

EDINBURGH  
INSTRUMENTS



# PRECISION RAMAN

Best-in-class Raman microscopes  
for research and analytical requirements  
backed with world-class customer  
support and service.



[edinst.com](http://edinst.com)

# Molecular structure, vibrational spectroscopic studies and NBO analysis of the 3,5-dichlorophenylboronic acid molecule by the density functional method

S. Ayyappan,<sup>a,b</sup> N. Sundaraganesan,<sup>c\*</sup> M. Kurt,<sup>d</sup> T. R. Sertbakan<sup>d</sup> and M. Özduran<sup>d</sup>



In this study, the Fourier-transform infrared (FT-IR) and FT-Raman spectra of 3,5-dichlorophenylboronic acid (3,5-dcpba) were recorded in the solid phase. The structural and spectroscopic analysis of the 3,5-dichlorophenylboronic was made by using density functional harmonic calculations. There are three conformers for this molecule. The computational results diagnose the most stable conformer of 3,5-dcpba as the ct form. The geometrical parameters and energies have been obtained for all three conformers from DFT (B3LYP) with 6-311++G(d,p) basis set calculations. The vibrations of stable and unstable conformers of 3,5-dcpba are researched by using quantum chemical calculations. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes calculated with the scaled quantum mechanics (SQM) method. The stability of the molecule arising from hyperconjugative interactions and charge delocalization has been analyzed using the natural bond orbital (NBO) analysis. The results show that the charge in electron density (ED) in the  $\pi^*$  and  $\sigma^*$  antibonding orbitals and E2 energies confirms the occurrence of intermolecular charge transfer (ICT) within the molecule. Finally, the calculation results were applied to simulated infrared and Raman spectra of the title compound, which show agreement with the observed spectra. Copyright © 2010 John Wiley & Sons, Ltd.

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

**Keywords:** dichlorophenylboronic acid; DFT; B3LYP; IR and Raman spectra; NBO analysis

## Introduction

The boronic acid ligands have been incorporated into various biologically important compounds. A wide variety of boronic acid derivatives of divergent biologically important compounds have been synthesized as antimetabolites for a possible two-pronged attack on cancer.<sup>[1–3]</sup> In addition to the inhibition of tumor growth, the use of boron-10 neutron capture therapy<sup>[4]</sup> would be possible due to the preferential localization of boron compounds in the tumor tissue. Boronic acid analogs have been synthesized as transition-state analogs for acyl transfer reactions<sup>[5]</sup> and inhibitors of dihydrotase.<sup>[6]</sup> The boronic acid moiety has also been incorporated into amino acids and nucleosides as antitumor, antiviral agents.<sup>[7]</sup> Phenylboronic acid is a versatile building block in organic synthesis and an important intermediate in the synthesis of active compounds in agrochemical and pharmaceutical industries.<sup>[8]</sup> In order to study these biologically important type of molecules by density functional theory (DFT) methods, the necessary parameters had to be developed.

To the best of our knowledge, no DFT calculations and detailed vibrational IR and Raman analyses have been performed on the 3,5-dichlorophenylboronic acid (3,5-dcpba) molecule. A detailed quantum chemical study will aid vibrational modes of 3,5-dcpba and clarify the experimental data available for this molecule. DFT calculations have been reported to provide excellent vibrational wavenumbers of organic compounds if the calculated wavenumbers are scaled to compensate for the

approximate treatment of the electron correlation for basis set deficiencies and for the anharmonicity.<sup>[9–14]</sup>

As a continuation of the interest in boronic acid-containing compounds, experimental and theoretical analysis along with the energies of different conformations of the title molecule were optimized at the B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels of calculations. Vibrational wavenumbers of the three different forms were also calculated at the DFT-B3LYP level and vibrational assignments were carried out on the basis of total energy distributions (TED) and experimental data. In addition, natural bonding orbitals (NBO) analysis was also carried out in order to have any intramolecular charge transfer (ICT) within the molecule. The results of this work are presented herein.

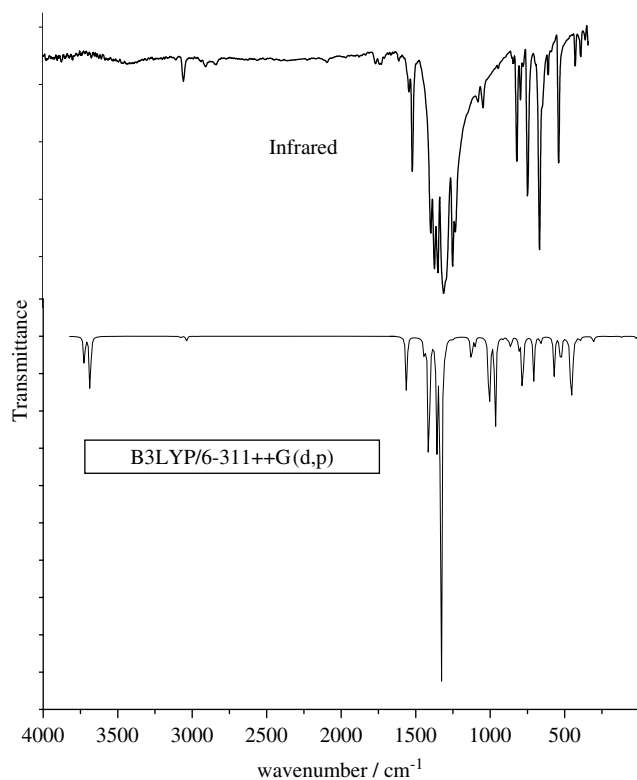
\* Correspondence to: N. Sundaraganesan, Department of Physics (Engg.) Annamalai University, Annamalai Nagar 608 002, Tamilnadu, India. E-mail: sundaraganesan\_n2003@yahoo.co.in

a Government College of Technology, Coimbatore 641 013, India

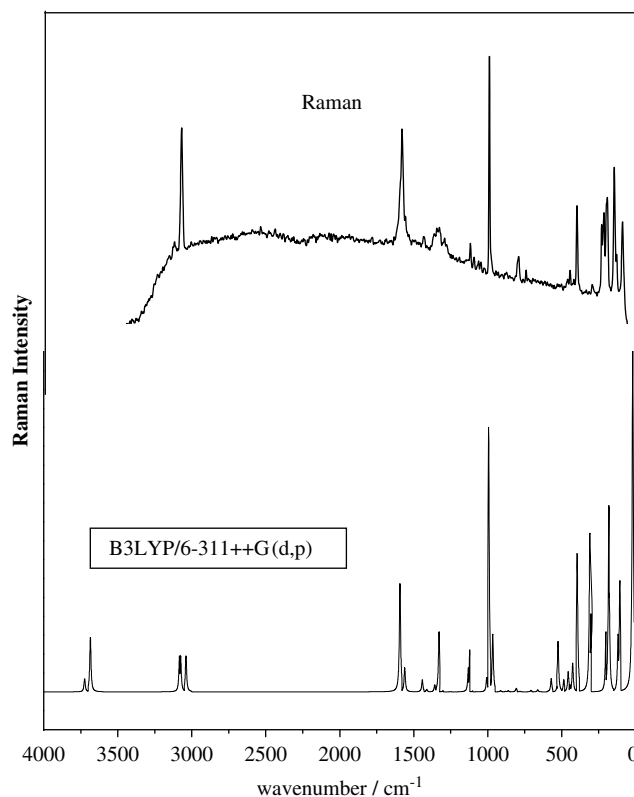
b Research and Development centre, Bharathar University, Coimbatore 641 046, India

c Department of Physics (Engg.) Annamalai University, Annamalai Nagar 608 002, India

d Ahi Evran Üniversitesi Fen Edebiyat Fakültesi Fizik Bölümü, Aşkpaşa Kampüsü 40100, Kırşehir-Türkiye



**Figure 1.** Comparison of the observed and computed FT-IR spectra of 3,5-dcpba.



**Figure 2.** Comparison of the observed and computed FT-Raman spectra of ~3,5-dcpba.

## Experimental

The 3,5-dcpba sample was purchased from the Acros Chemical Company with a stated purity of greater than 98% and it was used as such without further purification. The sample 3,5-dcpba is in solid form at room temperature. Fourier-transform infrared (FT-IR) spectra of the sample were recorded between 4000 and 400  $\text{cm}^{-1}$  on a Mattson 1000 FTIR spectrometer, which was also calibrated using polystyrene bands. The sample was prepared as a KBr disc. FT-Raman spectra of the sample were recorded on a Bruker RFS 100/S FT-Raman instrument using 1064-nm excitation from a Nd:YAG laser. 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. The measured experimental FT-IR, FT-Raman spectra and theoretically constructed spectra are shown in Figs 1 and 2.

## Calculations

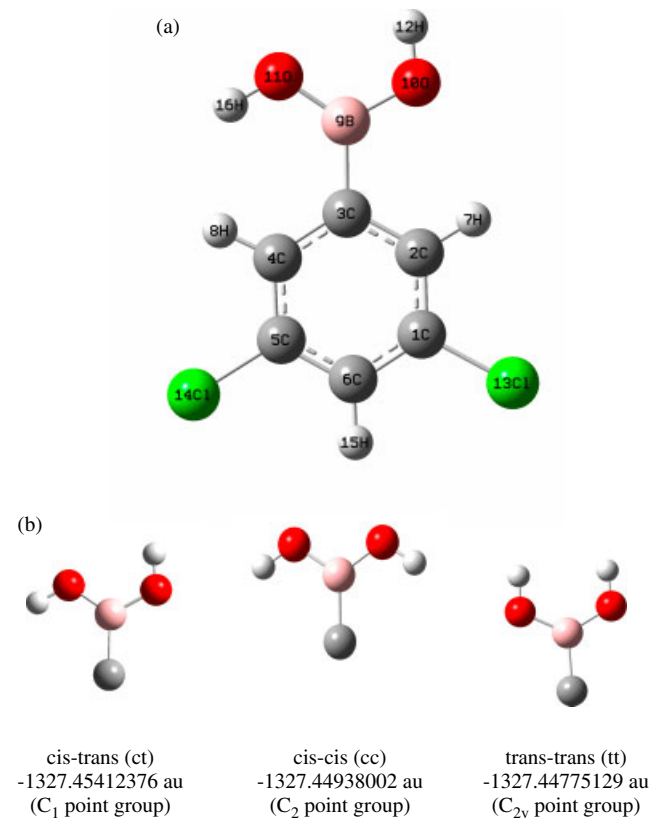
The molecular structure of 3,5-dcpba in the ground state (*in vacuo*) is optimized by B3LYP with the 6-311++G(d,p) and 6-31G(d) basis sets. There are no significant differences in the geometry and vibrational wavenumbers by the selection of the different basis sets, but we included two different basis sets, namely, (B3LYP/6-31G(d) and B3LYP/6-311++G(d,p)), only for geometric parameters. By using B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) methods, it was seen that all the vibrational wavenumbers for each form of the title molecule were positive. The calculated vibrational wavenumbers were scaled by using one global scaling factor of 0.964 for B3LYP/6-31G(d) and by using two scaling factors of 0.958 in the 1700–4000  $\text{cm}^{-1}$  region and 0.983 for

B3LYP/6-311++G(d,p) in the 0–1700  $\text{cm}^{-1}$  region.<sup>[15]</sup> The theoretically constructed FT-IR and FT-Raman spectra are shown in Figs 1 and 2.

Molecular geometry is restricted and all the calculations are performed by using Gauss view molecular visualization program<sup>[16]</sup> and Gaussian 03 program package on the personal computer.<sup>[17]</sup> 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 set. 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.

Finally, the NBO calculations<sup>[18]</sup> were performed using the NBO 3.1 program as implemented in the GAUSSIAN 03 W<sup>[17]</sup> package at the DFT/B3LYP/6-311++G(d,p) level in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the intermolecular delocalization or hyper conjugation. NBO analysis provides the most accurate possible 'natural Lewis structure' picture of  $\phi$ , because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra- and intermolecular interactions.

The second-order Fock matrix was used to evaluate the donor–acceptor interactions in the NBO basis.<sup>[19]</sup> The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (*i*) and acceptor (*j*), the stabilization energy  $E(2)$  associated with the



**Figure 3.** (a) Atom numbering scheme adopted in this study of 3,5-dcpba. (b) All the conformations of 3,5-dichlorophenylboronic acid.

delocalization  $i \rightarrow j$  is estimated as

$$E_2 = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i} \quad (1)$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$  and  $\varepsilon_j$  are the energies of  $\sigma$  and  $\sigma^*$  diagonal elements and  $F(i,j)$  is the off-diagonal NBO Fock matrix element.

## Results and Discussion

The molecule of 3,5-dcpba consists of 16 atoms and it has 42 normal vibrational modes. On the basis of a  $C_1$  symmetry, the 42 fundamental vibrations of the ct form of 3,5-dcpba can be distributed as 42A. The cc form of the molecule of 3,5-dcpba on the basis of the  $C_2$  symmetry can be distributed as 20A + 22B. If we take the  $C_{2v}$  symmetry of the tt form of this molecule into account, 42 normal vibrations can be distributed as 15A<sub>1</sub> + 5A<sub>2</sub> + 8B<sub>1</sub> + 14B<sub>2</sub>. In tt forms of the molecule, boronic acid and benzene ring are in the same plane. The cc and ct forms of the molecule have a nonplanar structure. The  $C_1$  structure was the lowest in energy at all levels. The molecular structure and numbering of the atoms of 3,5-dcpba are shown in Fig. 3(a). We reported some geometric parameters and vibrational wavenumbers for 3,5-dcpba by using B3LYP, comparing some observed bond lengths and bond angles.

The vibrational assignments of most of the fundamental vibrations of the molecule were straightforward based on their calculated TED values, as shown in Tables S2, S3 (Supporting information) and Table 1 (minimum energy). The calculated

wavenumbers of the molecule for the cc, tt and ct forms were compared with the corresponding observed IR and Raman spectra of the molecule, as shown in Tables S2 and S3 (Supporting Information) and Table 1 (minimum energy).

### Geometrical structures

The optimized structural parameters of 3,5-dcpba were calculated at the DFT/B3LYP level with the 6-31G(d) and 6-311++G(d,p) basis sets. Although the crystal structure of 3,5-dcpba has not been reported till now, the XRD crystal structure of closely related molecules like phenylboronic acid<sup>[20]</sup> has been compared with our calculated parameters, as shown in Table S1 (Supporting Information). The 3,5-dcpba molecule has three possible conformations: all-trans, all-cis and mixed trans-cis relative to the B-C bond. All conformation of 3,5-dcpba and its atomic numbering are shown in Fig. 3(a) and (b). 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. However, in the lowest-energy form of 3,5-dcpba, the -B(OH)<sub>2</sub> group is planar and, at all the computational levels, it does not lie in the plane of the benzene ring; the O-B-O plane was twisted by  $\sim 5^\circ$  for the 6,311++G(d,p) basis set and by  $\sim 14^\circ$  for the 6,31G(d) basis set.

In general, typical B-O distances are 1.359 Å<sup>[21]</sup> consistent with relatively strong  $\pi$ -interactions. Conversely, the C<sub>3</sub>-B<sub>9</sub> bond length is slightly greater than that typically found in boroxines, indicating a weakening of this bond by the electron-withdrawing nature of the ring part. However, by using HF/6-31G(d) levels of theory, for the few boronic acids including phenylboronic acid molecule, Chen *et al.*<sup>[19]</sup> found approximately the same value of this bond length. For the 3,5-dcpba molecule, B-O distances for different forms were found in the range of 1.364–1.372 Å.

Bond angles at B and C are consistent with sp<sup>2</sup> hybridization but with significant deviations from the expected 120° angle occurring in close proximity with the -B(OH)<sub>2</sub> substituent on C<sub>3</sub>. The theoretical results show that the -B(OH)<sub>2</sub> group is twisted by 14° and 5° relative to the ring part for the ct form by using 6-31G(d) and 6-311++G(d,p) basis sets. A potential energy scan with all the levels of theoretical approximation was performed along the C-C-B-O torsional angle of 3,5-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°. The resulting potential energy curve depicted in Fig. 4(a) and (b) shows the ct form for minimum energies. The B-C rotational barrier in the tt and cc forms was calculated to be about 2–3 kcal/mol (Fig. 4(a) and (b)), which is significantly high compared to the B-C barrier ct and tc forms of the molecule. From the calculations, the optimized structure of 3,5-dcpba was calculated to exist in a planar structure for the tt form, while the other forms of the molecule were calculated to exist as a near planar structure with C-C-B-O torsional angle of about 14 and 5 for the ct form, and 145 and 144 for the cc form, by using 6-31G(d) and 6-311++G(d,p) basis sets, respectively.

### NBO analysis

The NBO analysis provides an efficient method for studying intra- and intermolecular bonding and interaction among bonds,

**Table 1.** Experimental and calculated fundamental harmonic wavenumbers (in  $\text{cm}^{-1}$ )<sup>a</sup> infrared intensities<sup>b</sup> and Raman intensities<sup>c</sup> for 3,5-dclpa molecule (ct form)

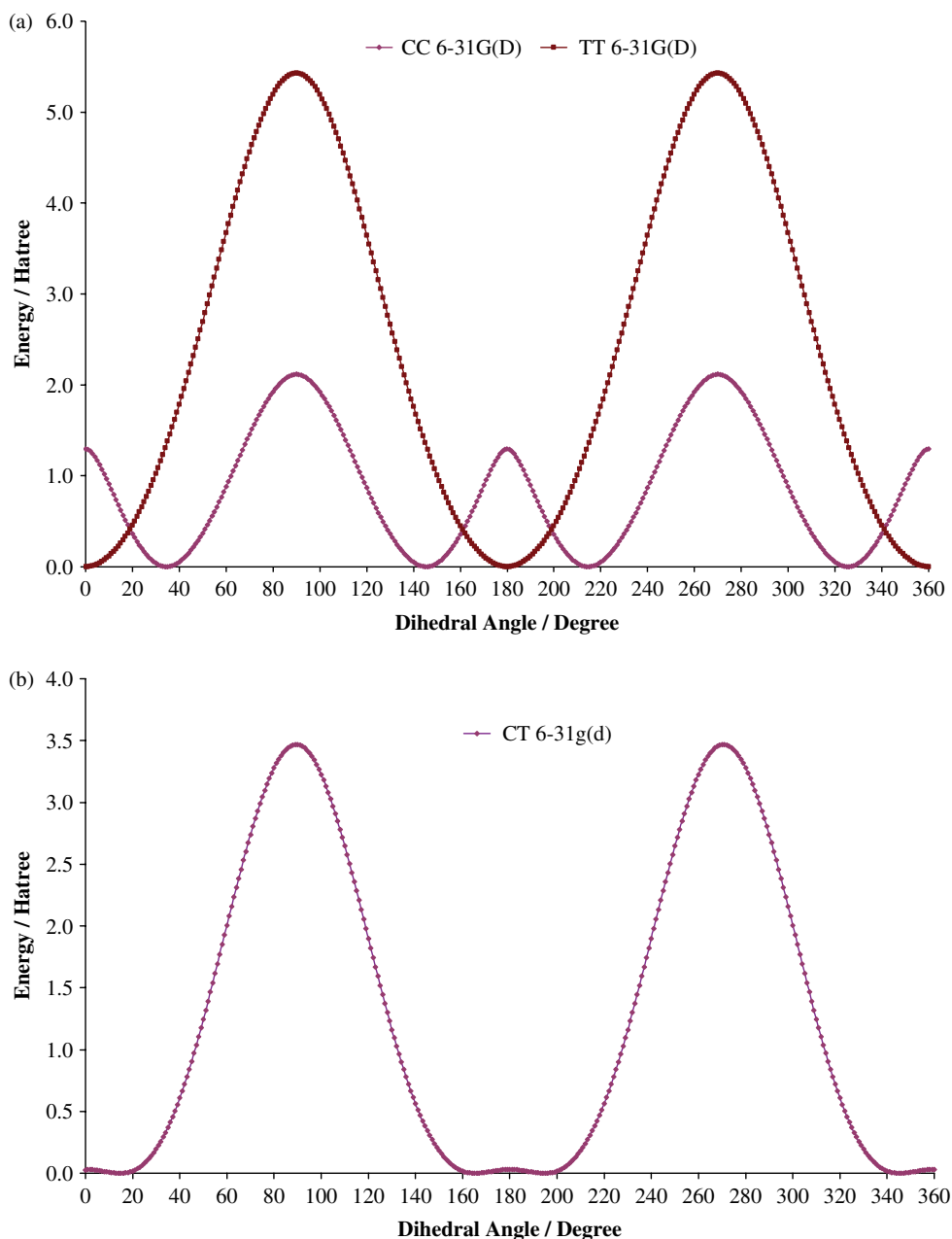
$\nu$	Sym	6-31G(D) 145.62660				6-311++G(D,P) 144.35195				Exp		TED ( $\geq 10\%$ )
		Freq	Scaled	$I_{\text{Infrared}}$	$I_{\text{Raman}}$	Freq	Scaled	$I_{\text{Infrared}}$	$I_{\text{Raman}}$	Infrared	Raman	
1	A	3807	3656	30.29	43.49	3887	3724	43.85	46.01	3443 w	3480vw	$n_{\text{OH}}(100)$
2	A	3769	3619	66.01	207.9	3847	3685	97.61	186.2	3397 w	3440vw	$n_{\text{OH}}(100)$
3	A	3245	3116	0.31	66.84	3218	3083	0.87	67.18	3069m	3101 w,sh	$n_{\text{CH}}(100)$
4	A	3235	3106	0.37	58.81	3210	3075	1.43	55.98	2925 m	3069n	$n_{\text{CH}}(100)$
5	A	3191	3064	9.40	66.46	3172	3039	7.26	66.26	2852 m	3045 w,sh	$n_{\text{CH}}(100)$
6	A	1639	1574	0.63	34.25	1621	1593	0.55	36.61	1570 m	1584 vs	$n_{\text{CC}}(66)+d_{\text{HCC}}(15)$
7	A	1607	1543	67.65	8.24	1588	1561	79.45	8.79	1561 s	1559 w	$n_{\text{CC}}(67)+d_{\text{HCC}}(18)$
8	A	1482	1423	33.41	3.21	1467	1442	29.77	3.47	1416 vs	1434vw	$n_{\text{CC}}(47)+d_{\text{HCC}}(25)$
9	A	1462	1404	283.08	1.40	1436	1412	243.69	0.82	1392 vs	1409vw	$n_{\text{OB}}(45)+d_{\text{HCC}}(14)+n_{\text{CC}}(14)$
10	A	1413	1357	71.91	1.55	1381	1358	147.78	1.91	1355 vs	1366 w	$n_{\text{OB}}(36)+n_{\text{CC}}(30)+d_{\text{HCC}}(20)$
11	A	1373	1319	513.80	15.40	1352	1329	552.37	16.28	1295 vs	1326 w	$n_{\text{OB}}(30)+n_{\text{BC}}(22)+d_{\text{HOB}}(17)+d_{\text{HCC}}(12)$
12	A	1343	1290	7.80	0.29	1324	1301	11.15	0.28	1278 s	1297 w	$n_{\text{CC}}(56)+d_{\text{HCC}}(42)$
13	A	1293	1241	1.28	0.06	1274	1252	3.22	0.05	1239 m,sh	1239vw	$d_{\text{HCC}}(55)+n_{\text{CC}}(42)$
14	A	1162	1116	29.69	3.53	1150	1130	24.02	4.97	1128 w	1123 w	$n_{\text{CC}}(32)+d_{\text{HOB}}(14)+d_{\text{HCC}}(11)$
15	A	1151	1105	17.84	9.99	1140	1121	15.94	9.11	1106 w,sh	1098 m	$n_{\text{CC}}(47)+d_{\text{HCC}}(24)+n_{\text{CCl}}(15)$
16	A	1134	1089	14.43	0.48	1122	1103	12.96	0.19	1094 w	1082 w,sh	$d_{\text{HCC}}(41)+n_{\text{CC}}(40)$
17	A	1039	998	151.47	3.15	1024	1007	142.36	2.55	994 w	998 s,sh	$d_{\text{HOB}}(79)+n_{\text{OB}}(18)$
18	A	1013	972	25.01	26.00	1011	994	6.80	45.55	969vw	995 vs	$d_{\text{CCC}}(35)+n_{\text{CC}}(31)+d_{\text{HOB}}(13)$
19	A	998	958	135.41	12.73	982	965	142.34	9.44	952vw	952vw	$d_{\text{HOB}}(55)+n_{\text{OB}}(22)$
20	A	930	893	3.38	0.86	929	913	2.39	0.15	894vw	892vw	$G_{\text{HCCC}}(36)+G_{\text{HCCB}}(26)+G_{\text{HCCCl}}(25)$
21	A	895	859	0.30	1.22	895	880	6.64	0.08	873 m	859vw	$G_{\text{HCCC}}(41)+G_{\text{HCCCl}}(36)+G_{\text{HCCB}}(14)$
22	A	880	845	28.14	0.29	876	861	19.00	0.16	848 w	857vw	$G_{\text{HCCCl}}(42)+G_{\text{HCCC}}(25)+G_{\text{HCCB}}(11)$
23	A	825	792	14.86	0.41	821	807	15.96	0.54	802 m	798 w	$n_{\text{BC}}(22)+n_{\text{CCl}}(17)+n_{\text{OB}}(16)+d_{\text{CCC}}(14)$
24	A	800	768	101.77	0.02	796	782	106.49	0.06	773 m	767vw	$n_{\text{CCl}}(54)+d_{\text{CCC}}(24)$
25	A	708	680	39.47	0.02	719	707	61.31	0.17	692 m,sh	685vw	$G_{\text{OBCC}}(26)+G_{\text{HCCC}}(25)+G_{\text{CCCC}}(22)$
26	A	661	634	30.41	0.43	673	662	12.07	0.18	668 w	639vw	$G_{\text{HOBO}}(29)+G_{\text{CCCC}}(21)+G_{\text{OBCC}}(19)$
27	A	594	570	42.45	3.00	580	570	53.08	1.05	598 s	570vw	$G_{\text{HOB}}(44)+G_{\text{HOBO}}(37)$
28	A	537	516	12.05	1.19	542	533	6.61	0.38	524vw	525vw	$G_{\text{CCCC}}(16)+d_{\text{OBO}}(11)+G_{\text{HCCC}}(10)$
29	A	534	513	35.29	2.80	534	525	45.35	3.72	494 w,sh	508vw	$d_{\text{OBO}}(20)+d_{\text{OBC}}(10)$
30	A	505	485	1.91	1.18	494	486	3.26	0.79	487 m	491 w	$d_{\text{OBC}}(23)+d_{\text{BCC}}(19)+d_{\text{CCCl}}(14)$
31	A	484	465	162.38	1.28	464	456	130.33	1.23	452 m	466 m	$G_{\text{HOBO}}(53)+G_{\text{HOB}}(42)$
32	A	441	424	2.18	2.17	450	442	18.48	0.42	425 w	425 m	$G_{\text{CCCC}}(22)+G_{\text{HOB}}(12)+n_{\text{CCl}}(11)+G_{\text{OBCC}}(11)$
33	A	430	413	2.64	1.24	433	426	3.48	1.56	407 w,sh	404 s	$d_{\text{CCCl}}(31)+d_{\text{CCC}}(21)+n_{\text{CCl}}(18)$
34	A	403	387	7.09	6.93	403	396	6.49	6.99	387 w,sh	387 w,sh	$n_{\text{CCl}}(45)+d_{\text{CCC}}(25)$
35	A	314	301	5.24	4.31	316	311	4.37	5.66	302 w	302 w	$n_{\text{BC}}(23)+d_{\text{OBO}}(22)+n_{\text{CCl}}(13)+d_{\text{OBC}}(12)$
36	A	308	296	4.95	2.79	308	303	5.86	2.70	287 w,sh	287 w,sh	$d_{\text{OBC}}(43)+d_{\text{CCCl}}(34)$
37	A	208	200	0.47	1.95	204	201	0.66	1.06	200 s	200 s	$G_{\text{CCCC}}(44)+G_{\text{HCCCl}}(24)+G_{\text{CCCC}}(13)$
38	A	185	177	0.43	2.42	184	181	0.34	3.01	178vw	178vw	$G_{\text{CCCl}}(43)+G_{\text{HCCCl}}(14)+G_{\text{BCCC}}(10)+G_{\text{BCCH}}(10)$
39	A	184	176	0.44	3.37	182	179	0.26	1.57	173vw	173vw	$d_{\text{CCCl}}(83)$
40	A	117	112	1.06	0.53	121	119	1.43	0.47	-	-	$d_{\text{BCC}}(62)+d_{\text{OBC}}(15)$
41	A	107	102	0.38	1.00	109	107	0.05	0.76	97 w	97 w	$G_{\text{BCCC}}(34)+G_{\text{CCCC}}(23)+G_{\text{OBCC}}(12)+G_{\text{BCCH}}(10)$
42	A	29	28	2.70	0.25	21	21	2.92	0.11	24vw	24vw	$G_{\text{OBCC}}(95)$

m, Middle; s, strong; vs, very strong; w, weak; vw, very weak; sh, shoulder; G, torsion; d, bending; n, stretching.

<sup>a</sup> Wavenumbers in  $\text{cm}^{-1}$ .<sup>b</sup> Intensities in  $\text{km/mol}$ .<sup>c</sup> Raman scattering activities in  $\text{\AA}^2/\text{amu}$ .

and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbitals, acceptor orbitals and the interacting stabilization energy that resulted from the second-order micro-disturbance theory are reported.<sup>[22,23]</sup> The larger the  $E^{(2)}$  value, the more intense is the interaction between electron donors and electron acceptors, i.e. a more donating tendency from electron donors to electron acceptors and a greater extent of

conjugation of the whole system. Delocalization of the electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the molecule at the B3LYP/6-311++G (d,p) level in order to elucidate the intramolecular rehybridization and delocalization of electron density within the molecule. The second-order perturbation theory



**Figure 4.** (a) Torsion profile of C–C–B–O (abbreviated as  $\theta$ ) in the title molecule cc and tt form by the B3LYP/6-31G(d) basis set. (b) Torsion profile of C–C–B–O in title molecule ct form by the B3LYP/6-31G(d) basis set.

analysis of Fock matrix in NBO analysis of 3,5-dcpba shows strong intramolecular hyperconjugative interactions, which are presented in Table 2.

The intermolecular hyperconjugative interactions are formed by the orbital overlap between  $\pi$  (C–C),  $\pi^*$ (C–C) and  $\sigma$ (C–C),  $\sigma^*$ (C–C) bond orbitals, which results in ICT, causing stabilization of the system. These interactions are observed as an increase in the electron density (ED) in the C–C antibonding orbital that weakens the respective bonds. The ED at the conjugated  $\sigma$  bonds ( $\sim 1.96e$ ) and  $\sigma^*$ ( $0.02e$ ) of the aromatic ring clearly demonstrates weak delocalization.

The strong intramolecular hyperconjugation interaction of the  $\pi$  electrons from C5–C6 to the  $\pi^*$  antibonding orbital of C1–C2 and C3–C4 bond shows an ED of 1.67e, leading to the stabilization of

$\sim 18.63$  KJ/mol. This enhanced  $\pi^*$  (C5–C6) NBO further conjugates with  $\pi^*$ (C2–C3), resulting in an enormous stabilization energy of 153.98 KJ/mol, as shown in Table 2. The most important interaction energy, related to the resonance in the molecule, is the electron donating from the LP(1) B9 atom to  $\pi^*$ (C3–C4), which leads to a strong stabilization energy of 170 KJ/mol. While chlorine atoms LP(3) Cl13 and LP(3) Cl14 lead to stabilization energies of 12.35 and 12.50 KJ/mol to  $\pi^*$  (C1–C2) and  $\pi^*$  (C5–C6) respectively, both chlorine atoms share an equal amount of energy to this bond.

The other important aspects of the NBO analysis show that the  $\pi^*$  (C1–C2) bonding conjugation with C3–C4 leads to an enormous stabilization energy of 306 KJ/mol. As in the case of the O–H bond,  $\sigma$  (O11–H12) and  $\sigma$  (O11–H16) conjugation

**Table 2.** Second-order perturbation theory analysis of Fock matrix on NBO basis

Donor ( <i>i</i> )	Type	ED/e	Acceptor ( <i>j</i> )	Type	ED/e	$E(2)^a$ (KJ/mol)	$E(J)-e(i)^b$ (a.u)	$F(i,j)^c$ (a.u)
C1–C2	$\sigma$	1.98086	C1–C6	$\sigma^*$	0.02918	3.48	1.29	0.060
			C2–C3	$\sigma^*$	0.02174	3.25	1.30	0.058
C1–C6	$\sigma$	1.97282	C1–C2	$\sigma^*$	0.02847	3.60	1.30	0.061
			C5–C6	$\sigma^*$	0.02881	3.73	1.29	0.062
			C5–Cl14	$\sigma^*$	0.03201	4.58	0.87	0.057
C1–Cl13	$\sigma$	1.98790	C2–C3	$\sigma^*$	0.02174	2.41	1.28	0.050
			C5–C6		0.02881	2.14	1.27	0.047
C2–C3	$\sigma$	1.96648	C1–C2	$\sigma^*$	0.02847	3.47	1.27	0.059
			C1–Cl13	$\sigma^*$	0.03258	5.09	0.84	0.058
			C3–C4	$\sigma^*$	0.02181	3.46	1.27	0.059
C2–H7	$\sigma$	1.97681	C3–C4	$\sigma^*$	0.02181	4.25	1.09	0.061
C3–C4	$\sigma$	1.65035	C2–C3	$\sigma^*$	0.02174	3.41	1.27	0.059
			C5–Cl14	$\sigma^*$	0.03201	4.94	0.85	0.058
			C1–C2	$\sigma^*$	0.02847	21.08	0.27	0.068
			C5–C6	$\sigma^*$	0.02881	21.79	0.26	0.068
C3–B9	$\pi$	1.96319	C1–C2	$\sigma^*$	0.02847	3.76	1.10	0.058
			C4–C5	$\sigma^*$	0.02909	3.85	1.09	0.058
			O10–H12	$\sigma^*$	0.00737	2.12	0.97	0.041
C4–C5	$\sigma$	1.98049	C3–C4	$\sigma^*$	0.02181	3.54	1.31	0.061
			C5–C6	$\sigma^*$	0.02881	3.51	1.29	0.060
C4–H8	$\sigma$	1.97822	C2–C3	$\sigma^*$	0.02174	3.96	1.10	0.059
			C5–C6	$\sigma^*$	0.02881	4.42	1.09	0.062
C5–C6	$\sigma$	1.97269	C1–Cl13	$\sigma^*$	0.03258	4.46	0.88	0.056
			C4–C5	$\sigma^*$	0.02909	3.72	1.30	0.062
	$\pi$	1.67380	C1–C2	$\pi^*$	0.36165	17.96	0.29	0.065
			C3–C4	$\pi^*$	0.35203	19.31	0.30	0.069
C5–Cl14	$\sigma$	1.98809	C1–C6	$\sigma^*$	0.02918	2.11	1.27	0.046
			C3–C4	$\sigma^*$	0.02181	2.44	1.29	
C6–H15	$\sigma$	1.97641	C4–C5	$\sigma^*$	0.02909	4.22	1.09	0.061
B9–O10	$\sigma$	1.99370	C3–C4	$\sigma^*$	0.02181	1.43	1.49	0.041
			C2–C3	$\sigma^*$	0.02174	0.98	1.49	0.034
O10–H12	$\sigma$	1.98609	C3–H9	$\sigma^*$	0.03147	2.20	1.20	0.046
O11–H16	$\sigma$	1.98600	B9–O10	$\sigma^*$	0.01949	3.06	1.23	0.055
B9	LP(1)	0.36517	C3–C4	$\pi^*$	0.35203	170.33	0.02	0.077
Cl13	LP(3)	1.92647	C1–C2	$\pi^*$	0.36165	12.35	0.33	0.061
Cl14	LP(3)	1.92860	C5–C6	$\pi^*$	0.38222	12.50	0.32	0.062
C1–C2	$\pi^*$	0.36165	C3–C4	$\pi^*$	0.35203	306.83	0.01	0.084
C5–C6	$\pi^*$	0.38222	C3–C4	$\pi^*$	0.35203	153.98	0.02	0.081

<sup>a</sup>  $E(2)$  means energy of hyperconjugative interaction (stabilization energy).

<sup>b</sup> Energy difference between donor and acceptor *i* and *j* NBO orbitals.

<sup>c</sup>  $F(i,j)$  is the Fock matrix element between *i* and *j* NBO orbitals.

with  $\sigma^*$  (C3–H9) and  $\sigma^*$  (B9–O10) leads to less stabilization energy of  $\sim 2.5$  KJ/mol, which shows that the  $\sigma$ (O–H) bonds do not have the stability to cause any change in the phenyl ring.

### Vibrational spectra

Calculations were made for a free molecule in vacuum, while experiments were performed for the solid sample; therefore, there are disagreements between calculated and observed vibrational

wavenumbers. The vibrational wavenumbers of the 3,5-dcpba molecule for the cc, tt and ct forms were compared with the corresponding observed IR and Raman spectra of the molecule and their TED assignments also remained mostly unchanged, as shown in Tables S2 and S3 (Supporting Information) and Table 1 (minimum energy).

The ct form of the title molecule had the lowest energy at all levels. All of calculated modes were numbered from the largest to the smallest frequency within each fundamental wavenumber,  $\bar{\nu}$ . On the basis of our calculations, and experimental infrared and

Raman spectra, we made a reliable one-to-one correspondence between our fundamentals and any of our frequencies calculated by the DFT (B3LYP) method.

### O–H vibrations

In the O–H region, very strong and broad bands in the spectra of some boronic acid molecules occur at *ca* 3300 cm<sup>-1</sup>. The assignment of these bands to O–H stretching vibrations is straightforward. In the spectra of phenylboronic acid,<sup>[24]</sup> pentafluorophenylboronic acid,<sup>[25]</sup> and 3- and 4-pyridineboronic acid,<sup>[26]</sup> *n*-butylboronic acid<sup>[27]</sup> absorption bands at 3280, 3467, 3410, 3320 and 3306 cm<sup>-1</sup> were assigned, which is typical for O–H bonded hydroxyl groups. The strength and broadening wavenumbers of these bands suggest that intramolecular hydrogen bonding occurs in different environments of boronic acids.<sup>[24]</sup> In accordance with the above conclusion, the two O–H stretching vibrations occur at 3443 and 3397 cm<sup>-1</sup> in the FT-IR spectrum. The same vibration occurs in the FT-Raman spectrum at 3480 and 3440 cm<sup>-1</sup>. The theoretically predicted wavenumbers by the B3LYP/6-31G(d,p) method for the most stable *ct* form show slightly on the higher side of wavenumbers at 3656 and 3619 cm<sup>-1</sup>, which may be due to intramolecular hydrogen bonding. As discussed in literature,<sup>[25,26]</sup> with halogen (F, Cl, Br, . . .) substitution, O–H stretching vibrations shift to a higher wavenumber region.<sup>[28]</sup> This means that, in the boronic acid part, O–H vibrations are sensitive due to halogen coordination. These bands are calculated at 3656 and 3619 cm<sup>-1</sup> with mode numbers 1 and 2 respectively. As expected, these two modes are pure stretching modes as evident from the TED column; they contribute almost 100%.

### C–H vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region of 3100–3000 cm<sup>-1</sup> due to aromatic C–H stretching vibration.<sup>[29]</sup> Our title compound 3,5-dcpba has three isolated C–H moieties. The scaled vibrations, mode numbers 3–5, correspond to the stretching modes of C2–H, C4–H and C6–H units. The benzene ring vibrations mode numbers 3–5 assigned to the aromatic C–H stretch computed in the range of 3083–3039 cm<sup>-1</sup> by the B3LYP/6-311++G(d,p) method show good agreement with the recorded FT-Raman bands at 3101–3045 cm<sup>-1</sup>. All the aromatic C–H stretching bands are found to be weak, and this is due to a decrease in the dipole moment caused by reduction of negative charge on the carbon atom. This reduction occurs because of the electron withdrawal on the carbon atom by the substituent due to the decrease in the inductive effect, which in turn is caused by the increase in the chain length of the substituent.<sup>[30]</sup> As expected, these three modes are pure stretching modes, as evident from the TED column; they contribute almost 100%.

The aromatic C–H in-plane bending vibrations lie in the region of 1230–970 cm<sup>-1</sup>.<sup>[31]</sup> In 3,5-dcpba, the medium strong bands at 1239, 1106 and 1094 cm<sup>-1</sup> in the FT-IR spectrum and 1239, 1098 and 1082 cm<sup>-1</sup> in the FT-Raman spectrum are assigned to the C–H in-plane bending vibration. They show good agreement with those that are theoretically computed by the B3LYP/6-311++G(d) method at 1252, 1121 and 1103 cm<sup>-1</sup> (mode numbers 13, 15 and 16). The bands observed at 894, 873 and 848 cm<sup>-1</sup> in the FT-IR spectrum and 892, 859 and 857 cm<sup>-1</sup> in the FT-Raman are assigned to C–H out-of-plane bending vibrations for the benzene ring of 3,5-dcpba. This also shows good agreement with theoretically scaled harmonic frequency values at 929, 880 and 861 cm<sup>-1</sup> in the B3LYP/6-311++G(d,p) method.

### B(OH)<sub>2</sub> vibrations

The B–O asymmetric stretching band of the phenylboronic acid occurs at 1370 cm<sup>-1</sup> in the infrared spectrum<sup>[24]</sup> and at 1375 cm<sup>-1</sup> for the phenylboronic acid linkage.<sup>[32]</sup> These bands are very intense and should also include the asymmetric stretching vibrations, which are located at 1349 and 1350 cm<sup>-1</sup> for phenylboronic and pentafluorophenylboronic acids, respectively.<sup>[24,33]</sup> Kahraman *et al.*<sup>[32]</sup> assigned the band around 1370 cm<sup>-1</sup> to the  $\nu$ (B–O) stretching vibrations for the homo- and heterotrimeric boron complexes. The corresponding bands were observed at 1392 cm<sup>-1</sup> as very strong bands in FT-IR and at 1409 cm<sup>-1</sup> as weak bands in FT-Raman spectra of the 3,5-dcpba molecule. These vibrations were calculated at 1410, 1412 and 1410 cm<sup>-1</sup> with the B3LYP/6-311++G(d,p) basis set (*cc*, *ct* and *tt* conformations, respectively). When two chlorine atoms are substituted at the third and fifth positions of the phenylboronic acid, the B–O vibration shifts to higher wavenumbers of  $\sim$ 22 cm<sup>-1</sup> in the FT-IR spectrum. The TED calculations show that the B–O stretching mode is a pure mode in the case of the *cc* form, whereas it is a mixed mode in the other two forms. The B–O–H deformation vibrations  $\delta$ (B–OH) were observed at 1002 cm<sup>-1</sup> in the infrared spectrum of the phenylboronic acid. This band was observed at 1197 cm<sup>-1</sup> for boric acid and at 994 cm<sup>-1</sup> for diphenylboronate.<sup>[24,26]</sup> The  $\delta$ (B–OH) vibrations of the 3,5-dcpba appear at 994 cm<sup>-1</sup> in the FT-IR spectrum. This vibration was calculated at 985, 1007 and 997 cm<sup>-1</sup> for *cc*, *ct* and *tt* conformations, respectively, at the B3LYP/6-311++G(d,p) level of theory. The B–C stretching bands were observed at 1080 and 1110 cm<sup>-1</sup> for vibrations of the arylboronic acid by Santucci and Gilman.<sup>[34]</sup> This band was observed at 1089 cm<sup>-1</sup> for phenylboronic acid by Faniran and Shurvell.<sup>[24]</sup> The corresponding bands were observed at 802 cm<sup>-1</sup> as medium bands in FT-IR. The B–C stretching band of 3,5-dcpba molecule was negatively shifted by  $\sim$ 280 cm<sup>-1</sup> for the chlorine substitution. This means that in the boronic acid part B–C vibrations are sensitive because of chlorine substitution.

### C–C vibrations

The ring carbon–carbon stretching vibrations occur in the region of 1625–1430 cm<sup>-1</sup>. In general, the bands are of variable intensity and are observed at 1625–1590, 1590–1575, 1540–1470, 1460–1430 and 1380–1280 cm<sup>-1</sup> from the wavenumber ranges given by Varsanyi<sup>[29]</sup> for the five bands in the region. In the present work, the wavenumbers observed in the FT-IR spectrum at 1570, 1561, 1416, 1278 and 1128 cm<sup>-1</sup> are assigned to C–C stretching vibrations. The same vibrations in the FT-Raman are at 1584, 1559, 1434, 1297 and 1123 cm<sup>-1</sup>. The symmetric ring-breathing mode was usually found to be near 1000 cm<sup>-1</sup> in the monosubstituted benzene ring. The ring-breathing mode at 1106 cm<sup>-1</sup> in FT-IR and the same vibration in FT-Raman at 1098 cm<sup>-1</sup> as a medium band coincide with the B3LYP/6-311++G(d,p) predicted value at 1121 cm<sup>-1</sup> for the most stable *ct* form. The TED of this vibration is a mixed mode, as evident from Table 1, mixing with the C–Cl stretching mode. The in-plane deformations are at higher wavenumbers than those of out-of-plane vibrations. Shimanouchi *et al.*<sup>[35]</sup> gave the wavenumber data for this vibration for different benzene derivatives as a result of normal coordinate analysis. The bands at 969, 773, 524 and 424 cm<sup>-1</sup> in both FT-IR and FT-Raman spectrum are assigned to the C–C–C deformation of the phenyl ring. The theoretically computed C–C–C out-of-plane and in-plane bending vibrational modes have been found to



be consistent with spectral data. The TED of these vibrations are not in the pure mode, as evident from the last column in Table 1.

### C–Cl vibrations

The vibrations belonging to the bond between the ring and halogen atoms are discussed here as mixing of vibrations is possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule.<sup>[36]</sup> Mooney<sup>[37,38]</sup> assigned vibrations of the C–X group (X = Cl, F, Br, I) in the wavenumber range of 1129–480 cm<sup>-1</sup>. The compounds with more than one chlorine atom exhibit very strong bands due to asymmetric and symmetric stretching modes. In view of this, the medium band in the FT-IR spectrum at 773 cm<sup>-1</sup> and a very weak band in the FT-Raman spectrum at 767 cm<sup>-1</sup> is assigned to the C–Cl stretching vibration. The computed TED for C–Cl stretching vibrations are shown along with the C–C–C in-plane bending vibration (mode number 24). The theoretical wavenumber of this vibration is 768 cm<sup>-1</sup> by B3LYP/6-31G(d,p) and it coincides well with the experimental data.

The C–Cl in-plane and out-of-plane bending vibrations are expected in the low-wavenumber region. The C–Cl in-plane bending vibrations predicted by B3LYP/6-31G(d) at 176 cm<sup>-1</sup> (mode number 39) show good agreement with the FT-Raman spectral value at 173 cm<sup>-1</sup> as a weak band. The TED corresponding to this mode almost contributes to 83%. The C–Cl out-of-plane bending vibrations are assigned in the FT-IR and FT-Raman spectra as a shoulder and strong band at 407 and 404 cm<sup>-1</sup>, respectively; they also show good agreement with the computed wavenumber by B3LYP/6-31G(d) at 413 cm<sup>-1</sup> (mode number 33).

### Conclusion

The NIR-FT-Raman and FT-IR spectral studies of 3,5-dcpba molecule were carried out for the first time. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. However, the difference between the observed and scaled wavenumber values of the O–H group fundamental is very large due to the presence of the intermolecular hydrogen bonds in the solid state. Therefore, the assignments made at the DFT level of theory with only reasonable deviations from the experimental values seem to be correct. The theoretically constructed FT-IR and FT-Raman spectra coincide with the experimentally observed FT-IR and FT-Raman spectra. Furthermore, the results of NBO analysis show that the charge in the electron density in the  $\pi^*$  and  $\sigma^*$  antibonding orbitals and  $E_2$  energies confirms the occurrence of ICT within the molecule. We hope that the results will be of help in the quest of the experimental and theoretical evidence for the title molecule in antitumor and antiviral agents.

### Acknowledgements

The visit of N. Sundaraganesan to Ahi Evran University was facilitated by the Scientific and Technical Research Council of Turkey (TUBITAK) BİDEB-2221. The financial support by Gazi University Scientific Research Projects Unit (BAP, project no.:

30-2005/3 and BAP, project no.: 30-2005/) is also politely acknowledged.

### Supporting information

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

### References

- [1] W. Tjarks, A. K. Anisuzzaman, L. Liu, S. H. Soloway, R. F. Barth, D. J. Perkins, D. M. Adams, *J. Med. Chem.* **1992**, *35*, 16228.
- [2] Y. Yamamoto, *Pure Appl. Chem.* **1991**, *63*, 423.
- [3] F. Alam, A. H. Soloway, R. F. Barth, N. Mafune, D. M. Adam, W. H. Knoth, *J. Med. Chem.* **1989**, *32*, 2326.
- [4] A. H. Soloway, R. G. Fairchild, *Sci. Am.* **1990**, *262*, 100.
- [5] D. A. Matthews, R. A. Alden, J. J. Birktoft, S. T. Freer, J. Kraut, *J. Biol. Chem.* **1975**, *250*, 7120.
- [6] D. H. Kinder, S. K. Frank, M. M. Ames, *J. Med. Chem.* **1990**, *33*, 819.
- [7] X. Chen, G. Liang, D. Whitmire, J. P. Bowen, *J. Phys. Org. Chem.* **1988**, *11*, 378.
- [8] A. Meud, M. Erbes, K. Forstinker, US Patent No 2002/0, **2002**, *16*, p 230.
- [9] N. C. Handy, C. W. Murray, R. D. Amos, *J. Phys. Chem.* **1993**, *97*, 4392.
- [10] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
- [11] F. J. Devlin, J. W. Finley, P. J. Stephens, M. J. Frisch, *J. Phys. Chem.* **1995**, *99*, 16883.
- [12] S. Y. Lee, B. H. Boo, *Bull. Korean Chem. Soc.* **1996**, *17*, 754.
- [13] S. Y. Lee, B. H. Boo, *Bull. Korean Chem. Soc.* **1996**, *17*, 760.
- [14] G. Rauhut, P. Pulay, *J. Phys. Chem.* **1995**, *99*, 3093.
- [15] N. Sundaraganesan, S. Ilakiamani, H. Saleem, P. M. Wojciechowski, D. Michalska, *Spectrochim. Acta* **2005**, *A61*, 2995.
- [16] A. Frisch, A. B. Nielsen, A. J. Holder, *Gauss View Users Manual*, Gaussian Inc. Pittsburg, **2000**.
- [17] M. J. Frisch, 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, 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, J. A. Pople, *Gaussian 03, Revision B.4*, Gaussian Inc.: Pittsburgh, **2003**.
- [18] E. D. Glendenning, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO Version 3.1*, TCI, University of Wisconsin: Madison, **1998**.
- [19] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
- [20] S. J. Rettig, J. Trotter, *Can. J. Chem.* **1977**, *55*, 3071.
- [21] P. N. Horton, M. B. Hurts house, M. A. Becket, M. P. Hankey, *Acta Cryst. Sect. E Struct. Rep.* **2004**, *E60*, 2204.
- [22] C. James, A. Amal Raj, R. Reghunathan, I. Hubert Joe, V. S. Jayakumar, *J. Raman Spectrosc.* **2006**, *37*, 1381.
- [23] J.-n. Liu, Z.-r. Chen, S.-f. Yuan, *J. Zhejiang Univ. Sci.* **2005**, *6B*, 584.
- [24] J. A. Faniran, H. F. Shurvell, *Can. J. Chem.* **1968**, *46*, 2089.
- [25] M. Kurt, *J. Mol. Struct.* **2008**, *874*, 159.
- [26] M. Kurt, T. R. Sertbakan, M. Özduran, *Spectrochim. Acta* **2008**, *70A*, 664.
- [27] M. K. Cyranski, A. Jezierska, P. Klimentowska, J. J. Panek, G. L. Zukowska, A. Sporzynski, *J. Chem. Phys.* **2008**, *128*, 124512.
- [28] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley: New York, **1959**.
- [29] G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*, Vol. 1 and 2, Academic Kiado: Budapest, **1973**.
- [30] N. Sundaraganesan, H. Saleem, S. Mohan, *Spectrochim. Acta* **2003**, *59A*, 2511.

- [31] A. J. Barnes, *Spectrochim. Acta* **1985**, 41A, 629.
- [32] G. Kahraman, O. Beskarcles, Z. M. Rzave, E. Piskin, *Polymer* **2004**, 45, 5813.
- [33] S. H. Brewer, A. M. Allen, S. E. Lappi, T. L. Chase, K. A. Briggman, C. B. Gorman, S. Franzen, *Langmuir* **2004**, 20, 5512.
- [34] L. Santuchi, H. Gilman, *J. Am. Chem. Soc.* **1958**, 80, 193.
- [35] T. Shimanouchi, Y. Kakiuti, I. Gamo, *J. Chem. Phys.* **1956**, 25, 1245.
- [36] M. Bakiler, I. V. Masler, S. Akyiiz, *J. Mol. Struct.* **1999**, 475, 83.
- [37] E. F. Mooney, *Spectrochim. Acta* **1964**, 20, 1021.
- [38] E. F. Mooney, *Spectrochim. Acta* **1963**, 19, 877.