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A Vibrational Spectroscopic Investigation of 2,2'-Bithiophene Using Experimental and DFT Methods

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Abstract

Organic compounds like 2,2’-Bithiophene (with a synonym. 2,2'-bithienyl, 2,2'-dithienyl)-containing bis(dioxaborin) have drawn significant concern in the area of materials science because of their electron affinity and luminescent properties. With this motivation, we have been concentrating on the properties and functions of 2,2'-Bithiophene. The vibrational frequencies of the molecule 2,2'-Bithiophene in the solid phase were recorded using the Fourier Transformed-Infrared (FT-IR) and FT-Raman spectrometers. Meanwhile, the molecular geometric parameters, the spectral wavenumbers, HOMO-LUMO analysis and the molecular electrostatic potential (MEP) of the 2,2'-Bithiophene molecule were computed at the B3LYP/ 6-311++G (d,p) level of the theory. Furthermore, a comparison between experimental and calculated values for the vibrational frequencies of the 2,2'-Bithiophene molecule exhibits a good agreement.

Keywords: 2,2’-bithiophene, FT-IR and FT-Raman spectroscopies, DFT method, conformational analysis

1. INTRODUCTION

The 2,2'-Bithiophene, ($C_8H_6S_2$), (or briefly BT) molecule which is a typical aromatic dimer gives us a basic knowledge about the aromatic compounds such as thiophene tetramer and higher oligomers. In the past over 30 years, the mentioned aromatic compounds (including thiophene, bithiophene and oligothiophene) have gained a great popularity since they are promising and extensively investigated materials in organic chemistry, medicine, pharmacology, and organic electronics

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fields. Thus, they can be used for the oligothiophene light-emitting diodes (OLEDs) which are taken places at the mentioned areas above [1-6].

Since the BT molecule, which has a well-known structure in gas and solid phases, forms, one of the most proper model molecules for understanding the structural features for polythiophene is focused on this study [7-14].

In this framework, we are interested with BT compound by considering its conformational analysis and the vibrational spectroscopic features. As a matter of fact, there are a great number of studies related to the main properties of torsion energy of the BT molecule using the semi-empirical and ab-initio calculations on different basis sets such as 3-21 G* and 6-31 G* [15-18]. Furthermore, the effect of external electric field on the potential energy surface of BT molecule was investigated using various basis sets at Hartree-Fock and DFT levels [19].

However, unlike the previous calculations, the conformational analysis results of title molecule in the present study were verified at the B3LYP/ 6-311++G(d,p) level which contain the diffuse and polarization functions of the theory and the computations were extended to a greater number of bond and dihedral angles of BT molecule.

On the other hand, a remarkable interest of the researchers for the vibrational spectrum on thiophene, BT molecule and its derivatives has continued for many years. In this framework, Orza et al. presented the assignments of the thiophene normal modes experimentally [20]. The infrared spectrum of 2,2'-Bithiophene was recorded by Furukawa et al. and Lopez et al.[21, 22]. Likewise, the assignments of the vibrational spectrum of thiophene, 2,2'-Bithiophene and higher oligomers were performed by Zerbi et al. [23]. Hernández et al. investigated the vibrational spectrum and ab-initio DFT calculations of 3,3'- and 4,4'-dimethyl substituted as the methyl-derivative of 2,2'-Bithiophene [24]. So as to obtain a deeper study for the conformational and geometrical properties and vibrational analysis of the BT molecule, we present here the theoretical and experimental investigations. Furthermore, it is well-known that the long-range intramolecular delocalization of the π-electrons along the adjacent rings which brings about a small HOMO-LUMO gap as a crucial parameter for adjustment to the properties of conducting polyphenes [25-28].

At the present work, unlike the- above mentioned study [23], we report in detail the results of the experimental and simulated vibrational (FT-IR and FT-Raman) spectra, the conformational analysis of the 2,2'-Bithiophene molecule in the solid phase, the optimized molecular geometry, HOMO-LUMO analysis and the electrostatic molecular potential map (MEP) of title molecule.

2. MATERIALS AND METHODS

2.1. Experimental

The 2,2'- Bithiophene compound in powdered form was purchased from the commercial company (Merck, 99.5 %). A Brucker IFS 66/S with PIKE Gladi ATR (Diamond) spectrometer was used at room temperature with 2 cm^{-1} resolutions for recording the FT-IR spectrum of BT molecule at interval 3500-400 cm^{-1}. The prepared sample for the measurement was compressed into self-supporting pellet and then, it was placed into an IR cell equipped with KBr window.

Likewise, a Brucker FRA 106/S spectrometer using 1064 nm excitation from a Nd: YAG laser whose the detector was a Ge-diode cooled to liquid nitrogen temperature was used for the FT-Raman spectrum of the mentioned compound at the interval 3500- 500 cm^{-1}.

2.2. Computational Details

Our calculations were verified by employing the Gaussian 03 program on an individual computer [29]. In order to determine the stable conformers of the 2,2'-Bithiophene molecule, a precise conformational analysis was performed. First, in the framework of the Molecular Mechanics Force Fields method, the conformational space of the title compound was scanned, and then, full geometry optimization for these structures were carried out at the B3LYP/6-311++G(d,p) level whose expansion is Becke–3–Lee Yang Parr (B3LYP) density functional theory method with 6–311++G(d,p) basis set in a ground state [30-32]. Secondly, after the determination of the geometrical optimization for a stable conformer, the vibrational frequency calculations were performed for the optimized structural parameters of this conformer.

It is well-known that the computed positive vibrational wavenumber values indicate that the optimized molecular structure is stable. On the other hand, since the computed wavenumber values at the mentioned level include the well-known systematic errors, they can be prevented by scaling the computed vibrational wavenumbers as 0.967 (under 1800 cm^{-1} for wave numbers) and 0.955 (over 1800 cm^{-1}) at the B3LYP/6-311++G(d,p) level of the theory [33, 34].

Table 1 The calculated at the B3LYP/6-311++G (d,p) level energy values of the conformers for the 2,2'- bithiophene molecule

Conf	E (Hartree)	E (kcal/mol)	ΔE (kcal/mol)	Dip. Mom. (Debye)
anti	-1104.949	-693366.52	0.000	0.288
s-cis	-1104.948	-693365.84	0.001	0.965

As for the attributes of fundamental vibrational modes of title molecule, the total energy distribution (TED) analysis by using VEDA 4 program were performed [35]. Likewise, the HOMO and LUMO analyses and molecular electrostatic potentials (MEP) calculations for the 2,2'-Bithiophene molecule were carried out at the B3LYP/6-311++G(d,p) level. Furthermore, by using the same level the plotting of both HOMO and LUMO orbitals and the map of the molecular electrostatic potential (MEP) in 3-dimensional (3D) were performed at the Gauss View 5 program.

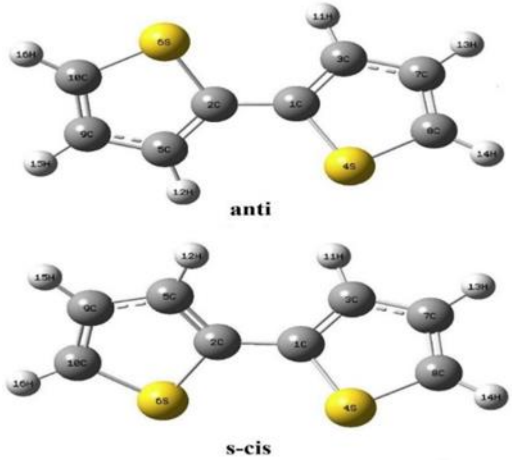

Figure 1 Two conformers of 2,2’-bithiophene molecule.

Meanwhile, the Raman activities were converted into Raman intensities in the framework of RaInt program by using the relationship:

$$Ii = 10^{-12} (n_0 - n_i)4 (1/n_i) S_i$$

where I_i is the Raman intensity, S_i is the Raman scattering activities, n_i is the wavenumber of normal modes, and no indicates the wavenumber of the excitation laser [36].

3. RESULTS AND DISCUSSION

3.1. Molecular optimization

The results of molecular geometry were exhibited that the BT molecule in solid-state has two stable conformers as indicated in Fig. 1. Molecular structure and atom numbering scheme of these conformers were given in Fig. 1. The most stable conformer of the title molecule with a DFT energy of -1104.949 Hartree, called anti conformer, which is given in Table 1.

Therefore, the optimized molecular geometric parameters at the B3LYP/6-311++G (d, p) level are tabulated in Table 2. A comparison between the calculated and experimental values for the bond lengths and bond angles in thiophene rings was also presented in Table 2.

Table 2 Theoretical geometric values at the B3LYP/6-311++G(d,p) level for anti-conformation of the 2,2'-bithiophene molecule

Bond lengths (Å)	Cal	Exp.*	Dihedral angles $(^0)$	Cal
C1,C2	1.451	1.456	C3,C1,C2,C5	153.6
C1,C3	1.376	1.370	C3,C1,C2,S6	-26.7
C1,S4	1.753	1.733	S4,C1,C2,C5	-26.7
C2,C5	1.376	1.370	S4,C1,C2,S6	152.9
C2,S6	1.753	1.733	C2,C1,C3,C7	-179.8
C3,C7	1.423	1.452	C2,C1,C3,H11	-1.2
C3,H11	1.082	1.124	S4,C1,C3,C7	0.5
S4,C8	1.733	1.719	S4,C1,C3,H11	179.1
C5,C9	1.423	1.452	C2,C1,S4,C8	179.5
C5,H12	1.082	1.124	C3,C1,S4,C8	-0.7
S6,C10	1.733	1.719	C1,C2,C5,C9	-179.8
C7,C8	1.366	1.363	C1,C2,C5,H12	-1.2
C7,H13	1.082	1.230	S6,C2,C5,C9	0.5
C8,H14	1.079	1.220	S6,C2,C5,H12	179.1
C9,C10	1.366	1.363	C1,C2,S6,C10	179.5
C9,H15	1.082	1.123	C5,C2,S6,C10	-0.7
C10,H16	1.079	1.122	C1,C3,C7,C8	0.1
Bond angles $(^0)$			C1,C3,C7,H13	179.5
C2,C1,C3	129.1	126.3	H11,C3,C7,C8	-178.5
C2,C1,S4	120.8	-	H11,C3,C7,H13	0.9
C3,C1,S4	110.2	111.8	C1,S4,C8,C7	0.8
C1,C2,C5	129.1	126.3	C1,S4,C8,H14	-179.2
C1,C2,S6	120.8	-	C2,C5,C9,C10	0.1
C5,C2,S6	110.2	111.8	C2,C5,C9,H15	179.5
C1,C3,C7	113.5	111.9	H12,C5,C9,C10	-178.5
C1,C3,H11	122.8	123.1	H12,C5,C9,H15	0.9
C7,C3,H11	123.7	-	C2,S6,C10,C9	0.8
C1,S4,C8	91.8	91.7	C2,S6,C10,H16	-179.2
C2,C5,C9	113.5	111.9	C3,C7,C8,S4	-0.6
C2,C5,H12	122.8	-	C3,C7,C8,H14	179.4
C9,C5,H12	123.7	125 .0	H13,C7,C8,S4	180.0
C2,S6,C10	91.8	91.7	H13,C7,C8,H14	0.0
C3,C7,C8	112.9	112.3	C5,C9,C10,S6	-0.6
C3,C7,H13	123.8	123.6	C5,C9,C10,H16	179.4
C8,C7,H13	123.3	-	H15,C9,C10,S6	180.0
S4,C8,C7	111.6	112.3	H15,C9,C10,H16	0.0
S4,C8,H14	119.8	-	C3,C1,C2,C5	153.6
C7,C8,H14	128.6	127.8		
C5,C9,C10	112.9	112.3		
C5,C9,H15	123.8	123.6		
C10,C9,H15	123.3	-		
S6,C10,C9	111.6	-		
S6,C10,H16	119.8	-		
C9,C10,H16	128.6	127.8		

*Experimental values have been taken from Refs [12, 15]

However, the experimental values of the three C_1-C_2 bond distances and the two C_1-S_4 lengths within the thiophene rings are assumed equal [12, 15]. Meanwhile, we must state that the experimental values are valid for solid phase while the theoretical calculations were verified for gaseous phase. By considering our calculations, the largest differences between experimental and calculated bond lengths are about 0.148 Å for the C_7-H_{13} bonds of the rings, which can be based on the low scattering factors of hydrogen atoms in the X-ray diffraction experiment.

Likewise, although some experimental bond angle values are missing in Table 2, the biggest difference for bond angles becomes 2.8° for the C_2-C_1-C_3 bond angles of the rings. As far as our knowledge up to now, the experimental and computed values of the dihedral angles of the BT compound do not exist in the literature. For this reason, we report only calculated dihedral angle values in Table 2.

However, the bond, C_1-C_2, which connects to two thiophene rings in the compound and has the intramolecular delocalization of the molecular π-electrons, was computed as 1.451 Å at the mentioned level and its experimental value was 1.456 Å [15]. As a result, it is clear that a good agreement with the results between the computed and experimental geometric parameters of the 2,2'-Bithiophene compound.

3.2. Vibrational frequencies

For BT molecule, ($C_8H_6S_2$), the experimental and simulated FT-IR and FT-Raman spectra are exhibited in Figs. 2 and 3 at the frequency interval 3500-3000 cm^{-1} and 2000-500 cm^{-1}, respectively. Since BT molecule includes 16 atoms, it has 42 fundamental vibrational modes. In Table 3, the experimental and computed at the B3LYP/6-311++G(d,p) level, the vibrational frequencies and vibrational frequency attributes of the mentioned molecule are listed. The PED analysis has been used in the assignments of vibrational frequencies.

As for the comparisons between the experimental vibrational wavenumbers of thiophene and BT molecules, first we can present the C-H stretching infrared frequency values of thiophene molecule which are 3126 cm^{-1} and 3098 cm^{-1} [20], whereas these experimental values for BT molecule were registered as 3107 cm^{-1} and 3080 cm^{-1}, respectively [23]

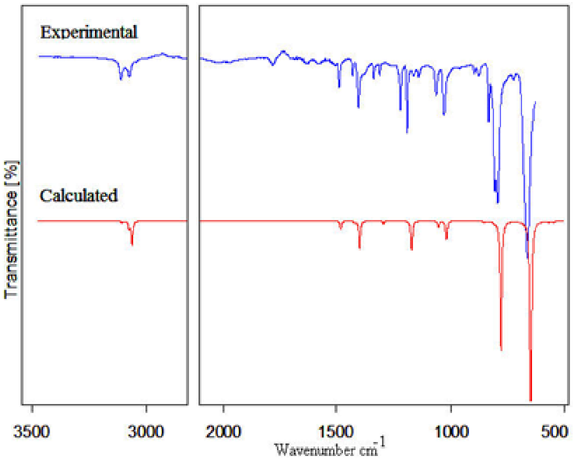

Figure 2 Experimental and theoretical FT-IR spectra of the 2,2’-bithiophene molecule

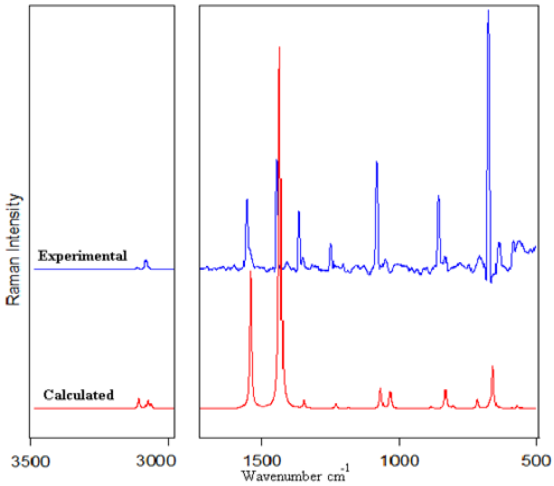

Figure 3 Experimental and theoretical FT-Raman spectra of the 2,2’-bithiophene molecule

Table 3 Comparisons of the experimental and computed at the B3LYP/6-311++G(d,p) level wavenumbers (cm^{-1}) of 2,2'-bithiophene molecule

Modes	Experimental		Theoretical				TED[c](%)
	IR	Raman	Unscaled[a]	Scaled[b]	I_{IR}	I_{Raman}	
1	-	-	3245	3099	0	4	84 ν(CH)
2	3104	3104	3245	3098	1	0	84 ν(CH)
3	-	3075	3210	3066	0	3	82 ν(CH)
4	-	-	3210	3065	3	0	82 ν(CH)
5	3069	-	3197	3053	11	0	80 ν(CH)
6	-	-	3196	3053	0	2	80 ν(CH)
7	-	1554	1591	1538	0	39	36 β(CCH)+ 32 ν(CC)+ 10 β(SCC)
8	1500	-	1544	1493	4	0	48 β(CCH)+ 25 ν(CC)
9	1441	1443	1481	1432	1	100	34 ν(CC)+ 30 β(CCH)
10	1416	1368	1460	1412	13	0	44 β(CCH)+ 34 ν(CC) +10 β(SCC)
11	1350	1351	1394	1348	0	2	46 β(CCH)+ 18 ν(CC) +10 β(CCC)+ 10 β(SCH)
12	1323	-	1353	1308	2	0	40 β(CCH)+ 20 ν(CC)
13	1234	1250	1274	1232	0	1	64 β(CCH)+ 12 ν(CC)+ 10 β(SCH)
14	1205	-	1226	1186	12	0	54 β(CCH)
15	-	-	1225	1185	2	0	21 ν(CC) +20 β(CCC)+ 16 β(CCH)+14 β(SCC) +12 ν(CS)
16	1079	-	1107	1070	3	0	64 β(CCH) +20 β(SCH)
17	-	1079	1102	1065	0	5	54 β(CCH) +20 β(SCH) + 10 ν(CC)
18	1045	-	1071	1035	9	0	50 β(CCH)+ 20 ν(CC) +10 β(CCC)
19	-	1046	1067	1032	0	4	52 β(CCH)+ 16 ν(CC) +10 β(CCC)
20	-	-	912	882	0	1	34 τ(HCCH)+ 26 τ(CCCH)+ 16 τ(SCCH)
21	914	-	910	880	0	0	36 τ(HCCH)+ 26 τ(CCCH)+ 16 τ(SCCH)
22	895	-	901	871	1	0	18 β(CCC) +14 τ(HCCH) +14 β(CCS)+ 12 β(CCH)+ 12 ν(CS)
23	852	856	858	830	1	4	16 ν(CS) +16 β(CCS)+ 16 β(CCC) + 14 β(CCH)+ 10 τ(CCCH)
24	-	-	839	811	1	0	40 τ(CCCH)+ 18 τ(HCCH)+ 14 τ(SCCH)
25	825	-	828	800	20	1	42 τ(CCCH)+ 20 τ(HCCH)+ 18 τ(SCCH)
26	813	-	826	799	43	0	20 ν(CS) +18 τ(CCCH)+ 12 β(CCH)+ 10 β(CCS)
27	-	709	741	716	0	2	28 ν(CS) +20 β(CCC)+ 17 β(CCH)
28	-	-	737	713	0	0	40 ν(CS) +20 β(CCH)+ 18 β(CCC)
29	-	-	696	673	5	0	40 τ(CCCH)+ 18 τ(CSCH)+ 18 τ(SCCH)+ 16 τ(HCCH)
30	684	-	693	670	100	1	38 τ(CCCH)+ 18 τ(CSCH)+ 16 τ(HCCH)+ 14 τ(SCCH)
31	-	670	681	658	0	10	16 β(CCC)+ 14 ν(CS) +10 τ(CCCH)
32	-	-	612	592	1	0	14 τ(CCCH)+ 12 τ(CCCS)+ 12 β(CCS)+ 10 ν(CS)
33	-	588	592	572	1	1	24 τ(CCCS)+ 20 τ(CCCH)+ 12 τ(CCCC)+ 10 τ(HCCH)+ 10 τ(SCCH)+ 10τ(CCSC)
34	-	-	575	556	0	0	22 τ(CCCS)+20 τ(CCCC)+16 τ(CCCH)+12 τ(SCCH)
35	-	-	524	507	2	0	20 τ(CCCC)+20 τ(CCSC)+18 τ(CCCS)+14 τ(CCCH)
36	-	-	468	453	3	1	22 τ(CCCS)+ 16 τ(CCCS)+ 14 τ(CCCH)+ 12 τ(CCCC)+ 12 τ(SCCH)
37	-	-	374	361	0	1	12 β(CCC)+ 12 β(CCS)
38	-	-	288	278	0	3	20 β(CCS)+ 12 τ(CCSC)+ 10 β(CCC)
39	-	273	280	270	0	1	28 τ(CCSC)+18 τ(CCCH)+18 τ(CCCS)+18 τ(CCCC)
40	-	-	124	120	0	2	16 β(CCC)+16 τ(CCCS)+14 β(CCS)+14 τ(CCCC)+12 τ(CCCH)+12 τ(CCCS)
41	-	-	111	107	1	1	29 τ(CCCC)+23 τ(CCCH)+22 τ(CCSC)+10 τ(SCCS)
42	-	-	38	37	0	17	44 τ(CCCS)+22 τ(SCCS)+21 τ(CCCC)

ν, stretching; β, bending; τ, torsion

[a] Unscaled computed values.

[b] In scaled values, the scaling factors 0.967 and 0.955 were used for wave numbers under 1800 cm^{-1} and above 1800 cm^{-1}, respectively.

[c] Relative intensities of IR normalized with highest peak absorption of 100.

[d] Relative intensities of Raman normalized with highest peak absorption of 100.[e] Only contributions ≥10% are tabulated.

By considering Table 3, the ν (CH) anti-symmetric stretching modes of BT molecule take place at 3104 cm^{-1} (IR/R), 3075 cm^{-1} (R) and 3069 cm^{-1} (IR) while their calculated at the mentioned level wavenumbers were found as 3098, 3066 and 3053 cm^{-1}, respectively [37-42].

The experimental infrared frequencies of thiophene for CCH bending mode were observed 1083 cm^{-1} and 1036 cm^{-1} [20]. In our study, the exp./cal. values for the β (CCH) in-plane bending modes in the rings of title molecule were found in the region (1500-1045) cm^{-1} (IR) and (1554-1046) cm^{-1} (R) / (830-716) cm^{-1}, respectively [37-42]. The experimental IR frequency values for BT molecule were registered in the region (1557- 1446) cm^{-1} [23].

Likewise, the experimental bands at 852, 825 and 813 cm^{-1} (IR) and 856 cm^{-1} and 709 cm^{-1} (R) can be assigned to the C-S stretching mode of the mentioned compound [43, 44]. These mentioned bands were computed at the B3LYP/6–311++G(d,p) level as 830, 800, 799 and 716 cm^{-1}, respectively. However, the mentioned C-S band for thiophene molecule were observed 872 cm^{-1} [20]. Therefore, it can be easily said that the observed values of the ring infrared band for both thiophene and BT molecules exhibit a great similarity.

3.3. HOMO-LUMO analysis

It can be easily stated that the frontier molecule orbitals (FMOs) contain the HOMO and LUMO orbitals, which are deciphered as the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. The HOMO orbital is known as an electron donor while the LUMO is known as an electron acceptor. Therefore, the energy gap between HOMO and LUMO energies is a crucial and critical parameter for the fix of the molecular electrical features [45]. At the same time, for the molecules this energy gap provides the determination of chemical reactivity, polarizability, chemical hardness and softness, and electronegativity and so on [46]. For instance, if HOMO-LUMO gap is small for any molecule, the molecule becomes soft and reactive in chemical reactions.

In our study, Table 4 summarizes some calculated at mentioned level molecular properties for BT molecule. Furthermore, the 3D plots of HOMO and LUMO orbitals, their shapes and energy gaps of BT are given in Fig. 4.

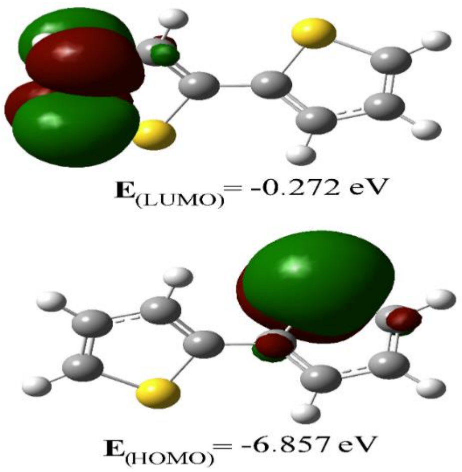

Figure 4 3D plots of HOMO and LUMO of the 2,2’-bithiophene molecule

By considering Table 4, the gap between HOMO and LUMO energy values becomes 6.585 eV. Furthermore, the calculated values at the mentioned level the total dipole moment μ, the chemical hardness η,the absolute electronegativity and the electrophilicity index (or, reactivity index) ω for BT compound were presented in Table 4 [47]. As we mentioned in the Introduction, if the energy gap between HOMO and LUMO orbitals is small because of the existence of the long-range delocalization of the π-systems on neighboring rings (on the intramolecular C1-C2 bond of the title molecule), it can be a tool for tuning conducting polyphenes [19].

3.4. MEP

The electrostatic potential (MEP) can be defined in terms of its relation to the interaction between total charge distribution of the compound and a unit positive test charge. Furthermore, since it is an important device in order to understand for the molecular interactions of a chemical compound and satisfies the correlations among the molecular features such as partial charges, dipole moments, electronegativity and chemical reactivity for molecule [48, 49].

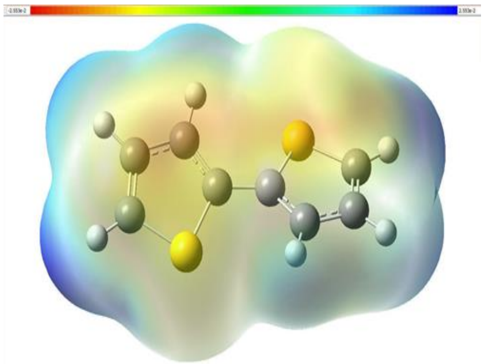

Figure 5 The MEP surface of the 2,2'-bithiophene molecule

Figure 5 exhibits the 3D plot of the MEP of BT compound and computed using the optimized molecular structure of the mentioned compound at the B3LYP/6-311++G(d,p) level. Furthermore, Fig. 5 demonstrates the electrostatic potentials at the surfaces represented by blue, red and green colors. In this content, the regions of negative and positive electrostatic potential are represented with the red and blue colored parts, respectively and the regions with zero potential are indicated by green color. Meanwhile, it can be remained that the electrophilic reactivity is related to the negative regions of molecular electrostatic potential while the nucleophilic reactivity is related to the positive ones. Therefore, in our study Fig. 5 indicates that the negative regions (with red color) are localized on the S4 and C5 atoms in the thiophene rings but the blue sites (positive regions) are localized on hydrogen atoms in rings of BT compound. On the other hand, the zero potential (green colored) are partly localized in out of rings. Therefore, the positive and negative regions are the localizations for the potential hydrogen bonds of title compound. With this study, a complementary information for the molecular structure, molecular electrostatic potentials (MEPs), and HOMO-LUMO analysis of BT molecule was verified and presented to other researchers of the mentioned compound.

Table 4 The calculated at the B3LYP/6-311++G(d,p) level some molecular properties (in eV) for 2,2'-bithiophene molecule

ET	E_{HOMO}	E_{LUMO}
-30067.453	-6.857	-0.272
μ (Debye)	η	χ
0.288	3.293	3.565

For the calculation the equations were taken from Ref.[47].

4. CONCLUSION

This work reports a new study about the BT compound, which is a starting agent for polythiophenes and presents an additional investigation in terms of the observed and calculated vibrational spectra. Theoretical examination was carried out at the B3LYP/6-311++G(d,p) level. In our work, the vibrational analysis results present that the relationship between spectroscopic properties such as IR and Raman and theoretical calculations is very useful since it gives basic knowledge of aromatic compounds that can be used for the oligothiophene light-emitting diodes (OLEDs).

Meanwhile, in order to fix the most stable state for BT molecule in solid-state, an examination was verified and the results obtained are confirmed the previous conformational studies, which were performed at the different levels of theory.

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Authors' Contribution

Ebru Karakaş Sarıkaya: Conceptualization, Formal analysis, Writing - original draft.
Ömer Dereli: Methodology, Funding acquisition, Resources.
Semiha Bahçeli: Corresponding Author, Writing - review & editing.
Feride Pınar Özturan: Investigation.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest was declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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