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Characterization of 3 fluoro-4-formylphenylboronic acid molecule with Density Functional Theory

Emine BABUR ŞAŞ[*1], Mustafa KURT[2]

Abstract

The geometric structure of 3-fluoro-4-fomylphenylboronic acid (3-4FPBA) molecule were investigated with DFT/B3LYP/6-311++G(d,p) level. The FT-IR and FT-Raman spectra were recorded for the title molecule. Theoretical wavenumber and Mulliken charges were also calculated by using the same method and compared theoretical wavenumber with experimental wavenumbers (FT-IR and FT-Raman) which have a good agreement. Furthermore, electronic structure properties of in the title molecule such as HOMO-LUMO and Molecular Electrostatic Potential (MEP) were investigated by TD-DFT method.

Keywords: 3-fluoro-4-fomylphenylboronic acid, 3-4FPBA, DFT, HOMO-LUMO.

1. INTRODUCTION

Boronic acids and their derivatives have an important place among the compounds due to their wide use. Boronic acids are naturally absent, but have been in the literature since 1860 [1]. Boronic acids and their derivatives have many applications in the field such as material science, analytical chemistry, medicine, biology, catalysis, organic synthesis and crystal engineering [2].

Biomedical applications of boronic acid-containing polymers and biological applications of specific dichlorophenylboronic acids have been investigated [3-5]. Half of the boronic acids are incorporated into nucleosides and amino acids as antiviral agents and anti-tumor [6]. In addition, derivatives of biologically important compounds have been synthesized as anti-metabolites for possible attack against cancer [7-9].

Phenylboronic acid is a compound that is soluble in most polar organic solvents. Phenylboronic acids are a versatile building block in organic synthesis. It is an important intermediate in the synthesis of active compounds in the pesticide and pharmaceutical industry [10]. Boronic acids, such as phenylboronic acid, are known to inhibit lipase (enzyme) acids [11]. This property of phenyl boronic acids has been used to disrupt epithelial barrier function to enhance the absorption of topically applied active agents [12]. Boric acid and certain phenyl boronic acids are some beta-lactamase inhibitors. Phenyl boronic acids have been shown to be effective against beta-lactam antibiotic-resistant bacteria as a consequence of Porin mutation [13, 14].

The infrared spectrum of phenylboronic acid was obtained by Fanniran and Shurvell in 1968 [15]. Crystal structure was first described by Retting and Trotter in 1977 with the x-ray diffraction method [16]. In the literature, no studies have been found on the structural and vibrational spectroscopy of 3-4FPBA molecules.

In this study, molecular geometric parameters, vibrational modes, HOMO-LUMO, MEP and Mulliken charge quantum chemical DFT / B3LYP method and 6-311G ++ (d,p) basis set of 3-4FPBA molecules were obtained and interpreted.

2. EXPERIMENTAL DETAILS

The 3-4 FPBA molecule was 97% pure from Across Organics and powder samples were supplied. Molecular FT-IR and FT Raman spectra were recorded

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[*] Corresponding Author Emine BABUR ŞAŞ Tel: +90 386 280 4748 e–mail address: baburemine@gmail.com

[1] Technical Sciences Vocational Schools, Ahi Evran University, Kırsehir, Turkey

[2] Department of Physics, Ahi Evran University, Kırsehir, Turkey

at 4000-400 cm^{-1} and 3500 -10 cm^{-1} regions. The FT-IR spectrum was obtained from a Perkin Elmer BX spectrometer using the KBr disc technique. The Dispersive Raman spectrum was also obtained using a Bruker RFS 100 / S FT-Raman instrument using a 1064 nm stimulated YAG laser.

3. COMPUTATIONAL DETAILS

All calculations in this study were performed with the Gaussian 09 program [17], DFT / B3LYP / 6-311G ++ (d,p) basis set [18,19]. By optimizing the molecule with this basis set, the molecular geometrical parameters, vibrational frequencies were calculated. In order to approximate the calculated vibration frequencies to the experimental vibration frequencies, these frequencies were multiplied by the scaling factor taken from certain references.

The molecular electrostatic potential surface (MEP) was demonstrated and evaluated in 2D and 3D dimensions, with a map showing the electron density of a molecule. The temperature capacity, entropy and enthalpy values were investigated for the different temperatures of the title molecule (100K-700K).

4. RESULTS

4.1. Geometric Optimization

The crystal structure of the working molecule is not present. Thus, the optimized molecule was compared to similar molecules [20, 21]. The 3-4FPBA molecule consists of a benzene ring, a group C = OH and a group B(OH)2. First, the possible four conformation of the 3-4FPBA molecule was determined by the orientation of the group B (OH) 2 and was named C1, C2, C3 and C4. The determined conformations were divided into new conformations according to the orientation of the oxygen atom in the C = OH group, and these conformations were named C1A, C2A, C3A and C4A. The conformation with the lowest energy was determined by calculating the energies of eight determined conformation. All conformations of the molecule are shown in Figure 1 and the energy values of conformation are given in Table 1.

Table 1 Calculated energies and energy differences for eight possible conformers of 3-4FPBA.

Conformers	Energy (Hartree)	Energy Differences(Hartree)
C1A	-621.00362825	0.01477
C2A	-621.01429300	0.00411
C3A	-620.99751615	0.02089
C4A	-621.00863912	0.00976
C1	-621.01586806	0.00253
C2	-621.01840131	0.00000
C3	-621.01840132	0.00000
C4	-621.01256937	0.00583

The calculation results show that C3 conformation is the lowest energy conformation of the 3-4 FPBA molecule and the lowest energy structure is shown in Fig 1. All data calculated for the molecule were made using this conformation.

First, the C3 conformation is optimized and the source [20] of the single molecule is given in Table 2 together with experimental X-ray data and the like molecule [21] to compare the geometrical parameters (bond lengths and angles) of this conformation.

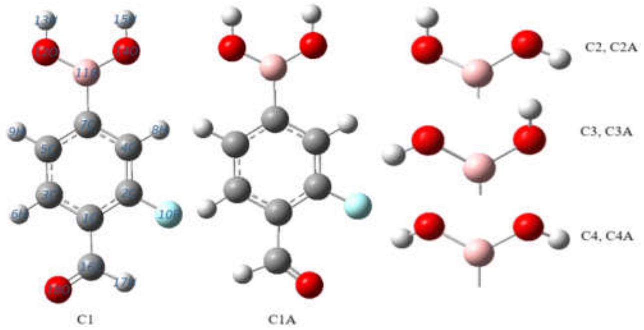


Figure 1. The possible conformation of the 3-4FPBA molecule

The bond lengths of the molecular boronic acid and the phenyl ring are compatible with each other as shown in Table 2. However, there are slight differences between the theoretical and experimental results. These differences can be attributed to the fact that theoretical calculations are made with the molecular gas and the experimental calculations are made with the solid state of the molecule.

The bond lengths indicated by the maximum deviation (deviation) of the 3-4FPBA molecule are the C-H bonds, which depend on the phenyl ring. The maximum deviation at the bond angles is seen at bond angle B12-O13-H16. The difference in these geometric parameters (bond angle and bond length) may be due to the intramolecular interaction of the fluorine atom and the boronic acid group attached to the phenyl ring.

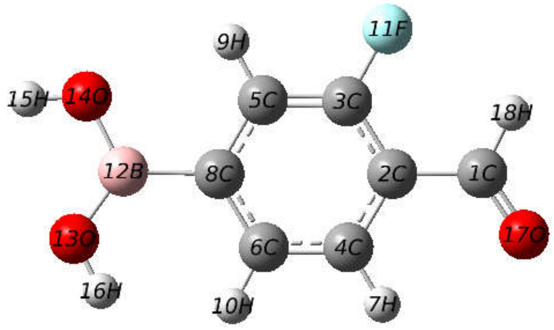


Figure 2. The lowest energy C3 conformation of the 3-4FPBA molecule

4.2. Vibration spectra

In the C3 conformation, 3-4FPBA molecules with C1 symmetry group have 18 atoms and 48 fundamental vibrations. Wavenumbers are calculated according to this conformation in the basis set of 6-311G ++(d,p) and are given in Table 3 by comparison with experimental values. For the calculated wave numbers to be fitted experimentally, the vibrational frequencies less than 1700 cm^{-1} are multiplied by 0.983 and the larger vibrational frequencies are multiplied by the 0.958 scale factors [22]. Experimental FT-IR, dispersive Raman spectra and theoretical Infrared and Raman spectra for 3-4FPA molecules is shown at Fig 3.

Table 2 The some geometrical parameters optimized in 3-4FPBA

Bond Length	3-4FPBA	X-Ray [1]	3FPBA [2]
C1-C2	1.4774	-	-
C1-O17	1.2176	-	-
C1-H18	1.1017	-	-
C2-C3	1.3975	1.365	1.387
C2-C4	1.4034	1.375	1.393
C3-C5	1.3823	1.377	1.384
C3-F11	1.3576	1.377	1.357
C4-C6	1.3864	1.387	1.393
C4-H7	1.084	0.93	1.084
C5-C8	1.4028	1.406	1.404
C5-H9	1.0835	0.93	1.083
C6-C8	1.4076	1.398	1.404
C6-H10	1.0853	0.93	1.086
C8-B12	1.5768	1.562	1.569
B12-O13	1.3676	1.366	1.373
B12-O14	1.3659	1.343	1.366
O13-H16	0.9631	0.855	0.96
O14-H15	0.9659	0.851	0.963
Bond Angles			
C3-C2-C4	117.3	118.4	118.2
C2-C3-C5	122.8	123.9	122.6
C2-C3-F11	119.0	118.1	118.5
C5-C3-F11	118.3	118	118.9
C2-C4-C6	120.8	119.7	120.2
C2-C4-H7	118.4	120.2	119.6
C6-C4-H7	120.8	120.2	120.3
C3-C5-C8	119.8	118.6	119.6
C3-C5-H9	119.3	120.7	119.7
C8-C5-H9	120.9	120.7	120.7
C4-C6-C8	121.3	121.8	121.4
C4-C6-H10	118.1	119.1	118.1
C8-C6-H10	120.7	119.1	120.5
C5-C8-C6	118.2	117.6	118.1
C5-C8-B12	119.0	120.1	119.3
C6-C8-B12	122.8	122.1	122.6
C8-B12-O13	124.6	122.7	124.3
C8-B12-O14	117.5	119	118.3
O13-B12-O14	117.8	118.2	117.4
B12-O13-H16	116.6	124	115.1
B12-O14-H15	113.3	116	112.6

Table 3. Comparison of the calculated and experimental vibrational wavenumbers (cm^{-1}) of 3-4FPBA.

	Experimental wavenumbers		**Theoretical wavenumbers**			
No.	FT-IR	FT-Raman	Scaled	I_{IR}	S_{ra}	I_{ra}
1			33	6.23	0.23	0.00
2			71	2.59	1.44	0.01
3		121	129	8.86	0.71	0.00
4			137	16.93	4.38	0.01
5		166	189	6.93	7.71	0.01
6		211	202	4.20	2.09	0.00
7			273	0.45	1.99	0.00
8			289	8.76	6.80	0.01
9		333	330	3.65	2.29	0.00
10			418	29.44	3.42	0.00
11			441	39.55	0.31	0.00
12			451	277.70	0.93	0.02
13			498	51.74	1.11	0.02
14	502		506	25.68	1.12	0.02
15		524	534	17.61	15.30	0.27
16			581	44.37	1.52	0.02
17			602	7.10	1.27	0.02
18	671		673	58.18	42.94	0.45
19		686	677	70.72	3.54	0.04
20	723		724	38.12	2.67	0.02
21	803	804	798	53.08	28.12	0.20
22			827	29.64	0.65	0.00
23	890		896	49.48	17.16	0.09
24	906	906	906	17.72	0.30	0.00
25			965	50.42	0.45	0.00
26			970	244.73	1.46	0.01
27			1010	230.67	3.55	0.01
28			1011	1.03	6.04	0.02
29	1078		1080	117.58	48.01	0.16
30		113	1120	30.43	8.25	0.03
31			1187	115.40	143.41	0.38
32	1217	1223	1207	104.81	51.68	0.13
33		1267	1273	28.41	55.01	0.12
34			1299	121.57	25.07	0.05
35			1327	853.17	79.01	0.16
36	1341		1345	289.05	6.71	0.01
37	1410	1397	1406	346.22	2.37	0.00
38			1416	33.99	31.16	0.05
39	1495	1494	1502	129.63	25.08	0.04
40	1560		1562	58.80	20.99	0.03
41	1620	1621	1628	86.69	871.05	1.00
42	1674	1672	1655	571.52	453.11	0.46
43	2967	2883	2874	111.97	298.32	0.05
44			3038	26.61	177.12	0.02
45			3067	9.51	157.88	0.02
46	3219	3072	3072	1.87	296.56	0.04
47	3450		3631	99.84	310.14	0.02
48			3665	73.28	108.90	0.01

The O-H strenght vibration is observed in boronic acids, usually close to 3300-3200 cm^{-1}. This band was found to be 3467 cm^{-1} in FT-IR for 2-fluorophenylboronic acid [24] at 3280 cm^{-1} in IR for the phenylboronic acid molecule [23], 3400 and 3332 cm^{-1} in FT-IR at 2,3 difluorophenylboronic acid molecule, and it was calculated to be 3685 and 3692 cm^{-1} [25]. It was calculated at 3631 and 3665 cm^{-1} in 3-4FPBA molecules and at 3450 cm^{-1} in FT-IR.

C-F stretching vibration is a mode in which the molecule is mixed with other modes. The C-F stretching vibration was generally observed as a strong band at 1000-1300 cm^{-1} in the IR spectrum [26, 27]. Narasimham et al. Observed a C-F stretching vibration at 1250 cm^{-1} in the IR spectrum [28]. This vibration band was calculated as 1187 and 1207 cm^{-1} in the 3-4FPBA molecule and 1217 cm^{-1} in the FT-IR.

The B-O asymmetric stretching vibration was observed at 1350 cm^{-1} in the IR spectrum of the phenylboronic acid molecule [22], 1385 cm^{-1} in the FT-IR spectrum and 1370 cm^{-1} in the FT-Raman spectrum of the 2-fluorophenylboronic acid molecule [23]. Vargas and colleagues in the boron complexes deposited the band 1370 cm^{-1} as the B-O stretching vibration band [29]. A symmetric strenght vibration at 1327 cm^{-1} in the 3-4FPBA molecule was calculated. These modes are theoretically calculated at a range of 1400-1350 cm^{-1} [30-32].

The C-H stretching vibration in the phenyl ring is observed in the range of 3000-3100 cm^{-1}, which is characteristic for these vibrations [29]. In this study, C-H stretching vibrations were calculated at 3038-3072 cm^{-1}, and this vibration was observed at 3072 cm^{-1} in FT-Raman and 3219 cm^{-1} in FT-IR. These bands are 100% pure bands.

4.3. Frontier molecular orbital analysis

The HOMO-LUMO orbital energies and energy difference, called frontier molecule orbitals (FMO), were calculated using the TD-DFT method in the basis set of 6-311++G(d,p). The difference between the HOMO-LUMO energy values is an important parameter in determining the energy range, the electrical properties of the molecule.

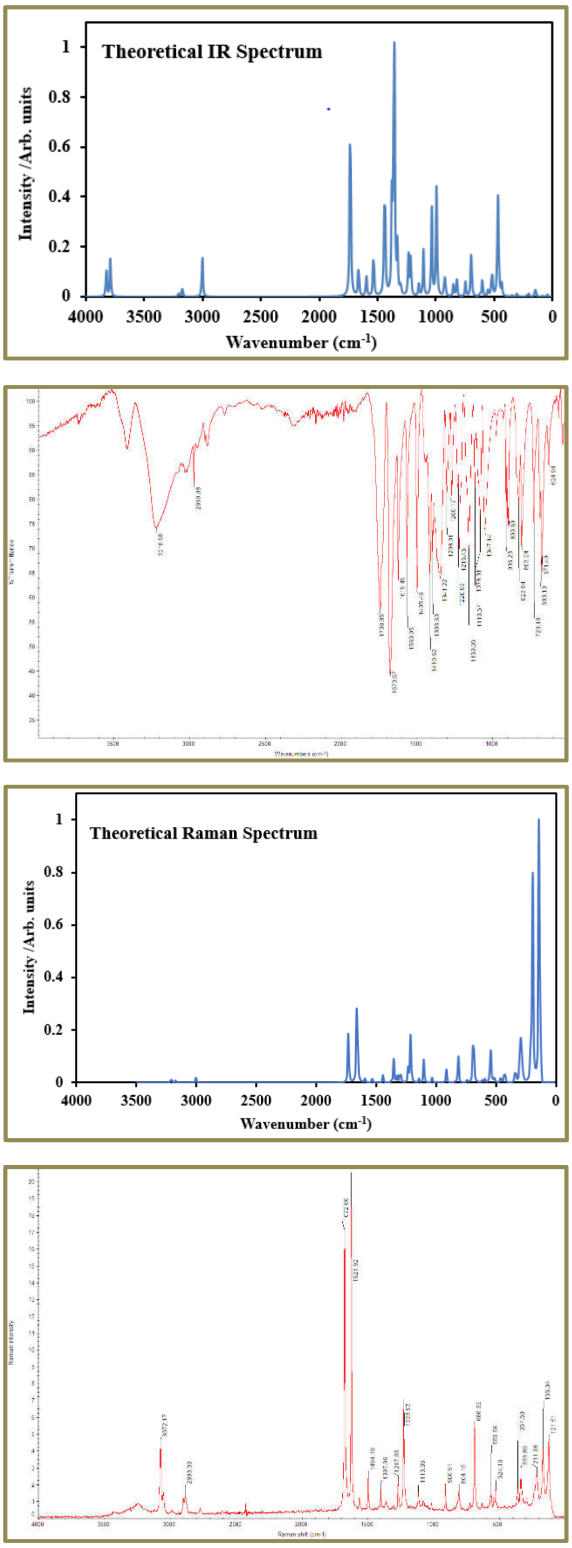


Figure 3. The experimental and theoretical IR and Raman spectra of the 3-4FPBA molecule

The energy range also describes the chemical stability of the molecule and the charge transfer involved in the molecule. Basically, the energy range determines the energy required to pass from the most stable core state in the molecule to an excited state [33].

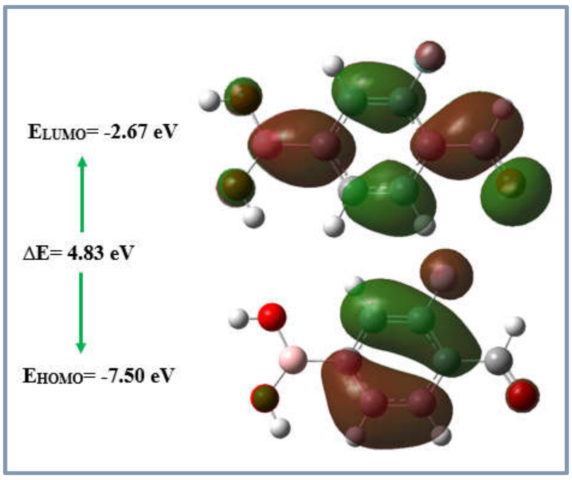


Figure 4. The frontier molecular orbitals of the 3-4FPBA for gas phase

The HOMO energy for the 3-4 FPBA molecule was calculated as -7.50 eV, the LUMO energy was -2.67 eV, the HOMO-LUMO energy difference was 4.83 eV, and it is given in Fig 4. In this graph, the red color is the positive phase and the green color is the negative phase. While the HOMO orbitals are concentrated in the ring, the LUMO orbitals are concentrated in the entire structure except hydrogen atoms.

Some parameters can be calculated using HOMO and LUMO energy values for a molecule. Chemical hardness, electronegativity and electrophilic index values in 3-4FPBA molecules were also calculated and given in Table 4. Intramolecular charge transfer of molecules with high chemical hardness values is low [34]

4. 4 Molecular Electrostatic Potential (MEP)

Molecular electrostatic potential (MEP) is a surface map showing the electron density of a molecule. A computational technique that is often used to determine effects such as nucleophilic reactions and electrophilic attack in a molecule. Reactants with a high tendency to give electrons when entering or exiting a reaction are called nucleophiles, while those with high tendency to take electrons are called electrofilms.

Nucleophilic and electrophilic reactions are displayed in different colors on the MEP surface map. The red color observed on this map has a negative potential, that is, blue and green colors showing electron-donating reactions show positive regions, that is, electron-withdrawing reactions. According to these results on the MEP surface map, the positive potential region (blue color) is around hydrogen and hydrogen atoms, while the negative potential region (red color) concentrates on electronegative atoms.

Table 4. The calculated energies values of 3-4FPBA

C*$_1$*simetri	**Gas**	**DMSO**	**Ethanol**
E_{total} (Hartree)	-474.5699	-474.5813	-474.4034
E_{HOMO} (eV)	-6.34	-6.45	-6.45
E_{LUMO} (eV)	-1.04	-1.25	-1.24
E_{HOMO-1} (eV)	-6.53	-6.62	-6.61
E_{LUMO+1} (eV)	-0.54	-0.62	-0.62
$E_{HOMO-1-LUMO+1\ gap}$ (eV)	**5.99**	**6.00**	**6.00**
$E_{HOMO-LUMO\ gap}$ (eV)	**5.30**	**5.21**	**5.21**
Chemical hardness (h)	2.65	2.60	2.61
Electronegativity (χ)	3.69	3.85	3.84
Chemical Potential (μ)	-3.69	-3.85	-3.84
Electrophilic index (ω)	2.57	2.85	2.83

These colors for the molecule -0.08751 a.u. (dark red) 0.08751 a.u. (dark blue) values and the electrostatic potential surface (MEP) of the molecule is given in Figure 5 as 3D surface. The highest positive potential in the molecule is around the hydrogen atom in the O-H group, with the most negative potential around the C = O double bond oxygen atom. In this case, the H atom contains a strong electron attractor and the O atom contains strong electron repulsion reactions.

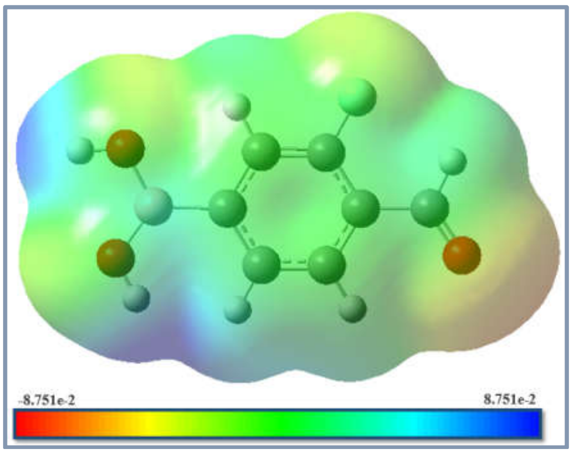
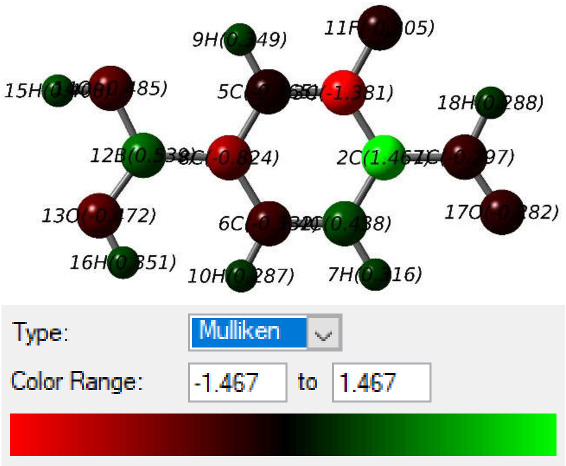


Figure 5. Molecular electrostatic potential (MEPs) 3D map for 3-4FPBA molecule

4.5. Mulliken atomic charges

Mulliken charge give a qualitative picture of a molecular population distribution [35]. However, this distribution does not fully reflect the electronegativities of each element. In some cases, an orbital can give a negative electron population, or an orbital can calculate more electrons than one. These depend strongly on the basis set used. Atomic charges are also used to define the molecular polarity of molecules [36]. The Mulliken charges distribution method is widely used despite some shortcomings. Mulliken charges experimental results are often used to make a qualitative set of estimates [37].



Type: Mulliken

Color Range: -1.467 to 1.467

Figure 6. The Mulliken charge distribution for 3-4FPBA

The Mulliken atomic charges of the 3-4FPA molecule were calculated using the DFT/B3LYP method and the basis set of 6-311++G(d,p) and in given Fig. 6. The values of the Mulliken atomic charges of the molecule are compared in Table 5 with 3-FFPA and FBA it is given.

In all of the molecules that are compared, the atom of bromine leads to the redistribution of the electron density. The C2 atom in the phenyl ring of the 3-4 FPBA molecule has a more positive value than the 3-FFBA molecule. The C2 carbon atom's Mulliken charge is so high from other molecules that it can originate from the group of the formula linked to that atom (C = OH). In the 3-FFBA and 3-4FPBA molecules, the fluorine-bonded (C-F) C3 atom has the most negative charge in the ring. This is because the electronegativity due to the halogen group of the fluorine atom is a high atom.

Table 5. Mulliken atomic charges of the molecule FBA, 3-FFBA ve 3-4FPBA

Atom	**FBA**	**3-FPBA**	**3-4FPBA**
C1			-0.30
C2	-0.02	0.44	1.47
C3	-0.44	-0.86	-1.38
C4	-0.35	-0.44	0.44
C5	0.19	0.60	-0.16
C6	0.21	0.14	-0.33
H7	0.16	0.17	0.32
C8	-0.68	-0.75	-0.82
H9	0.20	0.23	0.35
H10	0.11	0.12	0.29
F11/H	0.16	-0.17	-0.21
B12	0.53	0.53	0.54
O13	-0.37	-0.37	-0.47
O14	-0.38	-0.37	-0.49
H15	0.29	0.29	0.41
H16	0.23	0.24	0.35
O17			-0.28
H18			0.29

5. DISCUSSION

In conclusion, conformation of 3-4 FPBA molecule was determined and geometric optimization was done for lowest energy conformation. After the optimization, the vibrational spectra of the molecules were investigated experimentally and theoretically and these values were compared. The electronic properties of the molecule (HOMO-LUMO and MEP) were then looked at, and the calculations revealed that the electrophilic and nucleophilic reactions took place around which atoms. Calculated and experimentally obtained values were compared and it was seen that the fit between them was good.

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