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DFT simulations and vibrational spectra of 4-chloro and 4-bromophenylboronic acid molecules

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The experimental and theoretical vibrational spectra of 4-chloro- and 4-bromophenylboronic acids (abbreviated as 4Clpba and 4Brpba) were studied. The Fourier transform Raman and Fourier transform infrared (FTIR) spectra of 4Clpba and 4Brpba molecules were recorded in the solid phase. The structural and spectroscopic analyses of the molecules were made by using Hartree–Fock and density functional harmonic calculations. In both 4Clpba and 4Brpba only one form was most stable using B3LYP level with the 6–311++G(d,p) basis set. Selected experimental bands were assigned and characterized on the basis of the scaled theoretical wavenumbers by their total energy distribution (TED). Finally, geometric parameters as well as infrared (IR) and Raman bands were compared with the experimental data of the molecules. Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: halophenylboronic acids; vibrational spectra; Hartree–Fock; density functional theory; 6–311++G(d,p) basis set

Introduction

The boronic acid ligands have been used in biological, pharmaceutical, industrial, and various other applications. Recently, arylboronic acids have become the object of interest again because of their newer and wider applications.^[1–3] Wide synthetic applications were developed after Miyaura and Suzuki's discovery of palladium-catalyzed coupling of arylboronic acid with aryl halides.^[4] As compared with the earlier methods of the synthesis of biaryls, arylboronic acids used instead of various organometallic reagents are air- and water-stable compounds of low toxicity. Because of its versatility, Suzuki coupling is now the best way to obtain the aryl–aryl bond^[5] and is extended to alkylboronic acids.^[6,7] The other important synthetic application is Petasis synthesis of α -amino acids.^[3,8] Many other synthetic applications have been reviewed by Hall^[3] and Cuthbertson.^[9]

Biology and medicine are also the fields of numerous applications of boronic acids.^[3] They are used in anticancer therapy, both as boron neutron capture therapy (BNCT)^[10] and chemotherapeutic agents.^[11] They are also potent antiviral drugs.^[12] Fast and reversible formation of esters with polyols, reported in 1954 by Kuivila *et al.*,^[13] leads to the use of boronic acids as molecular receptors for sugars, enabling their detection in aqueous solutions. A variety of artificial receptors is used as chemosensors for saccharides with various types of detection, such as circular dichroism (CD), fluorescent, colored, electrochemical, and others.^[13,14] The use of these compounds for other bioanalytes is still in progress.

The use of boronic acid in crystal engineering in order to generate predictably organized crystalline materials was recently reviewed.^[15] There are also other fields in which boronic acids or their derivatives are used, e.g. as podand solvents^[16] or additivities to conducting polymers.^[17] The presence of hydroxy groups connected to a boron atom strongly influences the properties of boronic acids by formation of inter- and intramolecular hydrogen bonds. The reactivity, physical properties, ability of

complex formation, biological functions, and other features of these compounds are connected with their structures. Recently, the crystal structure of the dipeptide boronic acid and anticancer drug bortezomib in complex with proteasome was determined, which allowed the establishment of the binding mode of the acid to the proteasome's active sites.^[18] The use of boron compounds in the coupling reaction presents several advantages, such as stability to heat, oxygen, and water; flexibility towards functional groups; and commercial availability.^[19]

In recent studies, inhibition by boronic acids has been studied with some bacterial ureases and plant ureases. Ravi *et al.*^[20] reported that among boric acid, boronic acid, and 4-bromophenylboronic acid, the latter was found to be the most potent competitive inhibitor for pigeon pea urease. Manishkumar *et al.*^[21] reported supramolecular architecture in some 4-halophenylboronic acid including 4-chloro, 4-bromo and hydrates of 4-iodophenylboronic acid. In their work, only crystal geometry of 4-halophenylboronic acid molecules was discussed in detail.

To our knowledge, no theoretical Hartree–Fock (HF) or density functional theory (DFT) calculations, or detailed vibrational infrared (IR) and Raman analyses, have been performed on the 4-chlorophenylboronic acid and 4-bromophenylboronic acid (4Clpba and 4Brpba, respectively) molecules. A detailed quantum chemical study will aid in understanding the vibrational modes of the 4Clpba and 4Brpba and clarifying the experimental data available for these molecules. DFT calculations are known to provide excellent vibrational wavenumbers of organic compounds if the calculated wavenumbers are scaled to compensate for

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the approximate treatment of electron correlation, for basis set deficiencies, and for the anharmonicity effects.^[22–27] DFT is now accepted as a popular post-HF approach for the computation of molecular structure, vibrational wavenumbers, and energies of molecules by the *ab initio* community.^[28]

In this work, by using HF and B3LYP methods we calculated the vibrational wavenumbers of 4Clpba and 4Brpba molecules in the ground state to distinguish the fundamentals from the many experimental vibrational wavenumbers and geometric parameters. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

Experimental

The 4Clpba and 4Brpba samples were purchased from Acros Chemical Company with a stated purity of greater than 98% and were used as such without further purification. The samples of 4Clpba and 4Brpba are in solid form at room temperature. IR spectra of the samples were recorded between 4000 and 400 cm^{-1} on a Mattson 1000 Fourier transform infrared (FTIR) spectrometer which was calibrated using the 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 a Nd:YAG laser. The detector was a liquid-nitrogen-cooled Ge detector. Five hundred scans were accumulated at 4 cm^{-1} resolution using a laser power of 100 mW.

Calculations

The molecular structures of 4Clpba and 4Brpba in the ground state (*in vacuo*) were optimized by HF and B3LYP with the 6–311++G(d,p) basis set. There are no significant differences in geometry and vibrational wavenumbers by the selection of the different basis sets.

The Becke's three-parameter hybrid density functional, B3LYP,^[28,29] was used to calculate harmonic vibrational wavenumbers with the 6–311++G(d,p) basis set. It is well known in quantum chemical literature that among available functionals the B3LYP functional yields a good description of harmonic vibrational wavenumbers for small and medium-sized molecules.

Three sets of vibrational wavenumbers for these species were calculated with the hybrid method and then scaled by the corresponding scaling factors (see <http://srdata.nist.gov>). In the literature, there is no global scaling factor for the B3LYP/6–311++G(d,p) basis set. All calculations were performed by using Gauss View molecular visualization program^[30] and Gaussian 03 program package on a personal computer.^[31] The programs allows one to examine, graphically, the G03 generated IR spectra. Then the spectral numerical data was copied to the Microsoft Excel Program XP version where the spectral ranges were edited.

Results and Discussion

The molecules of 4Clpba and 4Brpba consist of 16 atoms; so it has 42 normal vibrational modes. Our first set of calculations involved the investigation of the possible conformations of 4Clpba and 4Brpba. There are three possible conformers for the

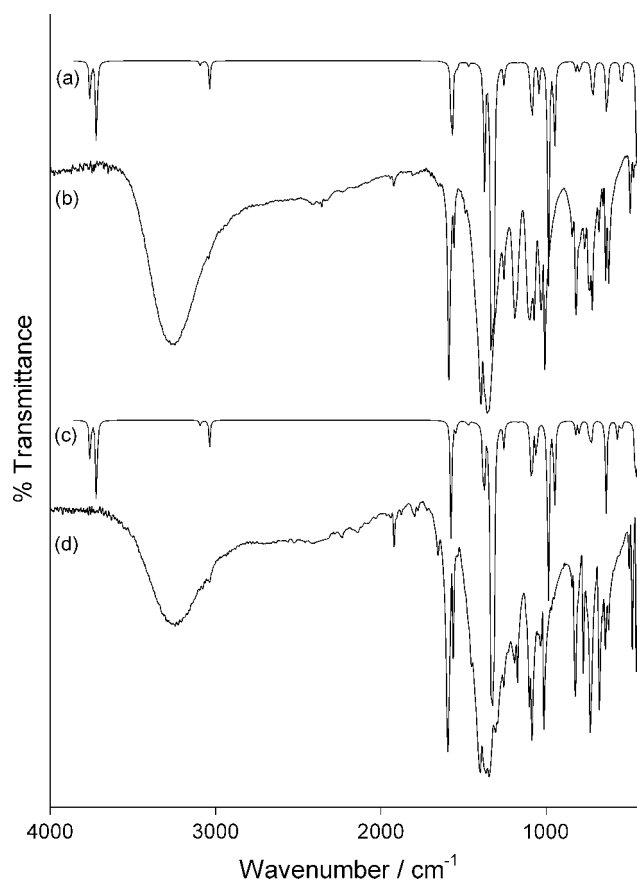


Figure 1. Comparison of the calculated and experimental IR spectra of the studied molecules: (a) simulated IR spectra of 4Brpba by using B3LYP/6–311G++(d,p) theory level; (b) experimental IR spectra of 4Brpba; (c) simulated IR spectra of 4Clpba by using B3LYP/6–311G++(d,p) theory level; (d) experimental IR spectrum of 4Clpba.

studied molecules, illustrated in Fig. S1 (Supporting Information), depending on the positions of the hydrogen atoms bonded to oxygen, i.e. whether they are directed away from or toward the benzene ring. Our calculations show that the three conformations do not differ greatly in energy, but demonstrate that the conformation *cis*–*trans* (abbreviated as *ct* = *tc*) has the lowest energy. On the basis of a C_s symmetry, the 42 fundamental vibrations of the *ct* and *tc* forms of 4Clpba and 4Brpba can be distributed as $13A'' + 29A'$. In the *cc*, *ct* (= *tc*), and *tt* forms of the molecules, boronic acid and the 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 4Clpba and 4Brpba are shown in Fig. S1 (Supporting Information). We have reported some geometric parameters and vibrational wavenumbers for 4Clpba and 4Brpba by using B3LYP and compared some observed bond lengths and bond angles for crystal structure of these molecules. Vibrational assignments are based solely on the B3LYP/6–311++G(d,p) calculations. The calculated wavenumbers of the molecule for the *tc* (or *tc*) form were compared to the corresponding observed IR and Raman spectra of the molecule as shown in Figure 1, Tables 1 and 2. The vibrational assignments of most of the fundamental vibration of the molecule was straightforward on the basis of their calculated total energy distribution (TED) values (Tables 1 and 2).

Table 1. Experimental and calculated fundamental harmonic wavenumbers^a infrared intensities^b and Raman scattering activities^c for the 4Clpba molecule (cis-trans form for selected 6-311++G(d,p) basis set)

ν	Assign.	Sym	HF			B3LYP			Raman	TED(> 10%)			
			Waven. ^a	Scaled	I_{infrared}^b	Wavenumber ^a	Scaled	I_{infrared}^b			Infrared		
1	ν_{OH}	A'	4234	3846	72.91	32.83	3888	3759	41.60	46.43	3276ms	3175vw	$\nu_{\text{OH}}(100)$
2	ν_{OH}	A'	4182	3799	150.93	122.81	3848	3720	91.84	180.65	3249ms	3106vw	$\nu_{\text{OH}}(100)$
3	ν_{CH}	A'	3365	3057	2.85	141.60	3201	3095	1.54	183.46	3081vw	3087vw	$\nu_{\text{CH}}(97)$
4	ν_{CH}	A'	3361	3053	4.98	66.78	3199	3093	3.71	51.28	3067w	3064vs	$\nu_{\text{CH}}(97)$
5	ν_{CH}	A'	3348	3042	1.06	41.02	3185	3079	0.79	45.79	3067w	3064vs	$\nu_{\text{CH}}(100)$
6	ν_{CH}	A'	3308	3005	27.65	72.02	3141	3036	26.24	86.55	1658w	1596vs	$\nu_{\text{CH}}(100)$
7	ν_{CC}	A'	1780	1617	125.93	73.60	1629	1575	117.44	91.46	1596vs	1596vs	$\nu_{\text{CC}}(64) + \delta_{\text{HCC}}(14)$
8	ν_{CC}	A'	1738	1579	13.83	2.50	1598	1545	10.60	1.61	1563s	1561vw	$\nu_{\text{CC}}(72) + \delta_{\text{HCC}}(12)$
9	δ_{HCC}	A'	1654	1502	8.22	0.49	1524	1473	5.33	0.94	1453m,sh	1488vw	$\delta_{\text{HCC}}(60) + \nu_{\text{CC}}(27)$
10	δ_{HCC}	A'	1531	1391	108.43	0.07	1425	1377	112.72	0.41	1401s	1488vw	$\delta_{\text{HCC}}(31) + \nu_{\text{CC}}(24) + \nu_{\text{OB}}(12)$
11	ν_{OB}	A'	1463	1329	270.46	2.45	1382	1336	248.77	12.01	1373m	1353w, 1343m	$\nu_{\text{OB}}(62) + \delta_{\text{HCC}}(15)$
12	ν_{OB}	A'	1448	1315	599.24	14.08	1365	1320	452.84	32.47	1350m	1353w, 1343m	$\nu_{\text{OB}}(31) + \nu_{\text{BC}}(26) + \delta_{\text{HOB}}(17)$
13	δ_{HCC}	A'	1433	1302	23.65	1.16	1330	1286	0.29	0.76	1310m, 1301m,sh	1297w	$\delta_{\text{HCC}}(79)$
14	δ_{HCC}	A'	1300	1181	2.13	3.86	1300	1257	24.88	0.23	1259m	1253vw	$\delta_{\text{HCC}}(74) + \nu_{\text{CC}}(22)$
15	ν_{CC}	A'	1256	1141	31.95	0.41	1212	1172	1.02	4.95	1194m, 1174s	1181w	$\nu_{\text{CC}}(65) + \delta_{\text{HCC}}(20)$
16	ν_{CC}	A'	1209	1098	115.70	0.32	1133	1095	43.49	0.55	1104vs	1095w	$\nu_{\text{CC}}(26) + \delta_{\text{CCH}}(15) \delta_{\text{CCC}}(12) + \delta_{\text{HOB}}(12)$
17	ν_{CC}	A'	1179	1071	17.55	21.62	1123	1086	53.49	2.39	1088vs	1085m	$\nu_{\text{CC}}(66)$
18	ν_{CC}	A'	1175	1067	16.12	21.60	1096	1060	46.98	48.17	1060w	1085m	$\nu_{\text{CC}}(67)$
19	Γ_{HCH}	A''	1110	1008	0.00	0.03	1032	998	5.53	1.85	1037m	1025m	$\Gamma_{\text{HCH}}(41) + \Gamma_{\text{HCCB}}(37)$
20	δ_{CCC}	A'	1106	1005	9.24	1.62	1022	988	201.52	2.32	1015s	1008m	$\delta_{\text{CCC}}(29) + \delta_{\text{HOB}}(20) + \delta_{\text{CCH}}(14) + \nu_{\text{CC}}(12)$
21	δ_{HOB}	A''	1096	996	194.82	1.10	996	963	0.00	0.03	973w	952vw	$\delta_{\text{HOB}}(56) + \nu_{\text{OB}}(16)$
22	Γ_{HCH}	A''	1065	968	0.57	0.02	983	950	101.41	1.88	956w	952vw	$\Gamma_{\text{HCH}}(43) \Gamma_{\text{CCH}}(23)$
23	δ_{HOB}	A'	1041	945	100.22	0.81	956	924	0.36	0.02	901vw	952vw	$\delta_{\text{HOB}}(62) + \nu_{\text{OB}}(31)$
24	Γ_{CCH}	A''	946	859	12.77	0.35	851	823	13.73	0.10	846w	952vw	$\Gamma_{\text{CCH}}(56) + \Gamma_{\text{HCCd}}(22) + \Gamma_{\text{BCCH}}(13)$

(continued overleaf)

Table 1. (Continued)

ν	Assign.	Sym	HF			B3LYP			Infrared	Raman	Exp. ^a	TED(> 10%)
			Waven. ^a	Scaled	I_{Infrared}^b	I_{Raman}^b	Wavenumber ^a	Scaled				
25	Γ_{CCCH}	A''	923	838	24.70	0.24	827	800	825s	803m	$\Gamma_{\text{CCCH}}(57) + \Gamma_{\text{HCCCl}}(19) + \Gamma_{\text{BCGH}}(17)$	
26	Γ_{CCCC}	A'	815	741	24.17	25.60	765	739	777s	724m	$\Gamma_{\text{CCCC}}(42) + \Gamma_{\text{CCCH}}(18) + \Gamma_{\text{CCCH}}(18)$	
27	ν_{CC}	A''	815	741	31.43	0.10	752	727	735s		$\nu_{\text{CC}}(24) + \delta_{\text{CCC}}(18) + \nu_{\text{CCl}}(15)$	
28	Γ_{OBCC}	A''	718	652	130.89	0.00	660	638	680s		$\Gamma_{\text{OBCC}}(29) + \Gamma_{\text{HOBOb}}(27)$	
29	δ_{CCC}	A'	690	627	0.90	6.68	645	623	643s,625m	628m	$\delta_{\text{CCC}}(54) + \delta_{\text{CCGH}}(18)$	
30	ν_{CCl}	A'	630	572	18.78	0.45	590	571	500w		$\nu_{\text{CCl}}(23) + \nu_{\text{BC}}(21) + \delta_{\text{OBOb}}(13) + \nu_{\text{OB}}(11)$	
31	Γ_{HOBc}	A''	591	537	18.14	1.22	565	546			$\Gamma_{\text{HOBc}}(38) + \Gamma_{\text{HOBOb}}(32)$	
32	Γ_{CCCC}	A''	513	466	70.76	0.23	475	459	481s	470vw	$\Gamma_{\text{CCCC}}(24) + \Gamma_{\text{CCCH}}(24) + \Gamma_{\text{HOBc}}(21)$	
33	δ_{OBOb}	A'	485	441	39.93	2.20	452	437	456vs	452vw	$\delta_{\text{OBOb}}(30) + \nu_{\text{CCl}}(27) + \delta_{\text{OBc}}(15)$	
34	Γ_{HOBH}	A''	479	435	74.82	0.42	451	436			$\Gamma_{\text{HOBH}}(30) + \Gamma_{\text{HOBc}}(27) + \Gamma_{\text{CCCC}}(17)$	
35	δ_{OBc}	A'	460	418	4.42	0.67	434	419			$\delta_{\text{OBc}}(46) + \delta_{\text{BCC}}(26)$	
36	Γ_{CCCC}	A''	435	395	47.94	0.29	399	386		352w	$\Gamma_{\text{CCCC}}(39) + \Gamma_{\text{CCCH}}(17) + \Gamma_{\text{HOBOb}}(17) + \Gamma_{\text{HOBc}}(15)$	
37	δ_{CCCl}	A'	319	290	2.16	0.22	297	287			$\delta_{\text{CCCl}}(67) + \delta_{\text{OBc}}(20)$	
38	ν_{BC}	A'	301	273	2.52	5.57	283	274		271w	$\nu_{\text{BC}}(23) + \delta_{\text{CCC}}(15) + \delta_{\text{OBOb}}(15) + \nu_{\text{CCl}}(11)$	
39	Γ_{CCCCl}	A''	269	244	0.19	1.44	244	236		258	$\Gamma_{\text{CCCCl}}(34) + \Gamma_{\text{HCCCl}}(17) + \Gamma_{\text{OBCC}}(13) + \Gamma_{\text{CCCCB}}(13)$	
40	δ_{BCC}	A'	153	139	2.31	0.32	143	138		169	$\delta_{\text{BCC}}(59) + \delta_{\text{OBc}}(24) + \delta_{\text{CCCl}}(11)$	
41	Γ_{BCCC}	A''	89	81	0.12	0.56	81	79		90	$\Gamma_{\text{BCCC}}(32) + \Gamma_{\text{CCCCl}}(19) + \Gamma_{\text{BCCH}}(12)$	
42	Γ_{OBCC}	A''	19	18	3.61	0.76	9	9			$\Gamma_{\text{OBCC}}(97)$	

Γ torsion; δ , bending; ν stretching.

^a Wavenumbers in cm^{-1} .

^b Intensities in km/mol .

^c Raman scattering activities.

Table 2. Experimental and calculated fundamental harmonic wavenumbers^a infrared intensities^b and Raman scattering activities^c for 4Brpba molecule (cis-trans form for selected 6–311++G(d,p) basis set)

ν	Assign.	Sym	HF			B3LYP			Exp. ^a				
			Wavenumber	Scaled ^a	I_{Infrared}^b	I_{Raman}^c	Waven.	Scaled ^a	I_{Infrared}^b	I_{Raman}^c	Infrared	Raman	TED(>10%)
1	ν_{OH}	A'	4234	3846	72.85	32.64	3888	3759	41.40	46.23	3276vs	3164vw	$\nu_{\text{OH}}(100)$
2	ν_{OH}	A'	4183	3800	154.49	128.81	3848	3720	93.99	189.12		3108vw	$\nu_{\text{OH}}(100)$
3	ν_{CH}	A'	3366	3058	2.36	135.18	3201	3095	0.97	173.67			$\nu_{\text{CH}}(99)$
4	ν_{CH}	A'	3362	3054	4.54	55.75	3199	3093	3.45	39.38		3080vw	$\nu_{\text{CH}}(96)$
5	ν_{CH}	A'	3348	3042	0.97	41.51	3184	3078	0.77	49.08	3058m, sh	3060s	$\nu_{\text{CH}}(100)$
6	ν_{CH}	A'	3307	3005	28.79	77.83	3140	3035	27.28	94.16			$\nu_{\text{CH}}(98)$
7	ν_{CC}	A'	1776	1614	128.56	81.07	1624	1571	127.81	99.67	1590vs	1588vs	$\nu_{\text{CC}}(63) + \delta_{\text{CCH}}(16)$
8	ν_{CC}	A'	1734	1575	11.20	1.85	1594	1542	9.12	1.46	1558m	1557vw	$\nu_{\text{CC}}(74) + \delta_{\text{CCH}}(11)$
9	δ_{CCH}	A'	1650	1499	6.18	1.20	1519	1469	4.58	1.59	1510vw, 1492w	1490vw	$\delta_{\text{CCH}}(59) + \nu_{\text{CC}}(26)$
10	ν_{OB}	A'	1528	1389	122.24	0.19	1422	1375	133.14	0.51	1397vs	1357w	$\nu_{\text{OB}}(25) + \delta_{\text{CCH}}(24) + \nu_{\text{CC}}(21)$
11	ν_{OB}	A'	1464	1330	255.27	2.42	1381	1335	242.22	14.26	1361vs	1341w	$\nu_{\text{OB}}(44) + \nu_{\text{CC}}(15)$
12	ν_{OB}	A'	1447	1315	609.34	15.20	1365	1320	450.94	36.80		1303w	$\nu_{\text{OB}}(37) + \nu_{\text{BC}}(23) + \delta_{\text{HOB}}(13)$
13	δ_{CCH}	A'	1434	1303	30.73	1.36	1331	1286	0.08	0.71	1258m		$\delta_{\text{CCH}}(84) + \nu_{\text{CC}}(14)$
14	ν_{CC}	A'	1303	1183	2.02	7.04	1298	1255	23.75	0.36			$\nu_{\text{CC}}(88)$
15	δ_{CCH}	A'	1255	1140	32.71	0.53	1214	1173	1.21	9.04	1194s	1179w	$\delta_{\text{CCH}}(75) + \nu_{\text{CC}}(23)$
16	δ_{CCH}	A'	1203	1092	95.90	3.82	1133	1095	36.34	0.56	1107s		$\delta_{\text{CCH}}(44) + \nu_{\text{CC}}(34)$
17	ν_{CC}	A'	1176	1069	3.58	0.12	1122	1085	52.99	6.56	1074s	1068m	$\nu_{\text{CC}}(29) + \delta_{\text{CCH}}(18) + \delta_{\text{HOB}}(17)$
18	ν_{CC}	A'	1160	1054	24.57	36.38	1080	1045	29.17	42.60	1034s	1021s	$\nu_{\text{CC}}(69) + \nu_{\text{CH}}(10)$
19	δ_{HOB}	A''	1110	1009	0.00	0.03	1028	994	11.53	3.69	1010vs	1004w	$\delta_{\text{HOB}}(34) + \delta_{\text{CCC}}(22) + \nu_{\text{CC}}(12)$
20	δ_{HOB}	A'	1102	1001	24.00	3.22	1021	987	218.25	1.78			$\delta_{\text{HOB}}(48) + \delta_{\text{CCC}}(18) + \nu_{\text{OB}}(11)$
21	Γ_{HCCH}	A'	1094	994	199.18	0.77	996	963	0.00	0.08			$\Gamma_{\text{HCCH}}(40) + \Gamma_{\text{CCH}}(25) + \Gamma_{\text{HCCBr}}(20)$

(continued overleaf)

Table 2. (Continued)

ν	Assign.	Sym	HF			B3LYP			Raman	Exp. ^a	TED(>10%)
			Wavenumber	Scaled ^a	I_{Infrared}^b	I_{Raman}^c	Waven.	Scaled ^a			
22	δ_{HOB}	A''	1065	967	0.36	0.08	950	99.81	2.08	$\delta_{\text{HOB}}(60) + \nu_{\text{OB}}(31)$	
23	Γ_{HCCH}	A'	1041	945	99.25	0.95	923	0.16	0.16	$\Gamma_{\text{HCCH}}(41) + \Gamma_{\text{CCCH}}(26)$	
24	Γ_{CCCH}	A''	946	860	7.73	0.30	823	9.49	0.05	$\Gamma_{\text{CCCH}}(56) + \Gamma_{\text{HCCBr}}(20) + \Gamma_{\text{HCCB}}(14)$	
25	Γ_{CCCH}	A''	920	836	25.07	0.16	798	16.27	0.08	$\Gamma_{\text{CCCH}}(51) + \Gamma_{\text{HCCB}}(18) + \Gamma_{\text{HCCBr}}(16)$	
26	δ_{CCC}	A''	804	730	44.44	0.31	752	24.54	22.94	$\delta_{\text{CCC}}(27) + \nu_{\text{CB}}(14) + \nu_{\text{CC}}(14)$	
27	Γ_{CCCC}	A'	799	726	24.88	26.78	714	30.66	0.20	$\Gamma_{\text{CCCC}}(40) + \Gamma_{\text{CCCH}}(25) + \Gamma_{\text{OBCC}}(17)$	
28	Γ_{HOB0}	A''	713	648	118.65	0.05	634	83.45	0.11	$\Gamma_{\text{HOB0}}(34) + \Gamma_{\text{CCCC}}(27) + \Gamma_{\text{CCCC}}(14)$	
29	δ_{CCC}	A'	689	626	0.85	6.35	621	0.78	5.22	$\delta_{\text{CCC}}(57) + \delta_{\text{CCH}}(18)$	
30	δ_{OB0}	A'	603	548	26.81	0.36	547	22.88	0.66	$\delta_{\text{OB0}}(19) + \nu_{\text{CB}}(16) + \nu_{\text{CB}}(14)$	
31	Γ_{HOBc}	A''	588	534	20.84	1.10	544	13.11	1.19	$\Gamma_{\text{HOBc}}(41) + \Gamma_{\text{HOB0}}(29)$	
32	Γ_{HOBc}	A''	503	457	81.82	0.35	452	121.87	0.60	$\Gamma_{\text{HOBc}}(21) + \Gamma_{\text{CCCH}}(18) + \Gamma_{\text{CCCC}}(16)$	
33	Γ_{HOBc}	A''	477	433	66.72	0.37	433	28.06	0.31	$\Gamma_{\text{HOBc}}(27) + \Gamma_{\text{CCCC}}(18) + \Gamma_{\text{HOB0}}(18) + \Gamma_{\text{CCCH}}(15)$	
34	δ_{OBc}	A'	457	415	6.45	0.57	416	6.13	0.74	$\delta_{\text{OBc}}(51) + \delta_{\text{CCB}}(27)$	
35	δ_{OB0}	A''	433	394	42.32	0.27	389	22.88	0.21	$\delta_{\text{OB0}}(31) + \nu_{\text{CB}}(29) + \delta_{\text{OBc}}(16) + \nu_{\text{BC}}(11)$	
36	Γ_{CCCC}	A''	432	393	23.77	1.02	384	23.54	0.23	$\Gamma_{\text{CCCC}}(41) + \Gamma_{\text{CCCH}}(16) + \Gamma_{\text{HOBc}}(16)$	
37	δ_{CCH}	A'	282	256	2.39	0.12	253	2.47	0.09	$\delta_{\text{CCH}}(63) + \delta_{\text{OBc}}(21)$	
38	ν_{BC}	A''	253	229	0.02	2.02	227	1.47	5.54	$\nu_{\text{BC}}(47) + \delta_{\text{CCC}}(14)$	
39	Γ_{CCCB}	A'	251	228	1.17	6.41	221	0.03	1.99	$\Gamma_{\text{CCCB}}(31) + \Gamma_{\text{HCCBr}}(17) + \Gamma_{\text{CCCB}}(17) + \Gamma_{\text{OCCB}}(13) + \Gamma_{\text{BCCH}}(12)$	
40	δ_{BCC}	A'	140	127	1.84	0.34	126	1.81	0.36	$\delta_{\text{BCC}}(53) + \delta_{\text{CCBr}}(22) + \delta_{\text{OBc}}(19)$	
41	Γ_{BCCC}	A''	79	71	0.05	0.21	68	0.04	0.09	$\Gamma_{\text{BCCC}}(28) + \Gamma_{\text{CCCB}}(24)$	
42	Γ_{OBCC}	A''	17	15	3.61	0.68	11	3.50	0.62	$\Gamma_{\text{OBCC}}(97)$	

m, medium; s, strong; vs, very strong; w, weak; vw, very weak; sh, shoulder; Γ , torsion; δ , bending; ν , stretching.

^a Wavenumbers in cm^{-1} .

^b Intensities in km/mol .

^c Raman scattering activities.

Geometrical structures

As the experimental values for 4Clpba and 4Brpba are known, the theoretically calculated values may give an idea about the geometry of these molecules and also an idea of how the geometry of these molecules changes from that of phenylboronic acid when we substitute C–X (X = Cl or Br) bonds in place of C–H bonds. The geometry parameters of the title molecules are given in Table S1 (Supporting Information), in accordance with the atom numbering scheme given in Fig. S1 (Supporting Information). 4Clpba and 4Brpba molecules can be all trans, all cis, or mixed trans–cis relative to the B–C bond. According to theoretical results, the ct conformation is the most stable for the 4Clpba and 4Brpba molecules. Both hydrogens 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 4Clpba and 4Brpba, the –B(OH)₂ groups are planar, and at all computational levels lie in the plane of the benzene ring. The calculated B–O and B–C bond lengths in 4Clpba and 4Brpba molecules are in good agreement with those found in the X-ray structure.^[21]

Theoretical calculations show that the C–H bonds of phenylboronic acid are approximately equal to those of 4Clpba and 4Brpba. Therefore similar treatments are valid between the C–C ring bond lengths and bond angles of these molecules by using B3LYP/6–31G(d) level of theory. For example, in the phenylboronic acid (pba) molecule, ring C–C bond lengths vary from 1386 to 1394 Å. In p3 and p4 molecules, these bond lengths vary from ~1.360 to 1.400 Å.^[32] In general, typical B–O distances are ~1.360 Å, consistent with relatively strong π -interactions.^[33] Conversely, the C–B bond length is slightly larger 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 a few boronic acids including the phenylboronic acid molecule Chen *et al.* found approximately same value for this bond length.^[34]

Bond angles at B and C are consistent with sp² hybridization but with significant deviations from the expected 120° angles occurring in close proximity the –B(OH)₂ substituent on C₄ atoms for 4Clpba and 4Brpba.

As can be seen in Table S1 (Supporting Information), there is good agreement for the bond angles at B and C₄. In the pentafluorophenylboronic acid molecule,^[35] while the C₅–C₄–B bond angle is ~122.6°, this bond angle varies from 122.9° to 123.3° for p3-boronic acid and p4-boronic acid formations.^[32] Experimental values of the corresponding bond angle is 122.0° for pba,^[36] 121.9° for 1,4 phenylenediboronic acid,^[37] 120.4° for 4Clpba, and 121.2° for 4Brpba molecules.^[21] Theoretical computed values of these angles are from 119.5° (HF) to 119.7° (B3LYP) for both 4Clpba and 4Brpba molecules. As can be seen in Table S1 (Supporting Information), there is excellent agreement between calculated and experimental bond angles by using the B3LYP level of theory.

The experimental results show that the –B(OH)₂ group is twisted by 21.4, 35.0, and 38.14°, relative to the ring group for phenylboronic acid,^[36] 1,4-phenylenediboronic acid,^[37] and pentafluorophenylboronic acid,^[35] respectively. For 4Clpba and 4Brpba, the corresponding measured values are 26.3 and 26.9°, respectively.^[21] The corresponding calculated values are different from these values (= 0°), because both the ring and the B(OH)₂ groups lie in the same plane.

Potential energy scans with the whole levels of theoretical approximation were performed along the C–C–B–O torsional

angle of 4Clpba and 4Brpba 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 C–C–B–O torsional angle was varied in steps of 10°. The resulting potential energy curve depicted in Fig. S2 (Supporting Information) show the ct form to have the minimum energy.

Vibrational spectra

In order to obtain the spectroscopic signature of the 4Clpba and 4Brpba molecules studied, we performed a wavenumber calculation analysis. Calculations were made for a free molecule in vacuum, while experiments were performed for solid samples, so there are disagreements between the calculated and observed vibrational wavenumbers. Vibrational wavenumbers were calculated for 4Clpba and 4Brpba molecules using the B3LYP method and a larger basis set. The theoretical wavenumbers obtained with the larger basis set (6–311++G**) are in good agreement with the experimental ones. Table 1 presents the calculated vibrational wavenumbers and experimental values. According to the theoretical calculation, the studied molecules were assumed to possess a planar structure of C_s point group symmetry. The 42 normal vibrations are distributed as 13A' + 29A' considering C_s symmetry. All the 42 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 wavenumber within each fundamental wavenumber, $\bar{\nu}$. On the basis on our calculations, as well as experimental IR and Raman spectra, we made a reliable one-to-one correspondence between the fundamentals and any of the wavenumbers calculated by the B3LYP method.

Owing to the lack of sufficiently detailed experimental data for the 4Clpba and 4Brpba molecules, the vibrational spectra were obtained by molecular orbital calculation using Gaussian 03. Because of the low IR and Raman intensity of some modes, it is difficult to observe them in the IR and Raman spectra. Vibrational modes of 4Clpba and 4Brpba were investigated by harmonic wavenumber calculations performed at the corresponding energy-optimized geometries. The assignments of the vibrational absorptions were made by the comparison with those of related molecules and also with the results obtained from the theoretical calculations. The descriptions of the modes presented here are only approximate, some of the vibrations being mixed together.

In the O–H region, very strong and broad bands occur at ~3300 cm⁻¹ in the spectra of some boronic acid molecules. The assignment of these bands to O–H stretching vibrations is straightforward. In the spectra of phenylboronic acid,^[38] pentafluorophenylboronic acid,^[35] and 3- and 4-pyridineboronic acids,^[32] the absorption bands at 3280, 3467 and 3410, and 3320 cm⁻¹ have been assigned to these vibrations. The experimental IR spectra of 4Clpba and 4Brpba molecules are very rich with bands in the 3000–3300 cm⁻¹ region, and from the strength and broadening of these bands we may suggest that intramolecular hydrogen bonds occur in different environments of boronic acid molecules. As seen in the tables, we selected some bands for comparing with the calculated wavenumber values of title molecules. The calculated values of O–H stretching modes are unreliable, because the differences between the calculated and experimental wavenumbers are very high for both molecules. In this region, the experimental

wavenumbers corresponding to these modes appear strong and broad in the IR spectra but weak in the Raman spectra. The TED values of O–H modes suggest that these are pure modes.

In the IR spectrum of 4Clpba molecule, four weak bands at 3099, 3081, 3067, and 3040 cm^{-1} are assigned to C–H stretching vibrations. In the Raman spectrum, two bands at 3087 and 3064 cm^{-1} are assigned to these vibrations. Similarly, for the 4Brpba, one middle band at 3058 cm^{-1} is also assigned to C–H stretching vibration, and the bands at 3080 (vw), and 3060 cm^{-1} (s) are assigned to these vibrations in the IR and Raman spectrum, respectively. The corresponding calculated values fall in the same region. In the high wavenumber region, TED calculations show that all the C–H stretching vibrations are pure modes. The corresponding computed bands at 3095, 3093, 3078, and 3035 cm^{-1} also show clear C–H stretching vibration.

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 the bending vibration of the C–C–H in the ring part. These bands are observed at 1649 (IR), 1657 (IR), 1634 (IR) and 1633 cm^{-1} (R), for pentafluorobenzene, α -bromopentafluorotoluene,^[39] and $\text{C}_6\text{F}_5\text{I}$ ^[40] molecules, respectively. With the $\text{B}(\text{OH})_2$ coordination, these modes do not change significantly. Therefore the modes at $\sim 1600 \text{ cm}^{-1}$ are insensitive to the $\text{B}(\text{OH})_2$ coordination. If we consider the phenylboronic acid case, the band at 1607 cm^{-1} is shifted to 1657 cm^{-1} for pentafluorophenylboronic acid. For the 4Clpba and 4Brpba molecules, these bands are observed at 1596 and 1591 cm^{-1} in the IR spectrum, and at 1596 and 1588 cm^{-1} in the Raman spectrum, respectively. These means that with the coordination of heavy atoms to the phenylboronic acid molecule, the band at 1607 cm^{-1} is shifted to 1591 and 1596 cm^{-1} negatively (see Table 1). However, the TED values in Tables 1 and 2 reveal that these modes are not characteristic and are coupled with the H–C–C bending vibration. But these may be almost pure modes as evidenced from 63 and 64% of TED (Tables 1 and 2) for the title molecules.

The other strong bands in the Raman spectra of 4Clpba and 4Brpba occur at 1404, 1370, 1349 cm^{-1} and at 1397, 1361 cm^{-1} in the IR spectrum. These bands are very intense and should include also the $\nu(\text{B–O})$ asymmetric stretching vibrations, which for phenylboronic and pentafluorophenyl boronic acid are located at 1349 and 1350 cm^{-1} , respectively.^[38,41] Vargas *et al.*^[40] assigned the band around 1370 cm^{-1} as the $\nu(\text{B–O})$ stretching vibration for the homo- and heterotrimeric boron complexes. The TED values in Tables 1 and 2 reveal that these modes are not characteristic but are coupled with H–C–C bending, C–C stretching, and H–O–B bending vibrations.

Stretching vibrations of double bonds usually give rise to very strong absorption bands. Therefore, it is possible that the high intensity of the B–O asymmetric stretching vibration could indicate some double bond character for the studied and phenylboronic acid molecules. The observed wavenumbers for the asymmetric B–O stretching vibrations in the title molecules are very similar to those reported by Faniran and Shurvell^[38] and in our previous papers for this vibration in the spectra of similar molecules.^[32,35]

Santucci and Gilman^[42] associated an absorption band between 1080 and 1110 cm^{-1} with a B–C stretching mode, $\nu(\text{B–C})$, in arylboronic acids. Faniran and Shurvell^[38] also assigned the bands at 1089 and 1085 cm^{-1} in the spectra of the normal and deuterated phenylboronic acids, respectively, and at 1084 cm^{-1} in diphenyl phenylboronate to the B–C stretching vibration. But in

the 1090–1140 cm^{-1} region we could not assign B–C stretching mode by using theoretical TED value owing to the lack of B–C modes.

Similar comparative analyses have been made for the other selected strong or medium bands. As seen in Tables 1 and 2 for TED values, the calculated modes are mixed with C–H, pyridine C–Cl, C–Br, C–C and boronic acid group modes in different proportions. Empirical assignments of the vibrational modes for peaks in the fingerprint region are difficult. In the wavenumber region of 600–1660 cm^{-1} the spectrum observed in the experiments closely resembles the calculated spectrum, except for differences in details. These wavenumbers in the same region are in reasonable agreement with experimental results (Tables 1 and 2).

Conclusion

Attempts have been made in the present work for calculation of the molecular conformational parameters and wavenumber assignments for the compounds 4Clpba and 4Brpba from FTIR and FT-Raman spectra. With regard to the C–B bonds, we considered the conformations cc, tt, and ct. We found a preference for the ct conformation for both molecules. With equilibrium geometries, the harmonic wavenumbers of 4Clpba and 4Brpba were determined and analyzed at DFT level of theory utilizing 6–311++G(d,p) basis sets. There is considerable mixing of the ring vibrational modes and also of the ring and substituent modes. The descriptions of the C–H, pyridine C–C, and boronic acid group modes are very difficult because of the low symmetry of the molecules, as there is no regularity in the change of wavenumbers of the analyzed bands with the position of the substituted $\text{B}(\text{OH})_2$ group in the aromatic ring. The fundamental vibrational modes were characterized by their TED.

Acknowledgements

Financial support by Gazi University Scientific Research Projects Unit (BAP, Project No: 30-2005/3) is gratefully acknowledged. We also thank Dr M. Tahir Gulluoglu for the Scaled Quantum Mechanical (SQM) program.

Supporting information

Supporting information may be found in the online version of this article.

References

- [1] A. Michaelis, P. Becker, *Ber Dtsch Chem Ges Berlin*. **1880**, 13, 52.
- [2] A. Michaelis, P. Becker, *Ber Dtsch Chem Ges Berlin*. **1882**, 15, 180.
- [3] D. G. Hall, *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine*, Wiley-VCH Verlag GmbH: Weinheim, **2005**.
- [4] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, 11, 513.
- [5] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, 102, 1359.
- [6] G. A. Molander, C.-S. Yun, *Tetrahedron* **2002**, 58, 1465.
- [7] *Boron Reagents for Suzuki Coupling*, Sigma-Aldrich, www.sigmaaldrich.com, **2007**.
- [8] N. A. Petasis, I. Akritopoulou, *Tetrahedron Lett.* **1993**, 34, 583.
- [9] E. Cuthbertson, *Boronic Acids: Properties and Applications*, Alfa Aesar: Heysham, **2006**.
- [10] A. H. Soloway, W. Tjarks, R. A. Barnum, F. G. Rong, R. F. Barth, I. M. Codogni, J. G. Wilson, *Chem. Rev.* **1998**, 98, 1515.
- [11] S. K. Kumar, E. Hager, C. Pettit, H. Gurulingappa, N. E. Davidson, S. R. Khan, *J. Med. Chem.* **2003**, 46, 2813.

- [12] W. Yang, X. Gao, B. Wang, *Med. Res. Rev.* **2003**, *23*, 346.
- [13] H. G. Kuivila, A. H. Keough, E. J. Soboczenski, *J. Org. Chem.* **1954**, *19*, 780.
- [14] T. D. James, S. Shinkai, *Top. Curr. Chem.* **2002**, *218*, 159.
- [15] K. E. Maly, N. Malek, J.-H. Fournier, P. Rodriguez-Cuamatzi, T. Maris, J. D. Wuest, *Pure Appl. Chem.* **2006**, *78*, 1305.
- [16] A. Sporzyński, A. Mioekiewicz, B. Gierczyk, R. Pankiewicz, G. Schroeder, B. Brzezinski, *J. Mol. Struct.* **2006**, *791*, 111.
- [17] H. S. Lee, Z. F. Ma, X. Q. Yang, X. Sun, J. McBreen, *J. Electrochem. Soc.* **2004**, *151*, 1429.
- [18] M. Groll, C. R. Berkers, H. L. Ploegh, H. Ovaa, *Structure* **2006**, *14*, 451.
- [19] C. M. Nunes, A. L. Monteiro, *J. Braz. Chem. Soc.* **2007**, *18*(7), 1443.
- [20] K. R. Charan Reddy, A. M. Kayastha, *J. Enzyme Med. Chem.* **2006**, *21*(4), 467.
- [21] M. R. Shimpi, N. SeethaLekshmi, V. R. Pediretti, *Cryst. Growth Des.* **2007**, *7*(10), 1958.
- [22] N. C. Handy, C. W. Murray, R. D. Amos, *J. Phys. Chem.* **1993**, *97*, 4392.
- [23] P. J. Stephens, F. J. Devlin, C. F. Chavalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
- [24] F. J. Devlin, J. W. Finley, P. J. Stephens, M. J. Frish, *J. Phys. Chem.* **1995**, *99*, 16883.
- [25] S. Y. Lee, B. H. Boo, *Bull. Korean Chem. Soc.* **1996**, *17*, 754.
- [26] S. Y. Lee, B. H. Boo, *Bull. Korean Chem. Soc.* **1996**, *17*, 760.
- [27] G. Rauhut, P. Pulay, *J. Phys. Chem.* **1995**, *99*, 3093.
- [28] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [29] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785.
- [30] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc.: Wallingford, CT, **2004**.
- [31] A. Frisch, A. B. Nielsen, A. J. Holder, *Gaussview Users Manual*, Gaussian: Pittsburgh **2003**.
- [32] T. R. Sertbakan, M. Özduran, M. Kurt, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2008**, *70*(33), 664.
- [33] P. N. Horton, M. B. Hursthouse, M. A. Becket, M. P. R. Hankey, *Acta Crystallogr E Struct. Rep.* **2004**, *E60*, o2204.
- [34] X. Chen, G. Liang, D. Whitmire, J. P. Bowen, *J. Phys. Org. Chem.* **1988**, *11*, 378.
- [35] M. Kurt, *J. Mol. Struct.* **2008**, *874*(1–3), 159.
- [36] S. J. Rettig, J. Trotter, *Can. J. Chem.* **1977**, *55*, 3071.
- [37] P. Rodriguez, C. G. Vargas, T. Marris, C. D. Wuest, H. Höpfl, *Acta Crystallogr.* **2004**, *E60*, o1316.
- [38] J. A. Faniran, H. F. Shurvell, *Can. J. Chem.* **1968**, *46*, 2089.
- [39] K. Koppe, PhD Thesis, *Synthesis, Reactivity, Structural and Computational Studies of [C₆F₅Xe]⁺ and [C₆F₅XeF₂]⁺ Salts*, Duisburg University, **2005**.
- [40] G. Vargas, I. Hernandez, H. Höpfl, M. Ochoa, D. Castillo, N. Farfan, R. Santillan, E. Gomez, *Inorg. Chem.* **2004**, *43*(26), 8490.
- [41] S. H. Brewer, A. M. Allen, S. E. Lappi, T. L. Chase, K. A. Briggman, C. B. Gorman, S. Franzen, *Langmuir* **2004**, *20*, 5512.
- [42] A. Fu, D. Du, Z. Zhou, *Spectrochim. Acta.* **2003**, *59A*, 245.