

# Infrared and Raman spectrum, molecular structure and theoretical calculation of 3,4-dichlorophenylboronic acid

Mustafa Kurt<sup>a,\*</sup>, T. Raci Sertbakan<sup>a</sup>, Mustafa Özduran<sup>a</sup>, Mehmet Karabacak<sup>b</sup>

<sup>a</sup> Department of Physics, Ahi Evran University, TR-40100 Kırşehir, Turkey

<sup>b</sup> Department of Physics, Afyon Kocatepe University, TR-03040 Afyonkarahisar, Turkey

## ARTICLE INFO

### Article history:

Received 5 November 2008

Received in revised form 14 December 2008

Accepted 16 December 2008

Available online 30 December 2008

### Keywords:

IR and Raman spectra

DFT

Dichlorophenylboronic acid

Vibrational frequencies

Molecular structure

## ABSTRACT

In this work, the experimental and theoretical study on the structures and vibrations of 3,4-dichlorophenylboronic acid (3,4-dcpba,  $C_6H_3B(OH)_2Cl_2$ ) are presented. The Fourier Transform Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) and the Fourier Transform Raman spectra ( $3500\text{--}5\text{ cm}^{-1}$ ) of the title molecule in the solid phase have been recorded. There are four conformers for this molecule. The computational results diagnose the most stable conformer of 3,4-dcpba as the *ct* form. The geometrical parameters and energies have been obtained for all four conformers from DFT (B3LYP) with 6-311++G(d,p) basis set calculations. The vibrations of stable and unstable conformers of 3,4-dcpba are researched with the aid of quantum chemical calculations. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The molecular structures, vibrational frequencies, Infrared intensities and Raman scattering activities were calculated. The spectroscopic and theoretical results are compared. The optimized bond lengths, bond angles and calculated frequencies showed the excellent agreement with the experimental results. The theoretical spectrogram for the Infrared and Raman spectrum of the title molecule has been constructed.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

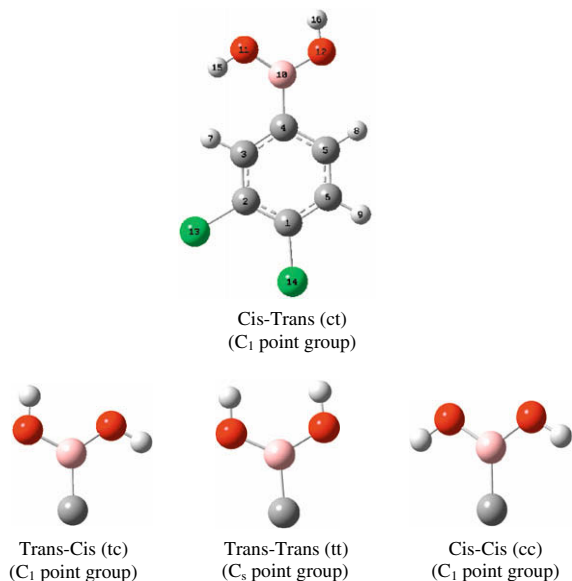
Organic compounds containing boron and boronic acids have been known for over a century. The boronic acid ligands have become an object of recent increasing interest due to their applications in crystal engineering, biology, medicine, analytical chemistry, organic synthesis, catalysis, supramolecular chemistry and materials science. A wide variety of boronic acid derivatives of divergent biologically important compounds have been synthesized as anti-metabolites for a possible two-pronged attack on cancer [1–8]. In addition to inhibition of tumor growth, the use of boron-10 neutron capture therapy [9] would be possible owing to the preferential localization of boron compounds in tumor tissue. Boronic acid analogs have been synthesized as transition state analogs for acyl transfer reactions [10] and inhibitors of dihydro-tase [11]. The boronic acid moiety has also been incorporated into amino acids and nucleosides as anti-tumor, anti-viral agents [12]. Phenylboronic acids are a versatile building block in organic synthesis and an important intermediate in the synthesis of active compounds in the agrochemical and pharmaceutical industries [13]. The biological application of particular dichlorophenylboronic acids was studied by Stabile et al. and Westmark and Smith [4,5].

*n*-Butylboronic acid were investigated using experimental and theoretical approaches [14]. Shimpi et al. [15] discussed crystal structures of 4-chloro- and 4-bromophenylboronic acids and hydrates of 2- and 4-iodophenylboronic acid in two different forms, which were by single-crystal X-ray diffraction methods. 2-Aminocarbonyl-phenylboronic acid and its corresponding ester, ethane-diol (2-aminocarbonyl) phenylboronate has been investigated computationally using both density functional theory and second-order Møller–Plesset perturbation theory [16]. The experimental and theoretical vibrational spectra of 4-chloro- and 4-bromophenylboronic acids were studied by Kurt [17]. Horton et al. [18] investigated crystal structure of pentafluorophenylboronic acid molecule. Infrared spectra of phenylboronic acid and diphenyl phenylboronate were studied by Faniran [19]. Kurt [20] investigated molecular structure and vibrational spectra of the pentafluorophenylboronic by density functional theory and *ab initio* Hartree Fock calculations. The molecular structures of phenylboronic acid and phenylboronic acid dimer were investigated experimentally using X-ray structural analysis and spectroscopic methods by Cyrański et al. [21].

Up to our knowledge no DFT calculations and detailed vibrational IR and Raman analysis have been performed on 3,4-dcpba molecule. The main aim of the study was the detailed description of 3,4-dcpba molecule using both experimental and computational techniques. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if

\* Corresponding author.

E-mail address: [kurt@gazi.edu.tr](mailto:kurt@gazi.edu.tr) (M. Kurt).



**Fig. 1.** The theoretical optimized possible four geometric structures with atoms numbering of 3,4-dcpba.

the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [22–26].

**Table 2a**

Geometric parameter set of 3,4-dichlorophenylboronic molecule for ct and tc form.

Parameter	ct Form		tc Form		Experiment [18,32]
	6-31G(d) $\theta = 13^\circ$	6-311++G(d,p) $\theta = 1^\circ$	6-31G(d) $\theta = 167^\circ$	6-311++G(d,p) $\theta = 178^\circ$	
C1–C2	1.401	1.398	1.401	1.398	1.372/–
C1–C6	1.398	1.395	1.398	1.395	1.378/–
C1–Cl14	1.746	1.746	1.746	1.746	1.334 (C–F)
C2–C3	1.395	1.393	1.395	1.393	1.384/1.389
C2–Cl13	1.749	1.749	1.749	1.749	1.342 (C–F)
C3–C4	1.402	1.399	1.401	1.399	1.385/1.404
C3–H7	1.087	1.085	1.087	1.085	–/1.000
C4–C5	1.406	1.404	1.406	1.404	1.374/1.402
C4–B10	1.572	1.569	1.572	1.569	1.579/1.568
C5–C6	1.391	1.388	1.391	1.388	1.374/1.390
C5–H8	1.086	1.083	1.086	1.083	–/1.000
C6–H9	1.085	1.083	1.085	1.083	–/1.000
B10–O11	1.372	1.372	1.372	1.372	1.362/1.378
B10–O12	1.366	1.366	1.366	1.366	1.355/1.362
O11–H15	0.966	0.960	0.970	0.963	0.82/0.75
O12–H16	0.970	0.963	0.966	0.960	0.92/0.75
C2–C1–C6	119.565	119.567	119.566	119.567	119.7/–
C2–C1–Cl14	121.539	121.501	121.541	121.501	120.1(CCF)/–
C6–C1–Cl14	118.896	118.933	118.893	118.932	120.1(CCF)/–
C1–C2–C3	119.569	119.632	119.567	119.632	119.2/–
C1–C2–Cl13	121.549	121.500	121.552	121.500	120.0(CCF)/–
C3–C2–Cl13	118.883	118.868	118.881	118.868	120.7(CCF)/–
C2–C3–C4	121.760	121.692	121.764	121.691	123.0/–
C2–C3–H7	117.219	116.967	117.211	116.968	–
C4–C3–H7	121.014	121.341	121.017	121.341	–/120.0
C3–C4–C5	117.588	117.617	117.584	117.618	115.3/120.0
C3–C4–B10	122.070	122.432	122.093	122.431	122.7/122.0
C5–C4–B10	120.342	119.951	120.324	119.951	121.9/120.8
C4–C5–C6	121.352	121.296	121.354	121.296	123.0/121.1
C4–C5–H8	119.257	119.264	119.259	119.264	–/120.0
C6–C5–H8	119.391	119.440	119.388	119.440	–/120.0
C1–C6–C5	120.164	120.197	120.164	120.197	119.4/–
C1–C6–H9	118.907	118.931	118.904	118.931	–
C5–C6–H9	120.928	120.872	120.932	120.872	–/120.0
C4–B10–O11	124.211	124.695	124.237	124.693	122.2/125.0
C4–B10–O12	117.900	117.899	117.888	117.901	118.2/118.8
O11–B10–O12	117.888	117.406	117.875	117.406	119.5/–
B10–O11–H15	113.892	115.734	113.910	115.732	115.6/111.0
B10–O12–H16	110.868	112.607	110.867	112.606	111.4/111.0

**Table 1**

Calculated energies and energy difference for four conformers of 3,4-dcpba by DFT (B3LYP/6-311++G(d,p)).

Conformers	Energy (Hartree)	Energy differences <sup>a</sup> (kcal/mol)
Cis–trans (ct)	–1327.45061616	0.000
Trans–cis (tc)	–1327.45060760	0.005
Trans–trans (tt)	–1327.44753271	1.935
Cis–cis (cc)	–1327.44463024	3.756

<sup>a</sup> Energies of the other three conformers relative to the most stable ct conformer.

3,4-dcpba is substituted benzene with two different functional groups; two Cl atoms and B(OH)<sub>2</sub> group. As model system boronic acid and two chloro atoms are chosen. The possible conformers of 3,4-dcpba molecule were searched. There are four conformers for 3,4-dcpba. As a continuation of the interest in boronic acid containing compounds, experimental and theoretical analyses were made in the present study. The energies of different conformation of the title molecule were optimized at B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) level of calculations. Cis–trans form is the more stable conformer than the other conformers. Vibrational frequencies of the four different conformers were also calculated at DFT–B3LYP level and vibrational assignments were made based on total energy distributions (TED) and experimental data. The results of this work are presented herein.

**Table 2b**  
Geometric parameter set of 3,4-dichlorophenylboronic molecule for cc and tt form.

Parameter	tt Form		cc Form		Experiment [18,32]
	6-31G(d) $\theta = 180^\circ$	6-311++G(d,p) $\theta = 180^\circ$	6-31G(d) $\theta = 33^\circ$	6-311++G(d,p) $\theta = 34^\circ$	
C1–C2	1.402	1.399	1.401	1.398	1.372/–
C1–C6	1.397	1.395	1.397	1.394	1.378/–
C1–C114	1.748	1.747	1.746	1.745	1.334 (C–F)
C2–C3	1.395	1.392	1.396	1.393	1.384/1.389
C2–C113	1.750	1.750	1.748	1.748	1.342 (C–F)
C3–C4	1.402	1.400	1.403	1.401	1.385/1.404
C3–H7	1.085	1.083	1.087	1.085	–/1.000
C4–C5	1.405	1.403	1.405	1.404	1.374/1.402
C4–B10	1.565	1.563	1.581	1.579	1.579/1.568
C5–C6	1.391	1.389	1.392	1.389	1.374/1.390
C5–H8	1.086	1.084	1.088	1.085	–/1.000
C6–H9	1.085	1.083	1.085	1.083	–/1.000
B10–O11	1.373	1.372	1.366	1.366	1.362/1.378
B10–O12	1.373	1.372	1.367	1.366	1.355/1.362
O11–H15	0.967	0.961	0.966	0.960	0.82/0.75
O12–H16	0.968	0.961	0.966	0.960	0.92/0.75
C2–C1–C6	119.682	119.725	119.536	119.492	119.7/–
C2–C1–C114	121.543	121.503	121.598	121.595	120.1(CCF)/–
C6–C1–C114	118.776	118.773	118.866	118.914	120.1(CCF)/–
C1–C2–C3	119.693	119.742	119.662	119.747	119.2/–
C1–C2–C113	121.393	121.349	121.452	121.389	120.0(CCF)/–
C3–C2–C113	118.915	118.909	118.887	118.864	120.7(CCF)/–
C2–C3–C4	121.356	121.231	121.706	121.675	123.0/–
C2–C3–H7	118.767	118.837	117.852	117.657	–
C4–C3–H7	119.877	119.932	120.431	120.652	–/120.0
C3–C4–C5	118.015	118.152	117.492	117.446	115.3/120.0
C3–C4–B10	120.589	120.525	120.919	120.984	122.7/122.0
C5–C4–B10	121.396	121.323	121.589	121.571	121.9/120.8
C4–C5–C6	121.198	121.067	121.520	121.481	123.0/121.1
C4–C5–H8	119.503	119.581	119.979	120.234	–/120.0
C6–C5–H8	119.299	119.352	118.489	118.268	–/120.0
C1–C6–C5	120.057	120.083	120.081	120.154	119.4/–
C1–C6–H9	118.940	118.958	118.968	118.985	–
C5–C6–H9	121.003	120.960	120.951	120.861	–/120.0
C4–B10–O11	117.749	117.956	122.228	122.489	122.2/125.0
C4–B10–O12	117.783	118.016	121.999	122.230	118.2/118.8
O11–B10–O12	124.468	124.029	115.773	115.282	119.5/–
B10–O11–H15	115.071	116.559	112.469	114.142	115.6/111.0
B10–O12–H16	115.120	116.684	112.351	114.031	111.4/111.0

## 2. Experimental

The compound 3,4-dcpba sample was purchased from Acros Chemical Company with a stated purity of greater than 98% and it was used as such without further purification. The sample is in solid form at room temperature. Therefore, the FT-IR spectrum ( $4000\text{--}400\text{ cm}^{-1}$ ) of KBr disc of the sample was recorded on a Perkin Elmer FT-IR System Spectrum BX spectrometer calibrated using polystyrene bands. The spectrum was recorded with a scanning speed of  $10\text{ cm}^{-1}\text{ min}^{-1}$  and the spectral resolution of  $4.0\text{ cm}^{-1}$ . FT-Raman spectra of the samples were recorded on a Bruker RFS 100/S FT-Raman spectra of the sample was recorded using 1064 nm line of Nd:YAG laser as excitation wave length in the region  $5\text{--}3500\text{ cm}^{-1}$  on a Bruker RFS 100/S FT-Raman. The detector is a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at  $4\text{ cm}^{-1}$  resolution using a laser power of 100 mW.

## 3. Calculations

In order to obtain stable structures, the geometrical parameters including for four forms of 3,4-dcpba in the ground state (in vacuo) were optimized at DFT by the B3LYP level of theory using the 6-311++G(d,p) basis set. There are no significant difference geometric and vibrational frequencies by the selection of the different basis sets. By using B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) methods, it was seen that all the vibrational frequencies for each form of the

title molecule were positive. The calculated vibrational frequencies scaled by using one global scaling factor of 0.963 for B3LYP/6-31G(d) and by using two scaling factors of 0.958 in the  $1700\text{--}4000\text{ cm}^{-1}$  region and 0.983 for B3LYP/6-311++G(d,p) in the  $0\text{--}1700\text{ cm}^{-1}$  region [27]. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of title molecule. The total energy distribution (TED) was calculated by using the SQM [28,29] program and the fundamental vibrational modes were characterized by their TED.

Molecular geometry calculations are performed by using Gaussian molecular visualisation program [30] and Gaussian 03 program package on the personal computer [31]. The Becke's three-parameter hybrid density functional, B3LYP, was used to calculate harmonic vibrational wavenumbers with the 6-31G(d) and 6-311++G(d,p) basis sets. It is well known in the quantum chemical literature that among available functionals the B3LYP functional yields a good description of harmonic vibrational wavenumbers for small and medium sized molecules.

## 4. Results and discussion

The molecular structure of 3,4-dcpba has not been studied by X-ray diffraction. As the experimental values for 3,4-dcpba are not known so, theoretically calculated values may give an idea about the geometry of this molecule. There are four possible conformers for 3,4-dcpba, illustrated in Fig. 1, dependent on the positions of

**Table 3a**

Experimental and calculated fundamental harmonic frequencies, Infrared intensities and Raman scattering activities for 3,4-dcpba molecule (ct form).

v	Freq	6-31G(d) $\theta = 13^\circ$			6-311++G(d,p) $\theta = 1^\circ$			Experimental			
		Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	Freq	Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	Infrared	Raman	TED ( $\geq 10\%$ )
1	3811	3659	28.17	41.18	3889	3725	41.67	43.12	3465w	3457vw	$\nu_{\text{OH}}(100)$
2	3769	3619	66.37	217.86	3846	3684	98.54	192.72	3425w	3415vw	$\nu_{\text{OH}}(100)$
3	3228	3100	3.7	143.8	3204	3069	1.74	151.73	2953m	3087m	$\nu_{\text{CH}}(99)$
4	3214	3086	0.92	50.28	3190	3056	0.15	45.18	2923m	3064m	$\nu_{\text{CH}}(100)$
5	3185	3059	11.49	66.22	3165	3032	9.04	67.53	2853m	3056m,sh	$\nu_{\text{CH}}(100)$
6	1642	1577	59.69	87.89	1622	1594	65.69	94.28	1591s	1590vs	$\nu_{\text{CC}}(63) + \delta_{\text{HCC}}(16)$
7	1597	1534	0.7	3.43	1580	1553	1.49	4.2	1562m	1577s,sh	$\nu_{\text{CC}}(74)$
8	1520	1460	12.96	1.15	1504	1478	12.06	1.77	1455m	1440w	$\delta_{\text{HCC}}(46) + \nu_{\text{CC}}(35)$
9	1445	1388	293.46	3.32	1414	1389	261.42	1.68	1379vs	1393vw	$\nu_{\text{OB}}(63)$
10	1395	1340	21	2.4	1370	1346	95.94	5.37	1344s,sh	1343w	$\nu_{\text{CC}}(34) + \delta_{\text{CC}}(29) + \nu_{\text{OB}}(19)$
11	1384	1329	508.61	32.75	1363	1339	531.43	37.18	1336vs	1340m	$\nu_{\text{OB}}(28) + \nu_{\text{BC}}(25) + \delta_{\text{HOB}}(17)$
12	1317	1265	2.46	5.24	1295	1272	4.41	5.01	1298vs	1262w	$\nu_{\text{CC}}(94)$
13	1301	1249	9.71	2.58	1288	1266	16.08	4.65	1245s	1249m	$\delta_{\text{HCC}}(68) + \nu_{\text{CC}}(22)$
14	1186	1139	9.88	2.47	1174	1154	7.05	1.83	1132m	1131m	$\delta_{\text{HCC}}(54) + \nu_{\text{CC}}(29)$
15	1160	1114	58.43	17.69	1149	1129	59.85	22.01	1105w,sh	1116w,sh	$\nu_{\text{CC}}(48) + \delta_{\text{HCC}}(24) + \nu_{\text{CCl}}(20)$
16	1141	1095	83.1	11.22	1129	1109	87.98	13.33	1091m	1091vw	$\nu_{\text{CC}}(37) + \delta_{\text{HOB}}(17) + \delta_{\text{CCH}}(11)$
17	1046	1004	49.27	6.55	1042	1024	39.91	10.83	1028m	1035m	$\delta_{\text{HOB}}(29) + \delta_{\text{CC}}(22) + \nu_{\text{CC}}(10)$
18	1038	996	178.52	5.08	1023	1005	177.31	3.49	997w	992vw	$\delta_{\text{HOB}}(48) + \delta_{\text{CC}}(15) + \nu_{\text{OB}}(12)$
19	996	957	95.29	2.19	994	977	0.08	0.07	962w	961vw	$\delta_{\text{HOB}}(63) + \nu_{\text{OB}}(28)$
20	986	947	0.99	0.53	982	965	89.65	2.51	951w	948vw	$\Gamma_{\text{HCCH}}(42) + \Gamma_{\text{HCCH}}(26) + \Gamma_{\text{HCCB}}(15)$
21	901	865	7.76	1.7	886	870	6.44	0.32	883w	865vw	$\Gamma_{\text{HCC}}(35) + \Gamma_{\text{BCCH}}(26) + \Gamma_{\text{HCC}}(25)$
22	850	816	17.63	2.01	849	834	16.49	0.11	830w	826w	$\Gamma_{\text{HCC}}(57) + \Gamma_{\text{HCCl}}(22) + \Gamma_{\text{HCCB}}(13)$
23	828	795	14.36	4.36	825	810	15.7	6.96	780w	803m	$\nu_{\text{CC}}(30) + \delta_{\text{CC}}(19) + \nu_{\text{BC}}(13) + \nu_{\text{OB}}(10)$
24	725	696	15.68	0.09	733	720	35.56	0.08	724w	699vw	$\Gamma_{\text{CCC}}(44) + \Gamma_{\text{HCC}}(22) + \Gamma_{\text{OBC}}(16)$
25	691	664	23.26	10.23	689	677	23	12.28	671vw	672s	$\delta_{\text{CC}}(34) + \nu_{\text{CC}}(17) + \nu_{\text{CC}}(11) + \delta_{\text{CCH}}(11)$
26	665	639	61.43	0.59	671	659	47.65	0.19	645vw	649w	$\Gamma_{\text{HOB}}(30) + \Gamma_{\text{OBC}}(27) + \Gamma_{\text{CCC}}(14)$
27	602	579	15.3	0.52	601	590	14.97	0.3	582vw	582vw	$\nu_{\text{CC}}(29) + \nu_{\text{BC}}(17) + \delta_{\text{CC}}(10)$
28	600	576	29.31	3	582	572	30.8	1.26	578vw	572vw	$\Gamma_{\text{HOB}}(34) + \Gamma_{\text{HOB}}(34)$
29	515	494	5.78	2.09	500	491	5.41	0.82	490vw	497vw	$\Gamma_{\text{HOB}}(19) + \Gamma_{\text{CCCC}}(14)$
30	490	471	63.82	5.2	495	486	43.67	5.37	472vw	472vw	$\delta_{\text{OBO}}(17) + \nu_{\text{CCl}}(14) + \Gamma_{\text{HOB}}(11)$
31	484	465	142.42	2.95	468	460	133.9	0.51	467vw	458m,sh	$\Gamma_{\text{HOB}}(36) + \Gamma_{\text{HOB}}(32)$
32	464	446	6.76	4.63	466	458	10.81	5.68	450vw	452s	$\delta_{\text{CCl}}(37) + \nu_{\text{CCl}}(15) + \delta_{\text{BCC}}(11)$
33	440	422	4.93	0.25	424	416	1.11	2.67	422vw	431w	$\Gamma_{\text{CCC}}(39) + \Gamma_{\text{CCCC}}(18) + \Gamma_{\text{HCC}}(17)$
34	424	407	2.72	2.18	420	412	30.31	0.67	410vw	406w	$\nu_{\text{CC}}(25) + \delta_{\text{OBC}}(20) + \delta_{\text{CC}}(12) + \delta_{\text{CCl}}(10)$
35	311	299	3.12	1.03	308	302	4.29	1.1	287s	287s	$\delta_{\text{CCl}}(31) + \delta_{\text{OBC}}(27)$
36	282	270	2.16	4.19	283	278	1.93	5.21	279m,sh	279m,sh	$\nu_{\text{BC}}(22) + \delta_{\text{OBO}}(16) + \delta_{\text{CC}}(14) + \nu_{\text{CC}}(10)$
37	266	255	0.66	0.8	271	266	0.45	0.48	256w	256w	$\Gamma_{\text{CCCC}}(48) + \Gamma_{\text{HCCl}}(14)$
38	199	191	0.11	1.93	200	196	0.18	1.88	184s	184s	$\delta_{\text{CCl}}(90)$
39	159	153	0.63	2.65	155	152	1.13	1.39	150m,sh	150m,sh	$\Gamma_{\text{CCCC}}(38) + \Gamma_{\text{CCCC}}(17)$
40	127	122	2.31	0.12	131	128	2.52	0.1	121s	121s	$\delta_{\text{BCC}}(61) + \delta_{\text{OBC}}(20)$
41	80	77	0.29	0.92	80	78	0.18	0.83	85s	85s	$\Gamma_{\text{HCC}}(30) + \Gamma_{\text{CCCC}}(20) + \Gamma_{\text{BCCH}}(11)$
42	28	27	3.3	0.24	10	9	3.88	0.01	26vw	26vw	$\Gamma_{\text{OBC}}(94)$

m: middle, s: strong, vs: very strong, w: weak, vw: very weak, sh: shoulder,  $\nu$ : stretching,  $\delta$ : bending,  $\Gamma$ : torsion, TED: total energy distribution. Frequency ( $\text{cm}^{-1}$ ), IR intensities:  $I^{\text{Infrared}}$  ( $\text{K mmol}^{-1}$ ), Raman scattering activities:  $S^{\text{Raman}}$  ( $\text{\AA} \text{amu}^{-1}$ ).

the hydrogen atoms bonded to oxygen, whether they are directed away from or toward the ring. Our calculations show that the four conformations for title molecule, do not differ greatly in energy, but demonstrate that conformation *cis-trans* (abbreviated as ct) has the lowest energy.

The molecule of 3,4-dcpba consists of 16 atoms, so it has 42 normal vibrational modes. On the basis of a  $C_s$  symmetry the 42 fundamental vibrations of 3,4-dcpba can be distributed as  $28A' + 13A''$  for the *trans-trans* (tt) form. The vibrations of the  $A'$  species are in plane and those of the  $A''$  species are out of plane. In this form boronic acid and benzene ring are in the same plane. In the *cis-cis* (cc), *cis-trans* (ct) and *trans-cis* (tc) forms of molecule are non-planar structure and have the  $C_1$  symmetry and the vibrational modes span the irreducible representations:  $42A$ . The molecular structure and numbering of the atoms of 3,4-dcpba are shown in Fig. 1. We reported some geometric parameters (bond lengths and bond angles) and vibrational frequencies for 3,4-dcpba by using DFT (B3LYP) by comparing experimental results. The vibrational assignments of most of the fundamental vibration of the molecule were straightforward on the basis of their calculated TED values. The calculated wavenumbers of the molecule for the cc, tt, tc and tc forms were compared to the corresponding observed Infrared and Raman spectra of the molecule as shown in Tables 3a–d.

## 5. Geometrical structures

The phenylboronic acid molecule was studied by X-ray diffraction [32]. Since the crystal structure of 3,4-dcpba is not available in the literature till now, the geometric parameters compared with the phenylboronic acid [32], bond lengths and bond angles. Total energies and geometry parameters of the molecule are given in Tables 1, 2a and b, in accordance with the atom numbering scheme given in Fig. 1. The 3,4-dcpba molecule can be *trans-trans*, *cis-cis*, mixed *trans-cis* relative to the B–C bond. According to theoretical results, the *cis-trans* (ct) conformation is the most stable. 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. But, in the lowest-energy form of 3,4-dcpba, the  $-\text{B}(\text{OH})_2$  group is planar and at the whole of computational levels, do not lie in the plane of the benzene ring the OBO plane was twisted by ca.  $1^\circ$  for 6-311++G(d,p) basis set and by ca.  $13^\circ$  for 6-31G(d) basis set.

In general, typical B–O distances are 1.359 Å [18] consistent with relatively strong  $\pi$ -interactions. Chen et al. [12] found approximately same value of this bond length by using HF/6-31G(d) levels of theory, for the few boronic acids including phenylboronic acid molecule. For the title molecule B–O distances

**Table 3b**

Experimental and calculated fundamental harmonic frequencies, Infrared intensities and Raman scattering activities for 3,4-dcpa molecule(tc form).

$\nu$	Freq.	6-31G(d) $\theta = 167^\circ$			6-311++G(d,p) $\theta = 178^\circ$				
		Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	Freq.	Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	TED ( $\geq 10\%$ )
1	3811	3659	28.09	41.14	3889	3725	41.65	43.14	$\nu_{\text{OH}}(100)$
2	3769	3619	66.47	217.64	3846	3684	98.90	192.73	$\nu_{\text{OH}}(100)$
3	3228	3100	3.69	143.75	3204	3069	1.77	151.68	$\nu_{\text{CH}}(99)$
4	3214	3086	0.91	50.25	3190	3056	0.16	45.17	$\nu_{\text{CH}}(100)$
5	3185	3059	11.61	66.29	3165	3032	9.02	67.59	$\nu_{\text{CH}}(100)$
6	1642	1577	59.74	88.02	1622	1553	65.39	94.27	$\nu_{\text{CC}}(63) + \delta_{\text{HCC}}(16)$
7	1597	1534	0.69	3.41	1580	1513	1.54	4.21	$\nu_{\text{CC}}(74)$
8	1521	1460	13.03	1.15	1504	1440	12.15	1.77	$\delta_{\text{HCC}}(46) + \nu_{\text{CC}}(35)$
9	1445	1388	293.06	3.31	1414	1354	262.02	1.69	$\nu_{\text{OB}}(63)$
10	1395	1340	3.20	2.42	1370	1312	95.75	5.35	$\nu_{\text{CC}}(34) + \delta_{\text{HCC}}(29) + \nu_{\text{OB}}(19)$
11	1384	1329	3.71	32.86	1363	1305	531.71	37.16	$\nu_{\text{OB}}(28) + \nu_{\text{BC}}(25) + \delta_{\text{HOB}}(17)$
12	1317	1265	10.86	5.24	1295	1240	4.38	5.05	$\nu_{\text{CC}}(94)$
13	1301	1249	9.67	2.58	1288	1233	16.26	4.63	$\delta_{\text{HCC}}(68) + \nu_{\text{CC}}(22)$
14	1186	1139	9.84	2.47	1174	1124	7.18	1.84	$\delta_{\text{HCC}}(54) + \nu_{\text{CC}}(29)$
15	1160	1114	58.43	17.62	1149	1100	60.07	22.00	$\nu_{\text{CC}}(48) + \delta_{\text{HCC}}(24) + \nu_{\text{CCl}}(20)$
16	1141	1095	83.21	11.29	1129	1081	87.75	13.34	$\nu_{\text{CC}}(37) + \delta_{\text{HOB}}(16) + \delta_{\text{CCH}}(11)$
17	1046	1004	49.14	6.56	1042	998	39.65	10.81	$\delta_{\text{HOB}}(29) + \delta_{\text{CCC}}(22) + \nu_{\text{CC}}(10)$
18	1037	996	178.73	5.07	1023	980	177.69	3.49	$\delta_{\text{HOB}}(49) + \delta_{\text{CCC}}(15) + \nu_{\text{OB}}(12)$
19	996	957	95.31	2.19	994	952	0.09	0.07	$\delta_{\text{HOB}}(63) + \nu_{\text{OB}}(28)$
20	986	947	0.96	0.53	982	940	90.06	2.49	$\Gamma_{\text{HCH}}(42) + \Gamma_{\text{HCC}}(26) + \Gamma_{\text{HCCB}}(15)$
21	901	865	7.73	1.70	886	848	6.43	0.32	$\Gamma_{\text{HCC}}(35) + \Gamma_{\text{BCCH}}(26) + \Gamma_{\text{HCCCl}}(25)$
22	850	816	17.62	2.01	849	813	16.47	0.11	$\Gamma_{\text{HCC}}(57) + \Gamma_{\text{HCCCl}}(22) + \Gamma_{\text{HCCB}}(13)$
23	828	795	14.34	4.36	825	790	15.79	6.97	$\nu_{\text{CCl}}(30) + \delta_{\text{CCC}}(19) + \nu_{\text{BC}}(13) + \nu_{\text{OB}}(10)$
24	725	696	15.67	0.09	733	702	35.29	0.10	$\Gamma_{\text{CCC}}(44) + \Gamma_{\text{HCC}}(22) + \Gamma_{\text{OBCC}}(16)$
25	691	664	23.27	10.24	689	660	23.05	12.27	$\delta_{\text{CCC}}(34) + \nu_{\text{CC}}(17) + \nu_{\text{CCl}}(11) + \delta_{\text{CCH}}(11)$
26	665	638	61.39	0.57	671	642	48.01	0.23	$\Gamma_{\text{HOB}}(30) + \Gamma_{\text{OBCC}}(27) + \Gamma_{\text{CCCC}}(14)$
27	602	579	15.24	0.47	601	575	14.97	0.30	$\nu_{\text{CCl}}(30) + \nu_{\text{BC}}(17) + \delta_{\text{CCC}}(10)$
28	600	576	29.64	3.04	582	557	30.69	1.26	$\Gamma_{\text{HOB}}(34) + \Gamma_{\text{HOB}}(34)$
29	514	494	5.93	2.13	500	479	5.73	0.91	$\Gamma_{\text{HOB}}(19) + \Gamma_{\text{CCCC}}(14)$
30	490	471	58.39	5.50	495	474	43.18	5.29	$\delta_{\text{OBO}}(17) + \nu_{\text{CCl}}(15)$
31	483	464	146.74	2.57	468	448	135.20	0.52	$\Gamma_{\text{HOB}}(38) + \Gamma_{\text{HOB}}(33)$
32	464	446	6.95	4.66	466	446	10.47	5.69	$\delta_{\text{CCl}}(137) + \nu_{\text{CCl}}(15) + \delta_{\text{BC}}(11)$
33	440	422	5.52	0.25	424	406	1.12	2.68	$\Gamma_{\text{CCCC}}(39) + \Gamma_{\text{CCCC}}(18) + \Gamma_{\text{HCCCl}}(17)$
34	424	407	2.77	2.19	420	402	29.54	0.68	$\nu_{\text{CC}}(25) + \delta_{\text{OBC}}(20) + \delta_{\text{CCl}}(12) + \delta_{\text{CCl}}(10)$
35	311	299	3.15	1.03	308	295	4.29	1.10	$\delta_{\text{CCl}}(31) + \delta_{\text{OBC}}(27)$
36	282	271	2.15	4.19	283	271	1.93	5.20	$\nu_{\text{BC}}(22) + \delta_{\text{OBO}}(16) + \delta_{\text{CCC}}(14) + \nu_{\text{CCl}}(10)$
37	266	256	0.65	0.80	270	258	0.44	0.48	$\Gamma_{\text{CCCC}}(48) + \Gamma_{\text{HCCCl}}(14)$
38	199	191	0.11	1.93	200	191	0.18	1.88	$\delta_{\text{CCl}}(90)$
39	159	153	0.64	2.65	155	148	1.13	1.39	$\Gamma_{\text{CCCC}}(38) + \Gamma_{\text{ClCC}}(117)$
40	127	122	2.32	0.12	130	124	2.55	0.10	$\delta_{\text{BC}}(61) + \delta_{\text{OBC}}(20)$
41	80	77	0.29	0.92	80	76	0.18	0.83	$\Gamma_{\text{BCC}}(30) + \Gamma_{\text{CCCC}}(20) + \Gamma_{\text{BCCH}}(11) + \Gamma_{\text{CCCC}}(10)$
42	27	26	3.36	0.24	12	11	3.85	0.01	$\Gamma_{\text{OBCC}}(94)$

 $\nu$ : stretching,  $\delta$ : bending,  $\Gamma$ : torsion, TED: total energy distribution.Frequency ( $\text{cm}^{-1}$ ), IR intensities:  $I^{\text{Infrared}}$  ( $\text{K mmol}^{-1}$ ), Raman scattering activities:  $S^{\text{Raman}}$  ( $\text{\AA}^2 \text{amu}^{-1}$ ).

including for different forms were found from 1.366 Å to 1.373 Å ranges. Bhat et al. [16] calculated B–C bond length 1.566 Å and 1.567 Å in the lowest form for phenylboronic acid using B3LYP and MP2 methods, respectively. The B–C bond length is calculated in the range of 1.563–1.581 Å for different forms. The calculated B–O and B–C bond lengths in 3,4-dcpba molecule are in good agreement with those found in the X-ray structure [32].

The C–X (F, Cl, Br...) bond length indicates a considerable increase when substituted in place of C–H. This has been observed even in benzene derivatives [33]. Chloro atoms are in the plane of the benzene ring. The C–Cl bond length is found ca. 1.75 Å. These bond lengths were also calculated in the range of 1.73–1.75 Å for similar molecules [34–36].

Bond angles at B and C are consistent  $sp^2$  hybridization but with significant deviations from the expected  $120^\circ$  angles occurring in close proximity the the  $-\text{B}(\text{OH})_2$  substituent on  $\text{C}_4$ . The theoretical results show that, the  $-\text{B}(\text{OH})_2$  group is twisted by  $13^\circ$  and  $1^\circ$  relative to the ring part for ct form, by using 6-31G(d) and 6-311++G(d,p) basis sets. Potential energy scan with the whole levels of theoretical approximation were performed along C–C–B–O torsional angle of 3,4-dcpba molecule 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  $10^\circ$ . The resulted potential energy curve depicted in Fig. 2 shows ct form for minimum energies. The B–C rotational barrier in tt and cc form was calculated to be about 2–3 kcal/mol (Fig. 2), which is significantly high as compared the B–C barrier ct and tc forms of molecule. From the calculations, optimized structure of 3,4-dcpba was calculated to exist in a planar structure for the tt form, while the other forms of molecule were calculated to exist as a near planar structure with C–C–B–O torsional angle of about  $13^\circ$  and  $1^\circ$  for the ct form,  $167^\circ$  and  $177^\circ$  for tc form, and  $33^\circ$  and  $34^\circ$  for cc form by using 6-31G(d) and 6-311++G(d,p) basis sets, respectively. All forms of the title molecule were predicted to have positive frequency by both basis sets (Tables 3a–d).

## 6. Vibrational spectra

We performed a frequency calculation analysis, in order to obtain the spectroscopic signature of the title molecule. Calculations were made for a free molecule in vacuum, while experiments were performed for solid samples, so there are disagreements between

**Table 3c**

Experimental and calculated fundamental harmonic frequencies, Infrared intensities and Raman scattering activities for 3,4-dclpba molecule (tt form).

$\nu$	Freq.	6-31G(d) $\theta = 180^\circ$			6-311++G(d,p) $\theta = 180^\circ$				
		Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	Freq.	Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	TED ( $\geq 10\%$ )
1	3790	3639	58.60	426.77	3872	3709	113.12	397.25	$\nu_{\text{OH}}(100)$
2	3785	3635	7.91	40.05	3868	3705	14.61	29.84	$\nu_{\text{OH}}(100)$
3	3225	3097	1.79	181.80	3201	3066	2.58	189.07	$\nu_{\text{CH}}(100)$
4	3224	3096	4.23	18.92	3199	3064	0.93	18.88	$\nu_{\text{CH}}(100)$
5	3209	3082	1.84	51.52	3185	3051	0.90	48.40	$\nu_{\text{CH}}(100)$
6	1642	1576	59.72	93.32	1622	1553	67.19	96.03	$\nu_{\text{CC}}(63) + \delta_{\text{HCC}}(15)$
7	1598	1534	1.24	3.44	1580	1513	1.66	4.39	$\nu_{\text{CC}}(75)$
8	1517	1457	9.24	0.59	1499	1436	9.10	1.04	$\delta_{\text{HCC}}(43) + \nu_{\text{CC}}(35)$
9	1433	1376	292.66	0.72	1407	1347	239.72	0.72	$\nu_{\text{OB}}(55)$
10	1393	1337	147.35	2.47	1365	1307	4.70	7.97	$\nu_{\text{OB}}(29) + \nu_{\text{BC}}(16) + \nu_{\text{CC}}(15) + \delta_{\text{HOB}}(12)$
11	1385	1330	255.32	15.95	1360	1302	3.50	17.01	$\nu_{\text{OB}}(24) + \delta_{\text{HCC}}(24) + \nu_{\text{CC}}(17) + \nu_{\text{BC}}(11) + \delta_{\text{HOB}}(10)$
12	1319	1267	5.91	4.39	1297	1242	11.31	4.69	$\nu_{\text{CC}}(94)$
13	1293	1242	9.63	1.39	1279	1225	17.16	2.61	$\delta_{\text{HCC}}(68) + \nu_{\text{CC}}(21)$
14	1183	1136	0.24	2.13	1170	1120	0.12	1.40	$\delta_{\text{HCC}}(56) + \nu_{\text{CC}}(30)$
15	1157	1111	63.37	25.51	1145	1096	57.87	29.75	$\nu_{\text{CC}}(54) + \nu_{\text{CC}}(22) + \delta_{\text{HCC}}(14)$
16	1137	1092	10.18	9.02	1123	1075	6.55	7.53	$\nu_{\text{CC}}(31) + \delta_{\text{CCH}}(23) + \delta_{\text{HOB}}(21)$
17	1046	1004	13.25	7.40	1043	999	23.61	13.00	$\delta_{\text{CCC}}(38) + \nu_{\text{CC}}(16) + \delta_{\text{CCH}}(13)$
18	1018	977	220.34	5.68	999	957	205.90	3.66	$\nu_{\text{OB}}(44) + \delta_{\text{HOB}}(37)$
19	982	943	0.00	0.54	984	942	0.02	0.10	$\Gamma_{\text{HCCB}}(41) + \Gamma_{\text{HCCB}}(27) + \Gamma_{\text{HCCB}}(15)$
20	945	907	184.24	7.63	940	900	158.72	5.74	$\delta_{\text{CCC}}(98)$
21	933	896	7.63	1.37	931	891	7.46	0.33	$\Gamma_{\text{HCCC}}(36) + \Gamma_{\text{BCCH}}(26) + \Gamma_{\text{HCCC}}(26)$
22	846	813	18.96	2.07	844	808	20.35	0.09	$\Gamma_{\text{HCCC}}(57) + \Gamma_{\text{HCCC}}(122) + \Gamma_{\text{HCCB}}(13)$
23	829	796	27.50	5.65	825	790	28.10	7.68	$\nu_{\text{CC}}(29) + \delta_{\text{CCC}}(18) + \nu_{\text{BC}}(13) + \nu_{\text{OB}}(13)$
24	726	697	8.72	0.01	753	721	10.73	0.06	$\Gamma_{\text{CCCC}}(45) + \Gamma_{\text{HCCC}}(22) + \Gamma_{\text{OBCC}}(16)$
25	689	661	23.06	10.98	687	658	22.60	13.04	$\delta_{\text{CCC}}(39) + \nu_{\text{CC}}(17) + \delta_{\text{CCH}}(15) + \nu_{\text{CC}}(11)$
26	660	633	47.60	0.22	681	652	48.96	0.12	$\Gamma_{\text{HOB}}(27) + \Gamma_{\text{OBCC}}(20) + \Gamma_{\text{CCCC}}(17)$
27	611	587	3.55	0.61	607	581	3.24	0.55	$\nu_{\text{CC}}(27) + \nu_{\text{BC}}(15) + \nu_{\text{OB}}(11) + \delta_{\text{OBO}}(11)$
28	569	547	144.36	5.39	558	534	85.42	1.42	$\Gamma_{\text{HOB}}(43) + \Gamma_{\text{HOB}}(19)$
29	504	484	52.07	7.02	501	479	51.11	7.24	$\nu_{\text{CC}}(20) + \delta_{\text{OB}}(20) + \delta_{\text{OBO}}(20) + \delta_{\text{CCC}}(11)$
30	492	472	72.72	5.32	478	457	111.32	1.95	$\Gamma_{\text{HOB}}(38) + \Gamma_{\text{CCCC}}(21)$
31	470	451	10.44	3.93	468	448	12.74	4.86	$\delta_{\text{CCC}}(35) + \nu_{\text{CC}}(16) + \delta_{\text{CCB}}(16) + \delta_{\text{HBC}}(12)$
32	448	430	15.80	0.37	447	428	35.55	0.08	$\Gamma_{\text{CCCC}}(42) + \Gamma_{\text{HCCC}}(20) + \Gamma_{\text{CCCC}}(18)$
33	430	413	11.40	2.82	428	410	11.58	2.76	$\nu_{\text{CC}}(29) + \delta_{\text{OB}}(18) + \delta_{\text{CCC}}(14) + \delta_{\text{CCC}}(13)$
34	402	386	0.08	0.39	379	363	0.18	0.11	$\Gamma_{\text{HOB}}(48) + \Gamma_{\text{HOB}}(48)$
35	306	294	2.13	0.88	305	292	1.81	1.02	$\delta_{\text{CCC}}(33) + \delta_{\text{OB}}(31) + \nu_{\text{CC}}(10)$
36	284	273	0.55	3.91	284	272	0.57	4.58	$\nu_{\text{BC}}(22) + \delta_{\text{CCC}}(15) + \delta_{\text{OBO}}(15) + \nu_{\text{CC}}(11)$
37	270	260	3.61	0.44	271	259	3.95	0.20	$\Gamma_{\text{CCCC}}(50) + \Gamma_{\text{HCCC}}(15)$
38	199	191	0.10	1.86	199	190	0.16	1.81	$\delta_{\text{CCC}}(90)$
39	163	156	2.26	2.47	161	154	2.75	1.41	$\Gamma_{\text{CCCC}}(38) + \Gamma_{\text{CCCC}}(17)$
40	124	119	2.02	0.19	125	119	1.95	0.16	$\delta_{\text{BC}}(63) + \delta_{\text{OB}}(22)$
41	81	78	1.19	0.69	81	77	1.24	0.69	$\Gamma_{\text{BCCC}}(29) + \Gamma_{\text{CCCC}}(11) + \Gamma_{\text{BCCH}}(11) + \Gamma_{\text{CCCC}}(21)$
42	46	45	0.02	0.05	49	46	0.01	0.01	$\Gamma_{\text{OBCCC}}(93)$

 $\nu$ : stretching,  $\delta$ : bending,  $\Gamma$ : torsion, TED: total energy distribution.Frequency ( $\text{cm}^{-1}$ ), IR intensities:  $I^{\text{Infrared}}$  ( $\text{K mmol}^{-1}$ ), Raman scattering activities:  $S^{\text{Raman}}$  ( $\text{\AA} \text{amu}^{-1}$ ).

calculated and observed vibrational wavenumbers. Experimental and calculated IR and Raman spectra are shown in Figs. 3 and 4. The calculated IR and Raman spectra are shown in Figs. 3 and 4 for comparative purposes, where the calculated intensity and activity is plotted against the harmonic vibrational frequencies. A comparison of Tables 3a–d shows that the vibrational frequencies of the cc conformer lie very close and their TED assignments are also mostly unchanged.

The ct form of structure was the lowest in energy at all levels. The experimental wavenumbers are tabulated in Table 3a together with the calculated wavenumbers of ct form of studied molecule. All of the calculated modes are numbered from the largest to the smallest frequency within each fundamental wave numbers. On the basis on our calculations, and experimental Infrared and Raman spectra, we made a reliable one-to-one correspondence between our fundamentals and any of our frequencies calculated by the DFT (B3LYP) method. Comparison of the frequencies calculated at B3LYP with the experimental values reveals the over estimation of the calculated vibrational modes due to neglect of anharmonicity in real system.

In the O–H region very strong and broad bands in the spectra of some boronic acid molecules occur at ca.  $3300 \text{ cm}^{-1}$ . The assign-

ment of these bands to O–H stretching vibrations is straightforward. In the spectra of phenylboronic acid [19], pentafluorophenylboronic acid [20], 3 and 4-pyridineboronic acid [37], *n*-butylboronic acid [14] absorption bands at  $3280 \text{ cm}^{-1}$ ,  $3467 \text{ cm}^{-1}$  and  $3410 \text{ cm}^{-1}$ ,  $3320 \text{ cm}^{-1}$  and  $3306 \text{ cm}^{-1}$  have been assigned, which is typical for OH bonded hydroxyl groups. The strength, broadening frequencies of these bands suggest that intramolecular hydrogen bonding occur in different environment of boronic acids [19]. The IR spectra of phenylboronic acid contains broad O–H stretching bands at  $3279$  and  $3350 \text{ cm}^{-1}$ , which transform to one sharp band at  $3467 \text{ cm}^{-1}$  and one broad band at  $3410 \text{ cm}^{-1}$  on formation of pfpba. As discussed in our previous papers [20,37], with the halogen (F, Cl, Br...) substitution, OH stretching vibrations shifted to higher wavenumbers region [38]. This means that in the boronic acid part, OH vibrations are sensitive due to halogen coordination. These bands calculated  $3659$  and  $3619 \text{ cm}^{-1}$  which modes ( $\nu_1, \nu_2$ ) of O11–H15 and O12–H16 units, respectively. As expected these two modes are pure stretching modes as it is evident from TED column, they are almost contributing 100%.

The heteroaromatic structure shows the presence of C–H stretching vibrations above  $3000 \text{ cm}^{-1}$  which is the characteristic

**Table 3d**

Experimental and calculated fundamental harmonic frequencies, Infrared intensities and Raman scattering activities for 3,4-dcpba molecule (cc form).

$\nu$	Freq.	6-31G(d) $\theta = 33^\circ$			6-311++G(d,p) $\theta = 34^\circ$				
		Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	Freq.	Scaled	$I^{\text{Infrared}}$	$S^{\text{Raman}}$	TED ( $\geq 10\%$ )
1	3812	3661	4.52	77.72	3891	3727	6.44	79.31	$\nu_{\text{OH}}(100)$
2	3811	3659	70.69	8.12	3890	3726	103.4	7.17	$\nu_{\text{OH}}(100)$
3	3224	3096	2.62	118.57	3200	3065	1.27	126.21	$\nu_{\text{CH}}(100)$
4	3197	3070	3.9	63.02	3174	3040	1.99	62.45	$\nu_{\text{CH}}(100)$
5	3180	3054	12.45	83.79	3160	3027	8.31	80.79	$\nu_{\text{CH}}(100)$
6	1638	1573	44.9	70.26	1619	1551	48.53	74.96	$\nu_{\text{CC}}(64) + \delta_{\text{HCC}}(15)$
7	1594	1531	4.01	5.32	1576	1509	5.57	6.34	$\nu_{\text{CC}}(74)$
8	1516	1456	8.46	1.1	1500	1437	9.29	1.53	$\delta_{\text{HCC}}(47) + \nu_{\text{CC}}(33)$
9	1454	1396	218.78	1.39	1418	1358	238.65	1.95	$\nu_{\text{OB}}(74)$
10	1401	1345	19.38	0.35	1381	1322	33.81	1.17	$\nu_{\text{CC}}(38) + \delta_{\text{HCC}}(32)$
11	1363	1309	659.15	44.74	1343	1286	644.87	44.23	$\nu_{\text{OB}}(35) + \nu_{\text{BC}}(25) + \delta_{\text{HOB}}(14)$
12	1314	1262	1.89	4.95	1291	1236	4.69	4.04	$\nu_{\text{CC}}(95)$
13	1295	1243	22.79	2.76	1283	1229	31.6	5.28	$\delta_{\text{HCC}}(67) + \nu_{\text{CC}}(21)$
14	1189	1142	16.18	2.95	1179	1129	16.23	2.17	$\delta_{\text{HCC}}(53) + \nu_{\text{CC}}(29)$
15	1158	1112	43.55	20.45	1147	1098	49.77	25	$\nu_{\text{CC}}(53) + \nu_{\text{CC}}(22) + \delta_{\text{HCC}}(17)$
16	1141	1095	64.46	3.69	1128	1080	66.02	7.66	$\nu_{\text{CC}}(35) + \delta_{\text{HCC}}(21) + \delta_{\text{HOB}}(16)$
17	1043	1002	52.6	7.64	1041	997	50.84	11.23	$\delta_{\text{CC}}(45) + \nu_{\text{CC}}(13) + \nu_{\text{CC}}(12)$
18	1019	979	281.27	0.37	1002	959	263.36	0.04	$\delta_{\text{HOB}}(90)$
19	1005	965	65.84	2.88	991	949	49.94	2.83	$\delta_{\text{HOB}}(59) + \nu_{\text{OB}}(32)$
20	971	933	2.42	0.53	975	934	4.93	0.08	$\Gamma_{\text{HCC}}(42) + \Gamma_{\text{HCC}}(29) + \Gamma_{\text{HCCB}}(13)$
21	917	881	6.15	1.52	906	867	6.5	0.21	$\Gamma_{\text{HCC}}(36) + \Gamma_{\text{HCCB}}(26) + \Gamma_{\text{HCC}}(25)$
22	844	811	13.94	2.1	838	802	16.82	0.21	$\Gamma_{\text{HCC}}(56) + \Gamma_{\text{HCC}}(20) + \Gamma_{\text{HCCB}}(15)$
23	829	796	19.95	4.08	825	790	20.84	6.18	$\nu_{\text{CC}}(29) + \delta_{\text{CC}}(19) + \nu_{\text{BC}}(13) + \nu_{\text{OB}}(10)$
24	728	699	16.25	0.21	733	702	17.42	0.45	$\Gamma_{\text{CCC}}(44) + \Gamma_{\text{HCC}}(21) + \Gamma_{\text{OBC}}(16)$
25	693	666	13.42	9.72	693	663	15.48	10.52	$\delta_{\text{CC}}(29) + \nu_{\text{CC}}(16) + \delta_{\text{CCH}}(11)$
26	660	634	35.2	1.07	667	638	39.42	1.9	$\Gamma_{\text{OBC}}(26) + \Gamma_{\text{HOB}}(16) + \Gamma_{\text{CCC}}(15)$
27	610	586	9.44	0.5	609	583	9.06	0.4	$\nu_{\text{CC}}(27) + \nu_{\text{BC}}(17) + \delta_{\text{BO}}(12) + \nu_{\text{OB}}(10)$
28	572	550	156.92	0.32	564	540	106.64	0.31	$\Gamma_{\text{HOB}}(66) + \Gamma_{\text{HOB}}(26)$
29	556	534	22.51	0.34	553	529	67.2	0.38	$\Gamma_{\text{CCC}}(15) + \Gamma_{\text{HOB}}(11) + \Gamma_{\text{OBC}}(10)$
30	498	478	1.52	4.61	495	474	2.19	3.86	$\Gamma_{\text{HOB}}(27) + \Gamma_{\text{HOB}}(27) + \nu_{\text{CC}}(12) + \delta_{\text{BO}}(12)$
31	489	469	9.91	5.01	488	467	8.79	4.8	$\Gamma_{\text{HOB}}(23) + \Gamma_{\text{HOB}}(23) + \nu_{\text{CC}}(18) + \delta_{\text{BO}}(11)$
32	458	440	7.9	2.2	456	436	8.7	2.39	$\Gamma_{\text{CCC}}(21) + \delta_{\text{CC}}(20)$
	444	427	0.13	1.99	442	423	0.13	1.73	$\Gamma_{\text{CCC}}(23) + \delta_{\text{CC}}(22) + \Gamma_{\text{CCC}}(11)$
34	420	403	2.67	1.28	418	400	1.99	1.25	$\delta_{\text{OBC}}(27) + \nu_{\text{CC}}(17)$
35	322	309	6.98	1.34	323	309	7.01	1.23	$\delta_{\text{CC}}(29) + \delta_{\text{OBC}}(16) + \nu_{\text{CC}}(10)$
36	276	265	2.22	4.21	276	264	1.99	5.13	$\nu_{\text{BC}}(23) + \delta_{\text{BO}}(16) + \delta_{\text{CC}}(14) + \nu_{\text{CC}}(10)$
37	251	241	4.08	1.18	249	238	4.75	0.67	$\Gamma_{\text{CCC}}(46) + \Gamma_{\text{CIC}}(13) + \delta_{\text{OBC}}(13)$
38	200	192	0.09	1.96	200	191	0.07	1.84	$\delta_{\text{CC}}(90)$
39	159	153	0.91	3.03	154	147	0.77	1.87	$\Gamma_{\text{CCC}}(35) + \Gamma_{\text{CIC}}(17) + \Gamma_{\text{OBC}}(14)$
40	115	111	6.15	0.23	119	114	5.4	0.27	$\delta_{\text{BC}}(65) + \delta_{\text{OBC}}(16)$
41	76	73	2.88	1.78	75	71	2.59	1.41	$\Gamma_{\text{BCC}}(31) + \Gamma_{\text{CCC}}(17) + \Gamma_{\text{BCH}}(12)$
42	52	50	0.16	1.11	41	39	0.29	0.93	$\Gamma_{\text{OBC}}(90)$

 $\nu$ : stretching,  $\delta$ : bending,  $\Gamma$ : torsion, TED: total energy distribution.Frequency ( $\text{cm}^{-1}$ ), IR intensities:  $I^{\text{Infrared}}$  ( $\text{K mmol}^{-1}$ ), Raman scattering activities:  $S^{\text{Raman}}$  ( $\text{\AA} \text{amu}^{-1}$ ).

region for ready identification of this structure [39]. In this region, the bands are not affected appreciably by the nature of the substituents. 3,4-dcpba has two adjacent and one isolated C—H moieties. The expected three C—H stretching vibrations correspond to 3, 4 and 5. The scaled vibration, lines of 3, 4 and 5 (Table 3a) corresponds to stretching modes of C5—H8, C6—H9 and C3—H7 units. As seen in Table 3a, three peaks (modes 3, 4 and 5) observed for the title molecule in the 2800–3500  $\text{cm}^{-1}$  range experimentally in the high frequency region which are 2853, 2923 and 2953  $\text{cm}^{-1}$  (FT-IR), 3056, 3064 and 3387  $\text{cm}^{-1}$  (FT-Raman). As expected, these three modes are pure stretching modes as it is evident from TED column, they are almost contributing 100%. The C—H in-plane bending frequencies appear in the range of 1000–1300  $\text{cm}^{-1}$  and C—H out-of-plane bending vibration in the range 750–1000  $\text{cm}^{-1}$  [40]. The CH in-plane bends are assigned to the FT-IR bands in the range from 1245 to 1105  $\text{cm}^{-1}$ . The CH out-of-plane bends are assigned to the FT-IR bands at 951, 883 and 830  $\text{cm}^{-1}$ . Both the in-plane and out-of-plane bending vibrations are described as mixed modes. The above conclusions are in very good agreement with literature values [39,41].

The experimental sharp and strong bands at ca. 1600  $\text{cm}^{-1}$  may come from the absorption due to the stretching vibration of the C—C bond, and bending vibration of the C—C—C in the ring part.

These bands observed at 1649  $\text{cm}^{-1}$  (IR), 1657  $\text{cm}^{-1}$  (IR), 1634 (IR)–1633 (Ra), for the pentafluorobenzene, alfa-bromo-pentafluoro-toluene [42] and  $\text{C}_6\text{F}_5\text{I}$  [43] molecules, respectively. With the  $\text{B}(\text{OH})_2$  coordination these mode are not changing significantly. Therefore the modes at ca. 1600  $\text{cm}^{-1}$  are insensitive with the  $\text{B}(\text{OH})_2$  coordination. If we consider phenylboronic acid case, the band at 1607  $\text{cm}^{-1}$  shifted to 1657  $\text{cm}^{-1}$  for pentafluorophenylboronic acid. For the title molecule, this band was observed at 1591  $\text{cm}^{-1}$  (IR) and 1590  $\text{cm}^{-1}$  (Ra) in experimental spectrum. This means that, with the coordination two chlorine atoms to the phenylboronic acid molecule, the band at 1607  $\text{cm}^{-1}$  shifted to 1591  $\text{cm}^{-1}$  negatively (see Table 3a). However, the TED values in Table 3a reveal that this mode is not characteristic and is coupled with HCC bending vibration. But this may be almost pure mode is evidenced from 63% of TED (Table 3a).

The other strong band in the spectrum of 3,4-dcpba occurs at 1379  $\text{cm}^{-1}$ . This band is very intense and should include also the  $\nu(\text{B—O})$  asymmetric stretching vibration, which for phenylboronic and pentafluorophenyl boronic acid are located at 1349  $\text{cm}^{-1}$  and 1350  $\text{cm}^{-1}$ , respectively [19,20]. Kurt [17] observed the B—O stretching vibration at 1373 and 1361  $\text{cm}^{-1}$  for 4-chlorophenylboronic acid and 4-bromophenylboronic acid, respectively. Vargas et al. [44] assigned the band around at 1370  $\text{cm}^{-1}$  as the  $\nu(\text{B—O})$

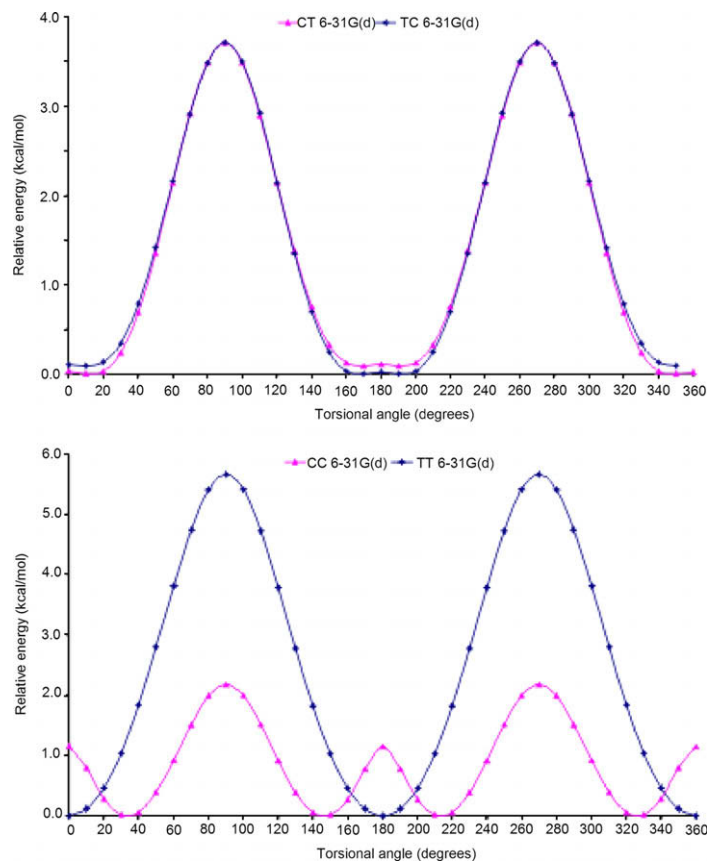


Fig. 2. Torsion profile of C-C-B-O (abbreviated as  $\theta$ ) in title molecule ct-tc form and cc-tt form by B3LYP/6-31G(d) basis set.

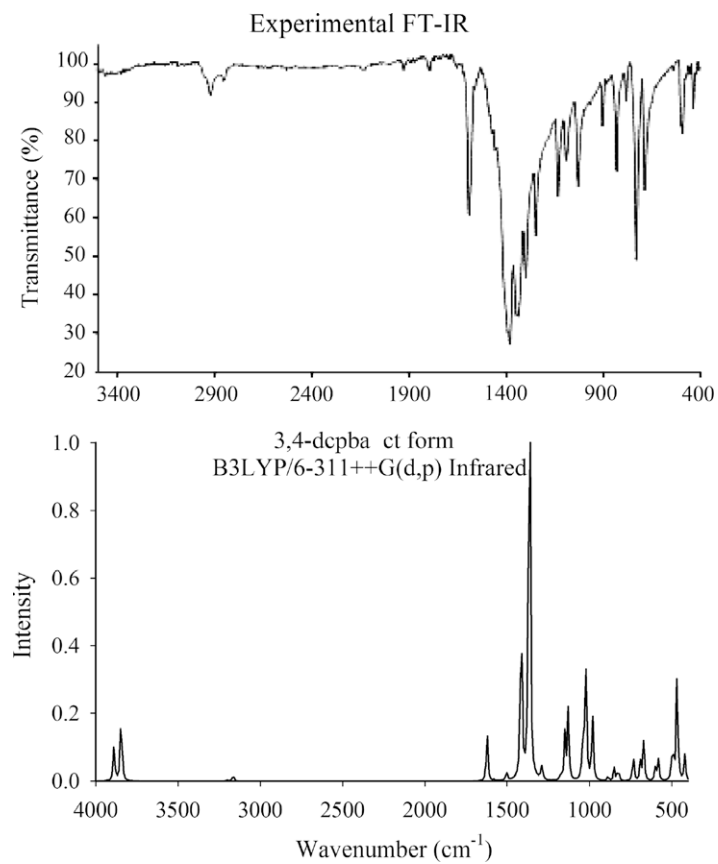


Fig. 3. Experimental FT-IR and calculated IR spectrum of 3,4-dcpba.



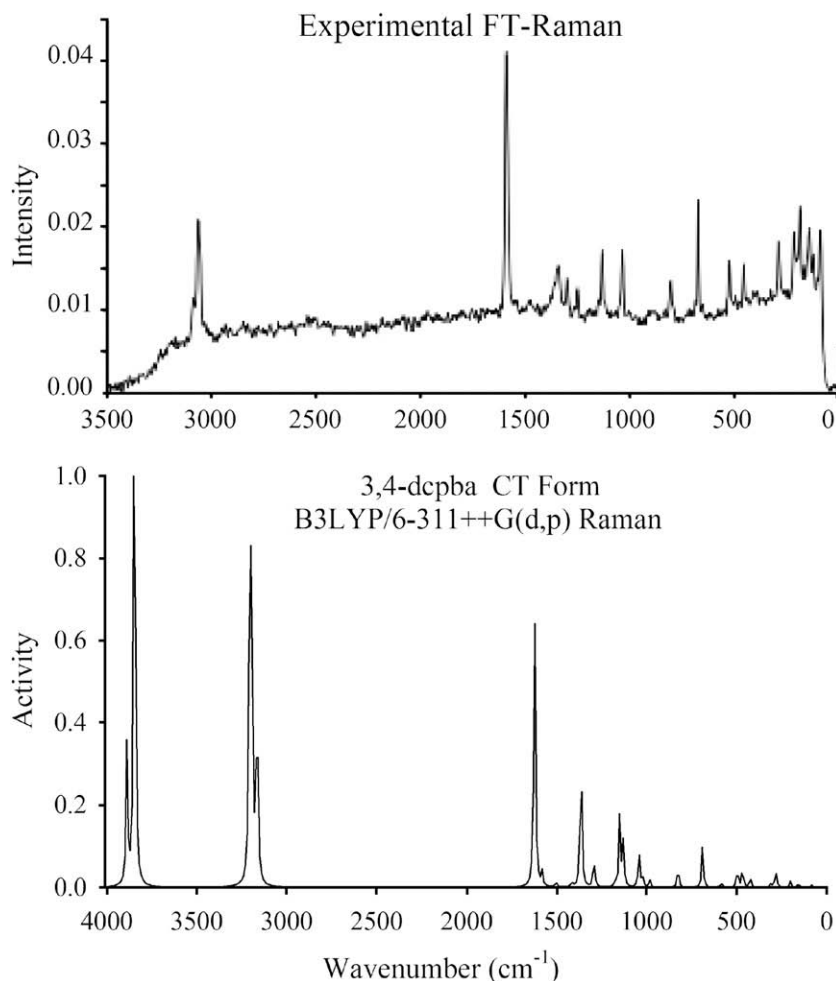


Fig. 4. Experimental FT-Raman and calculated Raman spectrum of 3,4-dcpba.

stretching vibrations for the homo- and heterotrimeric boron complexes. The broad band peaking at  $1390\text{ cm}^{-1}$  is observed the B–O asymmetric stretch for *n*-butylboronic acid by Cyrański et al. [14].

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 [19]. The observed frequency for the asymmetric B–O stretching vibrations in 3,4-dcpba are approximately similar than those reported by Faniran et al. [19] and our previous papers for this vibration in the spectra of similar molecules [17,20,37].

Santucci and Gilman [45] associated an absorption band between  $1080$  and  $1110\text{ cm}^{-1}$  with a B–C stretching mode  $\nu$  (B–C) in arylboronic acids. Faniran et al. [19] also assigned the band at  $1089$  and  $1085\text{ cm}^{-1}$  in the spectra of the normal and deuterated phenylboronic acids, respectively, and at  $1084\text{ cm}^{-1}$  in diphenyl phenylboronate to the B–C stretching vibration. For *n*-butylboronic acid, these vibrations are assigned at  $1147$  and  $1109\text{ cm}^{-1}$  by Cyrański et al. [14]. In the range of  $1090$ – $1140\text{ cm}^{-1}$ , we could not assign B–C stretching mode by using theoretical TED value due to lack of B–C modes.

Similar comparative analysis has been made for the other selected strong or medium bands. As seen in Tables 3a and b for TED values, calculated modes mixed with, C–H, pyridine C–Cl, C–C and boronic acid group modes in different proportions. Empirical assignments of vibrational modes for peaks in the fingerprint

region are difficult. In the wavenumber region of  $600$ – $1660\text{ cm}^{-1}$ , 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 (see Tables 3a–d).

## 7. Conclusion

Attempts have been made in the present work for the molecular parameters and frequency assignments for the compound 3,4-dcpba from the FT-IR and FT-Raman spectra. The equilibrium geometry, harmonic frequencies of 3,4-dcpba were determined and analyzed at DFT level of theory utilizing 6-31G(d) and 6-311++G(d,p) basis sets. The difference between the observed and scaled wave number values of most of the fundamentals is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at DFT levels of theory with only reasonable deviations from the experimental values seem to be correct.

## Acknowledgements

The Financial support by Gazi University Scientific Research Projects Unit (BAP, Project No. 30-2005/3) is also politely acknowledged.

## References

- [1] W. Tjarks, A.K.M. Anisuzzaman, L. Liu, S.H. Soloway, R.F. Barth, D.J. Perkins, D.M. Adams, *J. Med. Chem.* 35 (1992) 16228.
- [2] Y. Yamamoto, *Pure Appl. Chem.* 63 (1991) 423.
- [3] F. Alam, A.H. Soloway, R.F. Barth, N. Mafune, D.M. Adam, W.H. Knoth, *J. Med. Chem.* 32 (1989) 2326.
- [4] M.R. Stabile et al., *Bioorg. Med. Chem. Lett.* 21 (1996) 2501.
- [5] P.R. Westmark, B.D. Smith, *J. Pharm. Sci.* 85 (1996) 266.
- [6] N.A. Petasis, *Aust. J. Chem.* 60 (2007) 795.
- [7] E. Cuthbertson, *Boronic Acids: Properties and Applications*, Alfa Aesar, Heysham, 2006.
- [8] D.G. Hall (Ed.), *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*, Wiley-VCH, Weinheim, 2005.
- [9] A.H. Soloway, R.G. Fairchild, *Sci. Am.* 262 (1990) 100.
- [10] D.A. Matthews, R.A. Alden, J.J. Birktoft, S.T. Freer, J. Kraut, *J. Biol. Chem.* 250 (1975) 7120.
- [11] D.H. Kinder, S.K. Frank, M.M. Ames, *J. Med. Chem.* 33 (1990) 819.
- [12] X. Chen, G. Liang, D. Whitmire, J.P. Bowen, *J. Phys. Org. Chem.* 11 (1988) 378.
- [13] A. Meud, M. Erbes, K. Forstinker, US Patent No. 2002/0 161, 2002, p. 230.
- [14] M.K. Cyrański, A. Jezierska, P. Klimentowska, J.J. Panek, G.Z. Żukowska, A. Sporzyński, *J. Chem. Phys.* 128 (2008) 124512.
- [15] M.R. Shimpi, N.S. Lekshmi, V.R. Pedireddi, *Crystal Growth Des.* 7 (10) (2007) 1958.
- [16] K.L. Bhat, N.J. Howard, H. Rostami, J.H. Lai, Charles W. Bock, *J. Mol. Struct. (Theochem)* 723 (2005) 147.
- [17] M. Kurt, *J. Raman Spectrosc.*, 40 (2009) 29.
- [18] P.N. Horton, M.B. Hursthouse, M.A. Becket, M.P.R. Hankey, *Acta Cryst. E Struct. Rep.* E60 (2004) o2204.
- [19] J.A. Faniran, H.F. Shurvell, *Can. J. Chem.* 46 (1968) 2089.
- [20] M. Kurt, *J. Mol. Struct.* 874 (2008) 159.
- [21] M.K. Cyrański, A. Jezierska, P. Klimentowska, J.J. Panek, A. Sporzyński, *J. Phys. Org. Chem.* 21 (2008) 472.
- [22] N.C. Handy, C.W. Murray, R.D. Amos, *J. Phys. Chem.* 97 (1993) 4392.
- [23] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.* 98 (1994) 11623.
- [24] F.J. Devlin, J.W. Finley, P.J. Stephens, M.J. Frisch, *J. Phys. Chem.* 99 (1995) 16883.
- [25] S.Y. Lee, B.H. Boo, *Bull. Korean Chem. Soc.* 17 (1996) 760.
- [26] G. Rauhut, P. Pulay, *J. Phys. Chem.* 99 (1995) 3093.
- [27] N. Sundaraganesan, S. Ilakiamani, H. Saleem, P.M. Wojciechowski, D. Michalska, *Spectrochim. Acta A* 61 (2005) 2995.
- [28] P. Pulay, J. Baker, K. Wolinski, Green Acres Road, Suite A, Fayetteville, AR 72703, USA, p. 2013.
- [29] J. Baker, A.A. Jarzecki, P. Pulay, *J. Phys. Chem. A* 102 (1998) 1412.
- [30] A. Frisch, A.B. Nielsen, A.J. Holder, *Gaussview Users Manual*, Gaussian Inc., Pittsburg.
- [31] M.J. Frisch et al., *Gaussian 03, Revision B.4*, Gaussian Inc., Pittsburgh, PA, 2003.
- [32] S.J. Rettig, J. Trotter, *Can. J. Chem.* 55 (1977) 3071.
- [33] J.R. Durig, T.S. Little, T.K. Gounev, J.K. Gargner Jr., J.F. Sullivan, *J. Mol. Struct.* 375 (1996) 83.
- [34] M. Karabacak, M. Çınar, M. Kurt, *J. Mol. Struct.* 885 (2008) 28.
- [35] A.K. Rai, S. Kumar, A. Rai, *Vib. Spectrosc.* 42 (2006) 397.
- [36] M. Karabacak, M. Kurt, *Spectrochim. Acta A* 71 (2008) 876.
- [37] M. Kurt, T.R. Sertbakan, M. Özduvan, *Spectrochim. Acta A* 70 (2008) 664.
- [38] L.J. Bellamy, *The Infrared Spectra of Complex molecules*, Wiley, New York, 1959.
- [39] M. Silverstein, G. Clayton Basseler, C. Morill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1981.
- [40] N. Sundaraganesan, S. Ilakiamani, B.D. Joshua, *Spectrochim. Acta A* 67 (2007) 287.
- [41] G. Varsanyi, *Assignments of Vibrational Spectra of 700 Benzene Derivatives*, Wiley, New York, 1974.
- [42] <http://www.acros.be>.
- [43] Karsten Koppe, Ph.D. Thesis, Duisburg University, 2005.
- [44] G. Vargas, I. Hernandez, H. Höpfl, M. Ochoa, D. Castillo, N. Farfan, R. Santillan, E. Gomez, *Inorg. Chem.* 43 (2004) 8490.
- [45] L. Santucci, H. Gilman, *J. Am. Chem. Soc.* 80 (193) (1958).