectroscopy studies of a novel group of boron analogues of aminophosphonic acids," *The Journal of Physical Chemistry A*, vol. 116, no. 40, pp. 10004–10014, 2012.

[27] M. K. Cyrański, A. Jezierska, P. Klimentowska, J. J. Panek, and A. Sporzyński, "Impact of intermolecular hydrogen bond on structural properties of phenylboronic acid: quantum chemical and X-ray study," *Journal of Physical Organic Chemistry*, vol. 21, no. 6, pp. 472–482, 2008.

[28] A. Jezierska, J. J. Panek, G. Z. Zukowska, and A. Sporzyński, "A combined experimental and theoretical study of benzoxaborole derivatives by Raman and IR spectroscopy, static DFT, and first-principle molecular dynamics," *Journal of Physical Organic Chemistry*, vol. 23, no. 5, pp. 451–460, 2010.

[29] F. Jensen, *Introduction to Computational Chemistry*, John Willey and Sons, Chichester, UK, 2007.

[30] D. Michalska and R. Wysokiński, "The prediction of Raman spectra of platinum(II) anticancer drugs by density functional theory," *Chemical Physics Letters*, vol. 403, no. 1–3, pp. 211–217, 2005.

[31] N. M. O'Boyle and J. G. Vos, *GaussSum 0. 8*, Dublin City University, Dublin, Ireland, 2004, http://gausssum.sourceforge.net.

[32] J. L. M. Martin and C. van Alsenoy, *Gar2ped*, University of Antwerp, Antwerp, Belgium, 1995.

[33] D. G. Hall, *Boronic Acids. Preparation and Applications in Organic Synthesis, Medicine and Materials*, Wiley-VCH, Weinheim, Germany, 2011.

[34] M. Kurt, "An experimental and theoretical study of molecular structure and vibrational spectra of pentafluorophenylboronic acid molecule by density functional theory and ab initio Hartree Fock calculations," *Journal of Molecular Structure*, vol. 874, no. 1–3, pp. 159–169, 2008.

[35] N. Piergies, E. Proniewicz, Y. Ozaki, Y. Kim, and L. M. Proniewicz, "Influence of substituent type and position on the adsorption mechanism of phenylboronic acids: infrared, raman, and surface-enhanced raman spectroscopy studies," *The Journal of Physical Chemistry A*, vol. 117, no. 27, pp. 5693–5705.

[36] E. Podstawka, R. Borszowska, M. Grabowska, M. Drg, P. Kafarski, and L. M. Proniewicz, "Investigation of molecular structures and adsorption mechanisms of phosphonodipeptides by surface-enhanced Raman, Raman, and infrared spectroscopies," *Surface Science*, vol. 599, no. 1–3, pp. 207–220, 2005.

[37] E. Podstawka, A. Kudelski, and L. M. Proniewicz, "Adsorption mechanism of physiologically active l-phenylalanine phosphonodipeptide analogues: comparison of colloidal silver and macroscopic silver substrates," *Surface Science*, vol. 601, no. 21, pp. 4971–4983, 2007.

[38] E. Podstawka, A. Kudelski, P. Kafarski, and L. M. Proniewicz, "Influence of aliphatic spacer group on adsorption mechanisms of phosphonate derivatives of l-phenylalanine: surface-enhanced Raman, Raman, and infrared studies," *Surface Science*, vol. 601, no. 19, pp. 4586–4597, 2007.

[39] E. B. Wilson Jr., "The normal modes and frequencies of vibration of the regular plane hexagon model of the benzene molecule," *Physical Review*, vol. 45, no. 10, pp. 706–714, 1934.

[40] Y. Erdogdu, M. Tahir Güllüoğlu, and M. Kurt, "DFT, FT-Raman, FT-IR and NMR studies of 2-fluorophenylboronic acid," *Journal of Raman Spectroscopy*, vol. 40, no. 11, pp. 1615–1623, 2009.

[41] S. Ayyappan, N. Sundaraganesan, M. Kurt, T. R. Sertbakan, and M. Özduran, "Molecular structure, vibrational spectroscopic studies and NBO analysis of the 3,5-dichlorophenylboronic acid molecule by the density functional method," *Journal of Raman Spectroscopy*, vol. 41, no. 10, pp. 1379–1387, 2010.