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DFT, FT-Raman, FT-IR and NMR studies of 2-fluorophenylboronic acid

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The experimental and theoretical vibrational spectra of 2-fluorophenylboronic acid (2fpba) were studied. The Fourier transform Raman and Fourier transform infrared spectra of the 2fpba molecule were recorded in the solid phase. The structural and spectroscopic analysis of the molecule was carried out by using Hartree-Fock and density functional harmonic calculations. For the title molecule, only one form was found to be the most stable structure, by using B3LYP level with the 6-31++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). The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of the 2fpba molecule were calculated using the Gauge-Invariant- atomic orbital (GIAO) method in DMSO solution using IEF-PCM model and compared with the experimental data. Finally, geometric parameters, vibrational wavenumbers and chemical shifts were compared with available experimental data of the molecule. Copyright © 2009 John Wiley & Sons, Ltd.

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

Keywords: 2-fluorophenylboronic acid; FT-Infrared spectra; FT-Raman spectra; NMR spectra; torsional barrier

Introduction

The boronic acid ligands have been used in organic synthesis and catalysis, as well as in biological, pharmaceutical, industrial and various other applications. Boronic acids are used extensively in organic chemistry as chemical building blocks and intermediates, and the most widely used example is the Suzuki–Miyaura coupling, a useful synthetic route for biaryl compounds.[1,2] This reaction is used commercially in the synthesis of losartan, an antihypertensive medicine.[3] A wide variety of boronic acid derivatives of divergent biologically important compounds have been synthesized for use as anti-metabolites for a possible two pronged attack on cancer.[4–6] The synthesis of boron compounds for use in cancer treatment by ^{10}B neutron capture therapy (^{10}BNCT) has become an urgent goal in the light of a resurgence of interest in this field.[7,8] A vast array of ^{10}B-enriched compounds have been synthesized and tested in ^{10}BNCT.[9] They are used in anticancer therapy, both in ^{10}BNCT[9] and as chemotherapeutic agents.[10] They are also potent antiviral drugs.[11] Boronic acid analogs have been synthesized as transition state analogs for acyl transfer reactions[12] and as inhibitors of dihydrotase.[13] The boronic acid moiety has been incorporated into amino acids and nucleosides as anti-tumor and anti-viral agents.[14]

It's noted that vibrational spectra of arylboronic acid were reported by Santucci and Gilman.[15] Faniran and Shurvell[16] have assigned the infrared spectra of phenylboronic acid and deuterated phenylboronic acid. We reported theoretical calculations of vibrational spectra of 4-chloro and 4-bromo-phenylboronic acids,[17] 3-pyridine and 4-pyridineboronic acids[18] and pentafluorophenylboronic acid.[19] In the present paper, we report the results of calculated and experimental (IR, Raman and NMR) spectra of the 2fpba molecule, the calculations being on the basis of hartree-fock (HF) and density functional theory (DFT) approximations. To the best of our knowledge, neither detailed quantum chemical calculations nor the vibrational spectra of 2fpba have been reported. Therefore, the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various modes with greater wavenumber accuracy. DFT calculations have been performed to support our wavenumber assignments. Furthermore, we interpreted the calculated spectra in terms of total energy distributions (TED) and made the assignment of the experimental bands because of TED analysis results. Now, we also report the torsional barrier of the 2fpba by using HF and DFT (B3LYP) calculations.

Experimental

The 2-fluorophenylboronic acid sample was purchased from Sigma-Aldrich Chemical Company with a stated purity of greater than 98% and used as such without further purification. The sample of 2fpba is in solid form at room temperature. The infrared spectrum of the sample was recorded between 4000 and 400 cm^{-1} on a Mattson 1000 FT-IR spectrometer which was calibrated using polystyrene bands. The sample was prepared as a KBr disc. The FT-Raman spectrum of the sample was recorded between 3500 and 5 cm^{-1} region on a Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation from an Nd: YAG laser. A liquid nitrogen cooled Ge detector was used. The ^{1}H and ^{13}C NMR spectra were taken in DMSO solutions and all signals were referenced to TMS on a BRUKER DPX-400 FT-NMR spectrometer. All NMR spectra were measured at room temperature.

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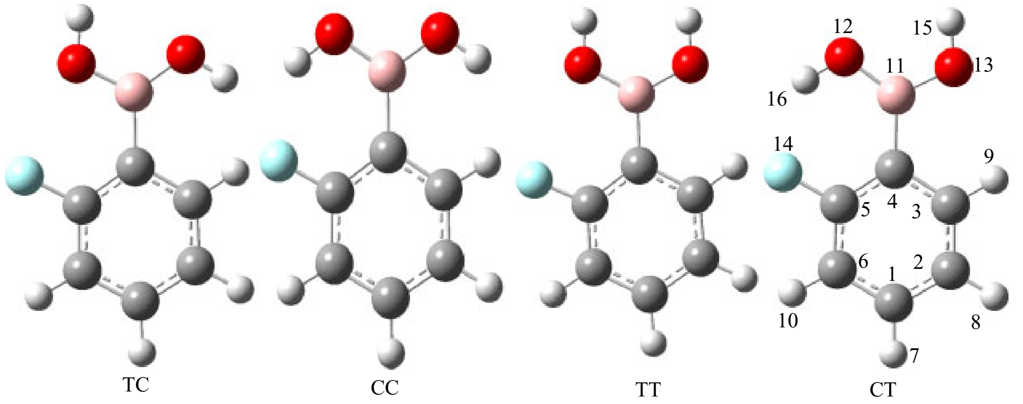

Figure 1. Kinds of 2fpba ligand conformation and atomic numbering. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

Computational Details

The initial molecular geometries were obtained at the RHF/6-31G* level of theory. The final molecular geometry was performed using the Kohn–Sham DFT with the 6-31++G (d,p) basis set and Becke three-parameter hybrid exchange correlation functional known as B3LYP.[20] Analytical evolution of the energy second derivative matrix Cartesian coordinates (Hessian matrix), at the same level of approximation, confirmed the nature of the potential surface minimum point associated with the optimized structures. Potential energy surface scanning around the C–B bond was performed with the 6-31++G(d,p) basis set. The total energy and vibrational wavenumbers were calculated by varying the torsion angle C–C–B–O with a grid point of 10° from 0° to 180°. The saddle point was determined and full geometry optimization was carried out at the transition state. As discussed in previous papers, the four conformations found were fully optimized using same basis set. The presence of an imaginary wave number denotes the nature of the saddle point.[17–19]

Density functionals for all studies reported in this paper have the following form:

$$E_{XC} = (1-a_0)E_X^{LSDA} + a_0E_X^{HF} + a_X\Delta E_X^{B88} + a_cE_C^{LYP} + (1-a_c)E_C^{VWN} \quad (1)$$

where the energy terms are the Slater exchange, the Hartree–Fock exchange and Becke's exchange functional corrections, and the gradient corrected correlation functional of Lee, Yang and Parr; the local correlation functional of Vosko, Wilk and Nusair RB3LYP with 6-31++G(d,p) levels of theory with the optimized geometries has been used to calculate all parameters of 2fpba molecule.

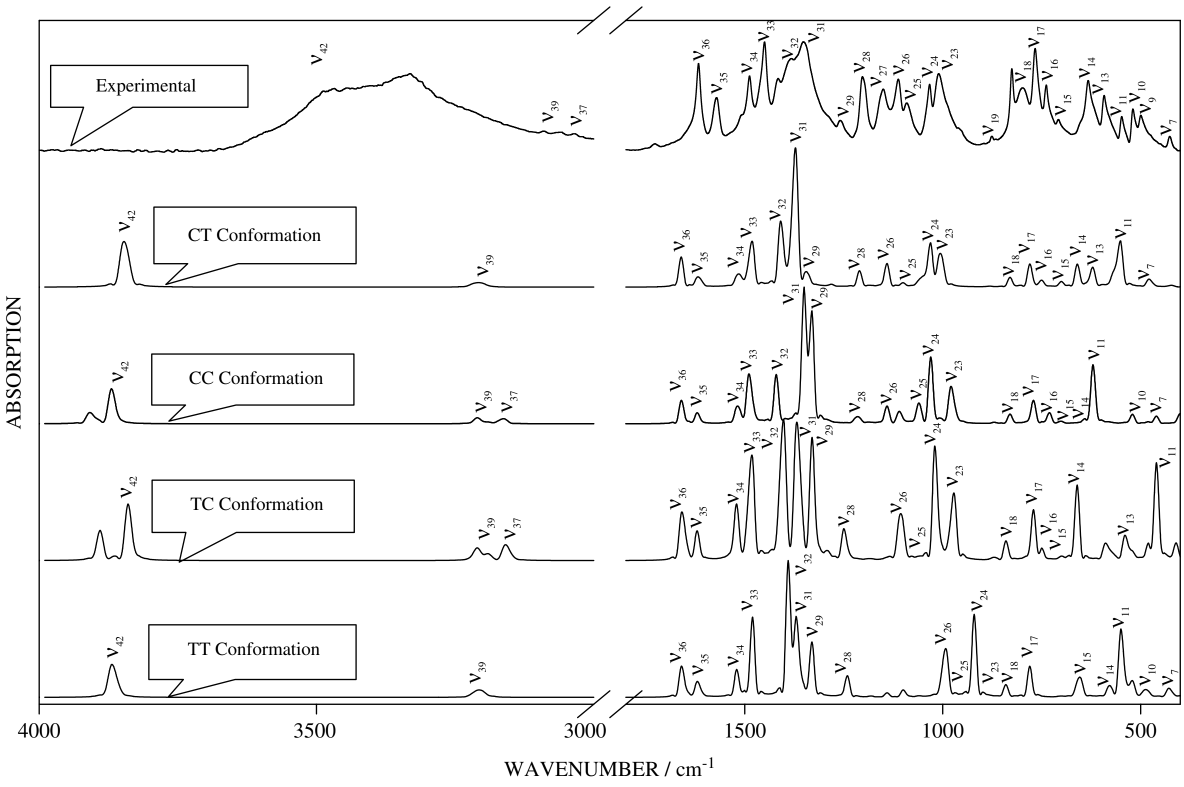

Figure 2. Theoretical and experimental infrared spectra of 2fpba molecule (in KBr).

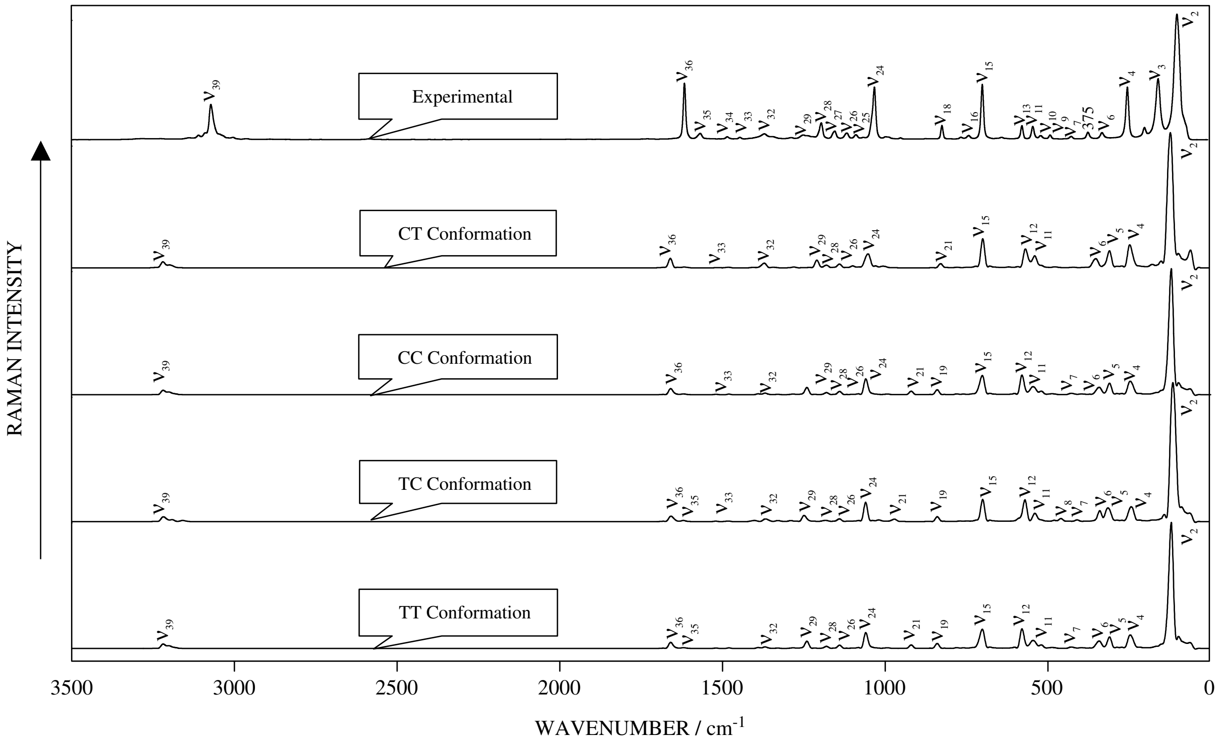

Figure 3. Theoretical and experimental Raman spectra of 2fpba molecule.

Vibrational wavenumbers for the studied sample are calculated with these methods and then scaled by corresponding scaling factors.[21] All the calculations are performed by using the Gauss-view molecular visualization program and the Gaussian 03 program package on a personal computer.[22] These calculations are valuable to gain insight into the vibrational spectroscopy and molecular parameters of structure.

Geometrical Structure

The optimized structure parameters of 2fpba were calculated by DFT/B3LYP level with the 631++G(d,p) basis set. Although the crystal structure of 2fpba has not been reported up till now, almost similar structure of the 3-fluorophenylboronic acid (3fpba) has been studied by x-ray diffraction.[23] All the geometrical parameters are optimized at the critical points and are reported in Table S2 (Supporting Information) together with conformations to compare with the x-ray data of the molecule of 3fpba. The 2fpba molecule has four possible conformations, all-*trans,* all-*cis* and mixed *trans-cis* relative to the B–C bond. All conformations of the 2fpba and its atomic numbering are shown in Fig. 1. Among these conformations the most stable one is the *cis-trans* (ct) state. Potential energy scan with all levels of theoretical approximation was performed along C–C–B–O torsional angle of 2fpba molecule in order to locate the structures that correspond to the energy minima. All the geometrical parameters were simultaneously relaxed during the calculations and the torsional angle was varied gradually in steps of 10°. The selected molecular properties of the all conformations are given in Table S1 (Supporting Information).

The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap is a typical quantity to

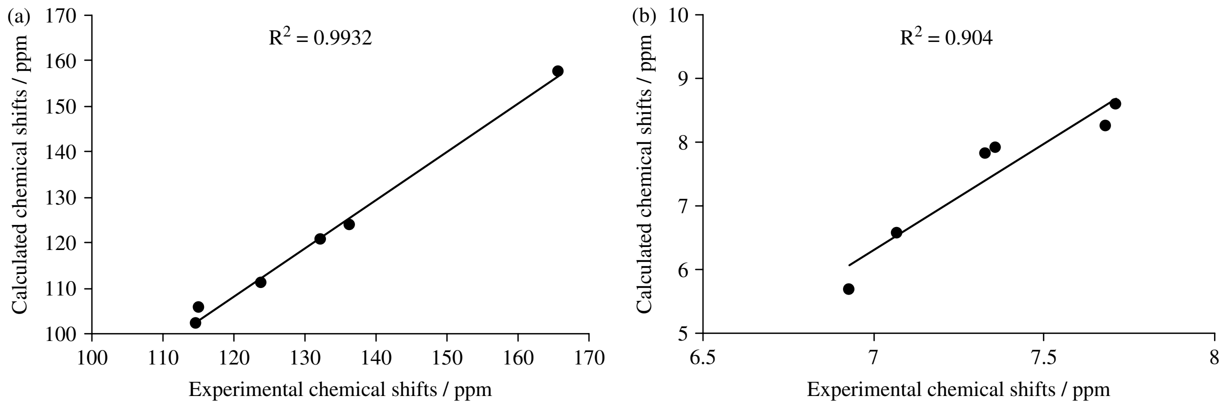

Figure 4. The linear regression between experimental and theoretical ^{13}C (a) and ^{1}H (b) NMR chemical shifts for 2fpba in CT conformation.

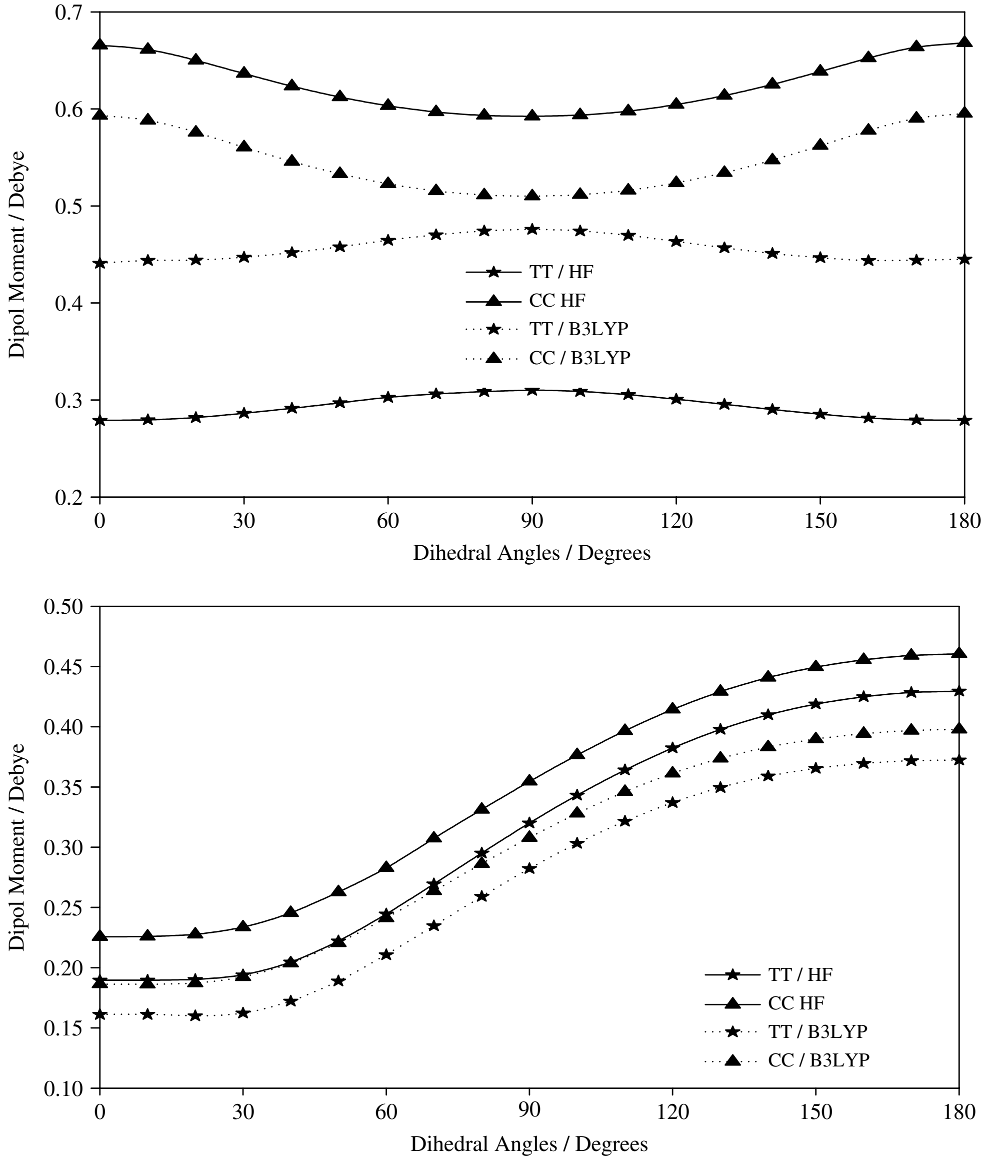

Figure 5. Dihedral angle ($C_5-C_4-B_{11}-O_{12}$) – dipole moment curves for 2fpba (in all conformations).

describe the dynamic stability of a molecule. According to the Koopman theorem, the energies of LUMO and HOMO can be described to a good approximation as

$$E_{\mathrm{LUMO}} = -|\mathrm{EA}|,\ E_{\mathrm{HOMO}} = -|\mathrm{IP}|,$$

where EA is the electron affinity and IP is the ionization potential. It can be seen from Table S1 (Supporting Information) that the HOMO of all conformations is mainly located on the phenyl ring and the fluorine atom. Meanwhile the LUMO is contributed mainly by the whole of molecule for all conformations with little contribution from the fluorine atom.[24]

Both O_{12} and O_{13} oxygens lone pairs of boronic acid have resonance interaction with the hydrogen in the O–B–O plane. The position of the $-B(OH)_2$ group is the lowest-energy planar form and at all of the computational levels it lies in the plane of the phenyl ring.[19] The $B(OH)_2$ group is planar for all computational levels, being in the plane of the ring. The calculated ring $-B(OH)_2$ (C4–B11) bond length in 2fpba molecule is 1.573 A° (ct), 1.589 A° (cc), 1.568 A° (tt) and 1.576 A° (tc). These bond lengths were compared with B–C distances in similar molecular structures (values of 1.579, 1.562 and 1.533 A° for crystals of pentafluorophenylboronic acid,[25] 3-fluorophenylboronic acid[23] and 3-bromophenylboronic acid,[26] respectively).

The optimized bond lengths of the C–C bond in ring systems are in the ranges 1.387–1.410 A° (ct), 1.387–1.410 A° (cc), 1.391–1.411 A° (tt) and 1.392–1.411 A° (tc). A similar treatment is valid for the C–C ring bond lengths for the x-ray structure of a similar molecule. For example, the bond length is observed in the range of 1.372 A° to 1.384 A° for pentaflurophenylboronic acid,[25] 1.365 A° to 1.406 A° for 3-flurophenylboronic acid[23] and 1.367 A° to 1.444 A° for bromophenylboronic acid.[26] As given in Table S2 (Supporting Information), the calculated B–O, C–C and B–C bond lengths in the 2-fpba molecule are in good agreement with those found in the x-ray data.

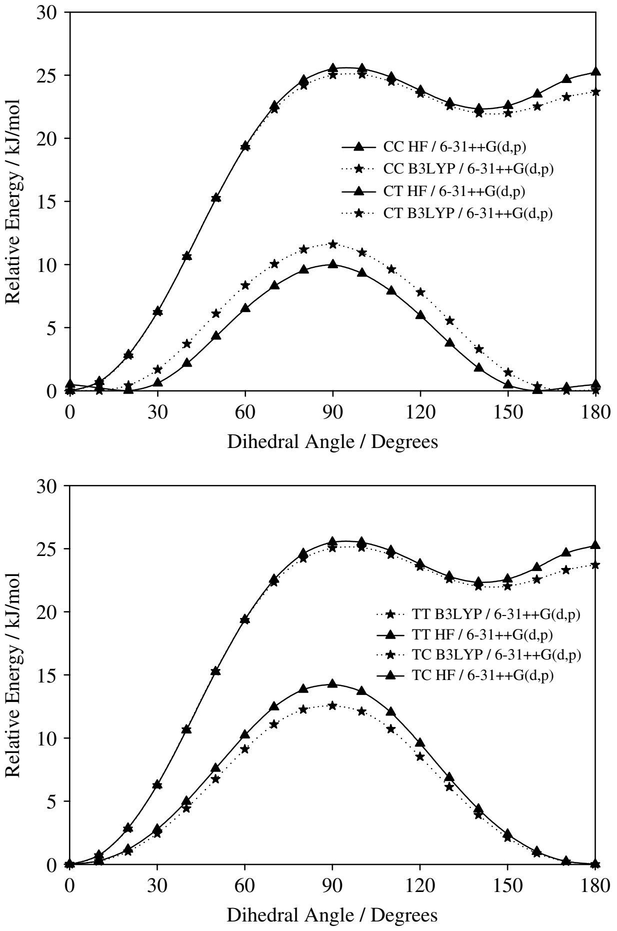

Figure 6. Dihedral angle ($C_5-C_4-B_{11}-O_{12}$)-energy curves for 2fpba (in all conformations).

Bond angles at B and C are consistent with sp^2 hybridization but with significant deviations from the expected 120° angle, occurring in close proximity to the $B(OH)_2$ substitute on C1. In the x-ray data of pentafluorophenylboronic acid molecules, the angles C5–C4–C3 [115.31°], F–C5–C4 [116.81°] and F–C3–C4 [117.20°] are significantly smaller than the other C–C–C and C–C–F angles, respectively.[25] The calculated bond angles are found to be: [C5–C4–C3; 114.5° (CC), 115.6° (TT), 115.0° (TT) and 115.4° (CT)], [F14–C5–C4; 118.8° (CC), 119.7° (TC), 118.5° (CT) and 119.7° (TC)] and [H9–C3–C4; 117.7° (CC), 118.0° (TT), 117.6° (TC) and 118.0° (CT)] for B3LYP/6-31++G(d,p) calculations.

Assignment of Fundamentals

In all conformations 2fpba belongs to C_S symmetry. The 2fpba molecule has 16 atoms. The 42 normal vibrations are distributed as 29 A′(in-plane) + 13A″(out-of-plane). All the vibrations are active in both IR absorption and Raman scattering. The calculated infrared and Raman wavenumbers together with experimental data of the title molecule are presented in Table 1. Theoretical and experimental (IR and Raman) spectra of 2fpba are given in Figs 2 and 3. The TED was calculated by using the scaled quantum mechanical program (SQM)[27] and the fundamental vibrational modes were characterized by their TED.

The theoretical Raman intensities (I_i^R) can be derived from the computed Raman scattering activities using the following equations:

$$I_i^R = C(\upsilon_0 - \upsilon_i)^4 . \upsilon_i^{-1} . B_i^{-1} . S_i \qquad (2)$$

where B_i is a temperature factor which accounts for the intensity contribution of excited vibrational states, and is represented by the Boltzmann distribution:

$$B_i = 1 - \exp\left(-\frac{h\upsilon_i c}{kT}\right) \qquad (3)$$

In Eqn (2) υ_0 is the wavenumber of the laser excitation line (in this work, we have used the excitation wave number $\upsilon_0 = 9398.5$ cm^{-1}, which corresponds to the wavelength of 1064 nm of a Nd : YAG laser), υ_i is the wavenumber of the normal mode (cm^{-1}), while S_i is the Raman scattering activity of the normal mode Q_i. I_i^R is given in arbitrary units (C is a constant equal 10^{-12}). In Eqn (3) h, k, c and T are Planck constant, Boltzmann constant, light-speed and temperature (in Kelvin), respectively. The B_i factor was assumed to 1, otherwise, the calculated Raman intensities for the bands below 300 cm^{-1} were extremely overestimated, in comparison to experimental intensity values.[28]

The carbon–carbon stretching modes of the phenyl group are expected in the range of 1620 to 1320 cm^{-1}.[16] In the present study, the carbon–carbon stretching vibrations of the 2fpba have been observed at 1617 (s) and 1573 (s) cm^{-1} in the FT-IR and 1617 (s) and 1565 (m) cm^{-1} in FT-Raman spectra. The corresponding theoretical values of these vibrations are 1625 (ct), 1622 (cc), 1621(tt) and 1620 (tc) cm^{-1}, and 1580(ct), 1582(cc), 1581(tt) and 1583 (tc) cm^{-1}. The in-plane and out-of-plane bending vibrations of the phenyl ring are presented in Table 1. These assignments are in good agreement with the literature. These bands are observed at 1649 (IR), 1657 (IR), 1634 (IR) and 1633 cm^{-1} (Ra) for the pentafluorobenzene and alfa-bromo-pentafluoro-toluene.[17–19] The C=C stretching mode in the phenyl ring is found in the IR spectrum at 1608 cm^{-1}.[15] At 1442 and 1420 cm^{-1} fairly strong and sharp bands were observed because of the benzene ring vibration in the phenyl boronic acid linkage (Ph–B); 1375 cm^{-1} (s): B–O band in $-B(OH)_2$ and 1345 cm^{-1} (s): strong stretching B–O band in phenylboronic acid linkage.[29] We also observed B-O a stretching vibration at 1385 cm^{-1} (vw, IR) and 1370 cm^{-1} (m, Ra). The very strong band at 1354 cm^{-1} belongs to the stretching B–O vibration in the experimental IR spectrum. The spectrum observed in the experiment closely resembles the calculated spectrum in details.

The presence of C–H stretching vibrations in the region 3000–3200 cm^{-1} is common for a heteroaromatic structure. In the high wavenumber region, the aromatic C–H stretching modes are observed at 3035 (w), 3061 (w) and 3091(w) cm^{-1} in the FT-IR spectrum and 3071(vs) and 3091(w) cm^{-1} in the FT-Raman spectrum, respectively. The calculated corresponding values fall within the same region. In this region, the TED calculations show that all the C–H stretching vibrations are pure modes. The corresponding computed bands at 3119, 3143 and 3150 cm^{-1} also show clear C–H stretching vibration. In the literature, the corresponding bands are observed at 3095, 3080, 3070, 3040 and 3020 cm^{-1} in the FT-Infrared spectrum for phenylboronic acid.[17,19] For 3-pyridineboronic acid, these bands are observed at 3099 and 3032 cm^{-1} in the FT-Infrared spectrum and at 3082 and 3050 cm^{-1} in the FT-Raman spectrum.[18] In the IR spectrum of 4-Cl-pba molecule, four weak bands at 3099, 3081, 3067 and 3040 cm^{-1} are assigned to C–H stretching vibrations. In the FT-Raman spectrum,

Table 1. Comparison of the observed and calculated vibrational spectra of free 2-fluorophenylboronic acid for B3LYP 6-31++G(d,p)

Mode		CT conformation			CC conformation			TT conformation			TC conformation					
		Waven.[a]	IR[c]	Ra.[d]	Waven.[a]	IR[c]	Ra.[d]	Waven.[a]	IR[c]	Ra.[d]	Waven.[a]	IR[c]	Ra.[d]	Exp. IR	Exp. Ra	TED[b] (10%)
ν_1	A″	62	0.30	0.15	19	0.07	0.25	29	0.09	0.32	−42	–	–			Γ_{OBCC} (98)
ν_2	A″	122	0.11	4.71	115	0.11	6.81	121	1.93	3.60	113	0.60	5.36		103 vs	Γ_{BCCC} (38)+Γ_{FCCB} (17)+Γ_{OBCC} (11)
ν_3	A′	176	1.22	0.06	196	0.70	0.04	166	1.84	0.02	173	0.36	0.03		161 s	δ_{BCC} (70)+δ_{OBC} (26)
ν_4	A″	241	0.06	1.39	240	0.52	1.77	240	1.23	0.91	239	0.03	1.19		256 s	Γ_{FCCC} (44)+Γ_{CCCC} (14)
ν_5	A′	306	0.36	1.10	316	2.17	1.85	305	0.31	0.67	308	2.45	1.38			ν_{BC} (19)+δ_{OBC} (31)+δ_{FCC} (19)
ν_6	A′	347	1.25	0.86	349	2.59	1.23	337	1.64	0.67	335	2.64	0.79		333 w	δ_{BCC} (46)+δ_{FCC} (19)
ν_7	A″	414	1.13	2.13	393	8.21	6.58	387	1.23	3.00	402	7.79	6.56	428 w	427 vw	Γ_{CCCC} (43)+Γ_{CCCH} (23)+Γ_{OBCC} (12)
ν_8	A′	466	5.40	3.98	450	5.43	4.17	417	9.03	6.86	449	46.38	12.15			δ_{FCC} (32)+δ_{OBC} (20)+δ_{OBO} (17)
ν_9	A″	511	0.21	5.34	471	1.11	12.25	475	7.83	4.09	467	6.67	5.04	500 m	493 vw	Γ_{CCCC} (31) Γ_{CCCH} (28) Γ_{FCCC} (13)
ν_{10}	A′	527	0.42	39.18	510	7.46	6.60	511	11.71	12.62	514	6.55	7.64	520 m	520 vw	δ_{CCC} (24) δ_{FCC} (20)
ν_{11}	A″	541	30.37	14.29	530	0.35	61.21	532	6.66	25.15	527	10.85	31.77	549 m	547 m	Γ_{HOBC} (45) Γ_{HOBH} (28) Γ_{HOBO} (10)
ν_{12}	A′	555	5.54	80.63	563	1.01	67.88	536	49.59	14.66	560	2.26	100			δ_{CCC} (25)
ν_{13}	A″	609	11.76	2.44	606	43.97	1.06	565	7.18	78.07	573	11.50	10.73	593 m	580 m	Γ_{HOBC} (51) Γ_{HOBO} (38)
ν_{14}	A″	644	11.40	0.53	620	2.95	1.33	640	23.07	0.17	646	34.91	0.81	634 s	641 vw	Γ_{HOBO} (42) Γ_{OBCC} (25) Γ_{CCCC} (12)
ν_{15}	A′	685	2.36	100	686	1.42	100	688	0.63	100	686	1.37	98.51	708 w	701 s	ν_{CC} (29) δ_{CCC} (25) ν_{BC} (18)
ν_{16}	A″	732	3.01	1.14	715	7.85	2.16	744	0.48	1.33	733	4.36	1.72	739 m	742 w	Γ_{CCCC} (33) Γ_{OBCC} (22) Γ_{CCCH} (16) Γ_{FCCB} (10)
ν_{17}	A″	761	12.27	2.01	755	19.34	2.15	762	21.38	2.34	755	25.19	2.18	768 vs	767 vw	Γ_{CCCH} (71) Γ_{HCCF} (12)
ν_{18}	A′	811	4.72	15.21	811	7.17	18.37	822	8.29	17.36	821	8.92	20.44	799 m	825 m	δ_{CCC} (33) ν_{FC} (27) δ_{CCH} (14)ν_{CC} (11)
ν_{19}	A″	864	0.35	0.11	851	0.82	0.08	865	0.61	0.05	854	1.38	0.15	877 vw		Γ_{CCCH} (46) Γ_{HCCH} (20) Γ_{HCCF} (17)
ν_{20}	A″	954	0.37	0.01	934	0.56	0.07	900	56.11	12.20	932	0.82	0.19			Γ_{HCCH} (46) Γ_{CCCH} (32)
ν_{21}	A″	981	0.02	0.03	955	40.22	16.10	955	0.71	0.03	952	45.08	14.40		950 vw	Γ_{HCCH} (65) Γ_{CCCH} (19)
ν_{22}	A′	983	25.93	8.16	969	0.03	0.01	972	52.93	2.84	967	0.06	0.01			ν_{OB} (45) δ_{BOH} (45)

Table 1. *(Continued)*

Mode		CT conformation			CC conformation			TT conformation			TC conformation			Exp. IR	Exp. Ra	TED^b (10%)
		Waven.^{a}	IR^c	Ra.^{d}	Waven.^{a}	IR^c	Ra.^{d}	Waven.^{a}	IR^c	Ra.^{d}	Waven.^{a}	IR^c	Ra.^{d}			
υ_{23}	A′	1010	25.64	3.92	1007	49.14	0.20	978	0.07	0.02	995	65.16	7.05	1011 s		δ_{BOH} (89)
υ_{24}	A′	1031	5.15	79.34	1038	14.28	97.41	1035	0.66	64.12	1037	0.50	78.51	1034 m	1033 s	υ_{CC} (65) δ_{CCH} (15)
υ_{25}	A′	1076	1.62	5.42	1083	10.94	4.56	1074	5.80	0.70	1081	36.77	1.32	1092 w	1089 w	δ_{CCC} (25) δ_{BOH} (16) δ_{CCH} (15)υ_{CC} (14)
υ_{26}	A′	1117	12.63	14.16	1117	13.59	17.38	1116	2.92	11.50	1117	0.69	13.33	1113 m	1116 m	δ_{CCH} (36) υ_{CC} (32)
υ_{27}	A′	1156	0.28	9.13	1160	0.96	8.54	1156	0.64	7.80	1159	0.72	7.88	1151 m	1154 m	δ_{CCH} (78) υ_{CC} (18)
υ_{28}	A′	1183	7.66	26.39	1188	8.19	28.96	1215	16.43	28.56	1220	18.82	34.27	1203 s	1197 m	υ_{FC} (37) υ_{CC} (29) δ_{CCH} (26)
υ_{29}	A′	1254	1.09	3.34	1260	1.00	4.34	1257	0.08	2.77	1262	2.50	3.90	1260 w	1251 vw	δ_{CCH} (56) υ_{CC} (22)
υ_{30}	A′	1313	5.01	1.55	1304	100	20.13	1301	35.51	1.51	1299	64.55	4.81			υ_{CC} (82)
υ_{31}	A′	1344	100	24.32	1321	92.74	25.02	1337	61.58	6.83	1336	97.28	17.56	1354 vs		υ_{BO} (29) υ_{BC} (26) δ_{BOH} (17)
υ_{32}	A′	1376	39.59	1.07	1389	34.80	2.32	1358	100	3.49	1373	100	7.17	1385 vw	1370 m	υ_{BO} (66)
υ_{33}	A′	1451	31.93	2.87	1454	51.10	4.53	1448	53.85	2.02	1451	74.23	2.94	1450 vs	1446 vw	δ_{CCH} (41) υ_{CC} (23) υ_{BO} (11)
υ_{34}	A′	1482	8.85	1.46	1483	16.87	1.24	1487	17.69	1.59	1489	28.65	1.76	1488 m	1484 vw	δ_{CCH} (49) υ_{CC} (30)
υ_{35}	A′	1580	7.65	3.74	1582	9.09	4.18	1581	14.22	3.14	1583	13.99	4.51	1573 s	1565 m	υ_{CC} (68) δ_{CCH} (15)
υ_{36}	A′	1625	14.86	33.63	1622	18.74	38.05	1621	27.43	27.86	1620	33.79	34.57	1617 s	1617 s	υ_{CC} (70)
υ_{37}	A′	3119	0.41	5.49	3095	5.87	7.54	3116	0.80	4.77	3087	10.47	6.79	3035 w		υ_{CH} (100)
υ_{38}	A′	3132	1.71	8.43	3125	1.77	8.01	3129	3.54	7.44	3122	2.55	7.10			υ_{CH} (100)
υ_{39}	A′	3143	2.16	7.05	3139	4.16	13.15	3142	4.21	3.61	3137	6.67	11.11	3061 w	3071 vs	υ_{CH} (98)
υ_{40}	A′	3150	0.56	18.22	3151	0.60	20.17	3147	1.46	17.20	3149	1.34	18.11	3091 w	3091 w	υ_{CH} (97)
υ_{41}	A′	3761	17.28	1.82	3783	31.48	1.27	3775	10.33	4.33	3754	29.91	7.35			υ_{OH} (99)
υ_{42}	A′	3762	19.27	6.01	3821	11.46	1.83	3786	21.13	7.87	3806	14.46	1.91	3467 s		υ_{OH} (99)

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; δ, bending; υ, stretching; Γ, torsion; IR, Infrared intensities; Ra, Raman intensities. ^{a} Scaling factor: 0.9781 ^{b} Total energy distribution calculated B3LYP 6-31++G(d,p) level for CT conformation. ^{c} Relative absorption intensities normalized with highest peak absorption equal to 100. ^{d} Relative Raman intensities calculated by Eqn (2) and normalized to 100.

two bands at 3087 and 3064 cm^{-1} are assigned to these vibration. Similarly, for the 4-Brpba, one middle strong band at 3058 cm^{-1} is also assigned to a C–H stretching vibration, and the bands at 3080 (vw) and 3060 (s) cm^{-1} are assigned to these vibrations in both, IR and Raman spectra.[17,19]

In the O–H region, very strong and broad bands in the spectra of some boronic acid molecules occur at ∼3300 cm^{-1}. The assignment of these bands to O–H stretching vibrations is straightforward. In the spectra of phenylboronic acid,[30] as well as of 3 and 4-pyridineboronic acids,[18] absorption bands were observed at 3280 and 3467 cm^{-1}, respectively. The O–H stretching modes are observed at 3467 cm^{-1} in the FT-IR spectrum for the 2fpba molecule. With the fluorine substitution, the OH stretching vibrations shifted to higher wavenumber values.[16–19,29] In the 2fpba molecule, the OH stretching vibration shifted by 187 cm^{-1} for the fluorine substitution. This means that in the boronic acid part, the O–H vibrations are sensitive because of fluorine coordination.

The B–O asymmetric stretching band of the phenylboronic acid occurs at 1370 cm^{-1} in the infrared spectrum[16] and at 1375 (s) for phenylboronic acid linkage.[29] These bands are very intense and should include also the asymmetric stretching vibrations, which for phenylboronic and pentafluorophenylboronic acids are located at 1349 and 1350 cm^{-1}, respectively.[18,30] Kahraman *et al.*[29] assigned the band around 1370 cm^{-1} to the υ(B–O) stretching vibrations for the homo- and heterotrinuclear boron complexes. The corresponding bands were observed at 1385 cm^{-1} in the FT-IR and 1370 cm^{-1} in the FT-Raman spectra of the 2fpba molecule. These vibration were calculated at 1376, 1389, 1358 and 1373 cm^{-1} with a B3LYP/6-31++G(d,p) basis set (respectively CT, CC, TT and TC conformations). When the fluorine atoms substituted at the second position of the phenylboronic acid, the B–O vibration shifted around 35 cm^{-1} in the FT-IR spectrum. The TED calculations show that the B–O stretching mode is clearly a pure mode in Table 1. The symmetric ring breathing mode was usually found near 1000 cm^{-1} in the monosubstituted benzene ring. However, the B–O–H deformation vibration δ(B–OH) was observed at 1002 cm^{-1} in the infrared spectrum of the phenylboronic acid. This band was observed at 1197 cm^{-1} for boric acid and at 994 (w) cm^{-1} for diphenylboronate.[16–19] The δ(B–OH) vibration of the 2fpba was observed at 1011 cm^{-1} in the FT-IR spectrum. This vibration was calculated at 1010, 1007, 978 and 995 cm^{-1} respectively for CT, CC, TT and TC conformations at B3LYP/6-31++G(d,p) level of theory. The B–C stretching bands were observed at 1080 and 1110 cm^{-1} for vibration of the arylboronic acid by Santucci and Gilman.[15] This vibration was observed at 1089 cm^{-1} for phenylboronic acid by Faniran and Shurvell.[16] The corresponding bands were observed at 1354 cm^{-1} in the infrared spectrum. The B–C stretching band of 2fpba molecule was shifted by 265 cm^{-1} for the fluorine substitution. This means that in the boronic acid part B–C vibrations are sensitive because of fluorine substitution.

The C–F in-plane bending wavenumber appears in the region 700–850 cm^{-1}. Sundaraganesan *et al.*[31] observed a strong band at 759 cm^{-1} in the FT-IR spectrum and a very strong band at 750 cm^{-1} in the FT-Raman spectrum for the 2-amino-4, 5-difluorobenzoic acid molecule. The C–F out-of-plane bending mode was identified as the 590 cm^{-1} band.[15,18,30–32] In the 2fpba molecule, we observed one band at 520 cm^{-1} both in the FT-IR and in the FT-Raman spectra. The corresponding calculated bands are at 527, 510, 511 and 514 cm^{-1} for CT, CC, TT and TC forms, respectively. However, the TED calculations show that a mixed mode of C–C–F in-plane bending and C–C–C in-plane bending occurs.

In the organic halogen compounds, the band due to C–F stretching vibrations may be found over a wide wavenumber range (1360–1000 cm^{-1}).[33] The C–F stretching vibration was observed at 1203 cm^{-1} (IR) and 1197 cm^{-1} (Ra) in spite of the TED distributions mixed mode. More detailed information is given in Table 1.

NMR Spectra

The molecular structure of the title compound was optimized. Then, gauge-including atomic orbital (GIAO) ^{13}C NMR and ^{1}H NMR chemical shifts calculations of the title compound were carried out by using B3LYP functional with 6-31++G(d,p) basis sets. The GIAO[34,35] method is one of the most common approaches for calculating isotropic nuclear magnetic shielding tensors. For the same basis set size, the GIAO method is often more accurate than other approaches.[36] The NMR spectra calculations were performed by using the Gaussian 03[22] program package. The calculations reported were performed in DMSO solution using the IEF-PCM model, rather than in the gas phase, in agreement with experimental chemical shifts obtained in DMSO solution.

Experimental and theoretical chemical shifts of 2fpba in ^{1}H and ^{13}C NMR spectra were recorded and the obtained data are presented in Table S3 (Supporting Information). The linear correlations between calculated and experimental data of ^{1}H and ^{13}C NMR spectra are noted. Correlation coefficients of ^{13}C NMR are determined as 0.9932 (CT conformation), 0.9914 (CC conformation), 0.9920 (TC conformation) and 0.9919 (TT conformation). Correlation coefficients of ^{1}H NMR are determined as 0.9044 (CT conformation), 0.8711 (CC conformation), 0.8673 (TC conformation) and 0.8919 (TT conformation). The data show a good correlation between predicted and observed proton and carbon chemical shifts. The correlations of NMR spectra are presented in Fig. 4 for the CT conformation. The agreement between the experimental and calculated data is satisfactory for carbon-13 and slightly worse for proton shifts. The protons are located on the periphery of the molecule and therefore are supposed to be more susceptible to molecular (solute–solvent) effects than carbons. For this reason the agreement between the experimental and the calculated data for proton is worse than that for carbon-13.[37]

All the theoretical chemical shifts of the ^{13}C NMR and ^{1}H NMR of the boronic acid group were smaller than the calculated values, while those of the ^{1}H NMR of the phenyl ring were larger than calculated values for the CT conformation.

The range of the ^{13}C NMR chemical shifts for a typical organic molecule usually is $>$100 ppm[38,39] and the accuracy ensures reliable interpretation of spectroscopic parameters. In the present paper, the ^{13}C NMR chemical shifts in the ring for the title compound are $>$100 ppm, as they would be expected. The C_5 atom which bonds to fluorine shows determined ^{13}C NMR shifts that are very high.

Torsional Barrier

The dihedral angles (C_5–C_4–B_{11}–O_{12}) are 0° and 90°; corresponding conformations are E0 and E90, respectively. The calculated torsional barrier and dipole moment results are shown in Table S4 (Supporting Information). The variations of the torsional barrier and the dipole moment with the dihedral angle for 2fpba are shown in Figs 5–6. The torsional barrier for 2fpba rotation was computed at the B3LYP and HF level with the 6-31++G(d,p) basis set.

Conclusion

This paper presents the experimental and theoretical vibrational IR and Raman spectra of the title molecule. The FT-IR and FT-Raman spectra have been recorded in the range 4000–400 cm^{-1} and 3500–5 cm^{-1}, respectively. Because of the lack of experimental information on the geometric structure available in the literature, theoretical calculations were compared with those for a similar molecule. All observed vibrational bands have been discussed and assigned with the help of TED values on the basis of our calculations. The molecular geometry and all of the vibrational wavenumbers of 2fpba in the ground state have been calculated by using the density functional method (B3LYP/6-31++G(d,p) level. A complete assignment of the fundamentals was proposed on the basis of the TED calculation.

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Supporting information

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

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