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Investigation of Conformation, Vibration and Electronic Properties of 2-Methoxythiophene Molecule by Theoretical Methods

Guventurk UGURLU
Kafkas University

Abstract: In this study, the structural parameters, vibrational frequency, the electronic energy, the dipole moment, the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy, the polarizability, hyperpolarizability and the potential energy curves (PEC) of 2-methoxythiophene molecule were calculated at Hartree-Fock (HF) and Density Functional Theory (DFT) with B3LYP (Becke 3 Parameter Lee-Yang-Parr) model using the 6-311++(d,p) basis set in gas phase. The potential energy curves of the molecule were performed as a function the θ[C3-C2-O-C6] torsion angle varying from 0-360º at 10º intervals. The dipole moment value of the molecule was calculated as 1.99 Debye by the DFT/B3LYP/6-311++G(d,p) method and as 2.24 Debye by the HF/6-311++G(d,p) method, respectively. The obtained vibrational wave numbers were scaled with appropriate scale factors and the assigning of these vibrational wavenumbers was made according to the potential energy distribution (PED) using the VEDA 4f program. Also, by using HOMO-LUMO energies, energy gap values, ionization energy, electron affinity, chemical potential, electronegativity, hardness and softness indices were obtained. The approximate geometry of the molecules in three dimensions was drawn in the GaussView 5.0 molecular imaging program, and all theoretical calculations were used with the Gaussian 09W package.

Keywords: 2- methoxythiophene, Vibration analysis, Potential energy curve (PEC), Hartree-Fock, Dipole moment

Introduction

Thiophene and its substituted thiophene units are one of the important compounds in both organic synthesis and materials, and are versatile compounds used in various fields such as organic synthesis and materials science. The studies on thiophene having unique electronic and optical properties due to its small band gap and high polarizability continue to increase rapidly. The monomer of the thiophenes has been used as building blocks in the fields of dyes, pharmaceuticals, agrochemicals. Poly- and oligo thiophenes, which are thiophene forms, are used in material chemistry. They have received much attention for their conductivity (Li et al. 2009; Nejati et al. 2011; Schon et al. 2001) and optical nature affected by external stimuli (Shiraki et al. 2010; Yao et al. 2013) and application in field-effect transistors (Bao et al. 1999; Kline et al. 2006), electroluminescent devices (Mehes et al. 2016; Shao et al. 2014), and solar cells (Yan et al. 2019; Briseno et al. 2010). Also, they have become very important materials in practical applications like field effect transistors (Yang et al. 2016), photovoltaic (Kim et al. 2016), chemical sensors (Kim et al. 2016), thermal emission detectors, electrochromic materials (Lv et al. 2016). In the study on the 2-Methoxythiophene molecule, crystal structure of the molecule was determined experimentally using X-ray structure analysis and spectroscopic methods (Blake et al., 1999). The same studies, intramolecular and intermolecular geometry of the molecule with thiophenes with oxygen-containing substituents were examined.

The physical and chemical properties of a substance are strongly related to both its geometrical and electronic structures. In this work, molecular structure, dipole moment, relative energies, rotational barriers, polarizability,

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first static hyper polarizability, potential energy curve, the electronic structure and HOMO-LUMO energies of above-mentioned molecule have been studied. Also, by using HOMO-LUMO energies, energy gap values, ionization energy, electron affinity, chemical potential, electronegativity, hardness and softness indices were obtained. The molecular structure using numbering scheme of 2-Methoxythiophene is given in Figure 1.

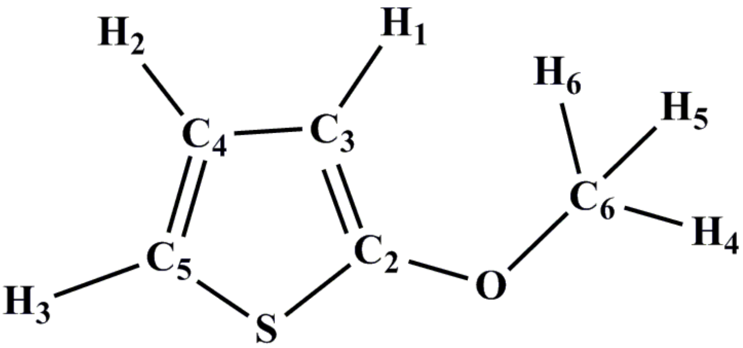


Figure 1. Molecular structure of 2-Methoxythiophene molecule numbering scheme

Method

Quantum-mechanical calculations on the title molecule was performed by the aid of Gaussian 09W program package and Gauss view 5.0 molecular visualization programs (Frisch et al., 2010; Dennington et al., 2009) in the gas phase. The structural parameters, vibrational frequency, the electronic energy, the dipole moment (μ), the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy, the polarizability (α), hyperpolarizability (β) and the potential energy curves (PEC) of 2-methoxythiophene molecule were calculated at Hartree-Fock (HF) and Density Functional Theory (DFT) with B3LYP (Becke 3 Parameter Lee-Yang-Parr) (Becke et al., 1988; Lee et al., 1988; Becke, 1993) model using the 6-311++(d,p) basis set in gas phase. In order to obtain the best stable structures, Conformational analysis of the molecule was performed as a function of dihedral angle which was varied between 0 and 360º with increments of 10º both HF/6-311++G (d,p) and B3LYP/6-31++G(d,p)level of theory

Results and Discussion

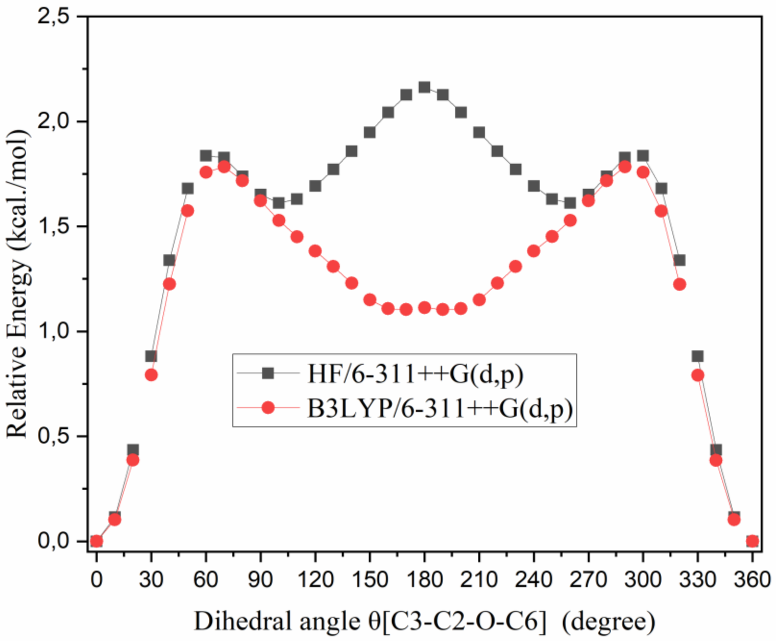


Figure 2. The potential energy curves of 2-Methoxythiophene molecule

Conformational Analysis and Torsional Barriers

The dihedral angle was defined as: θ[C3-C2-O-C6]. The dihedral angle θ is the C2-O single bond about which internal rotation forms clearly different conformations. The potential energy curves of the title molecule performed at both HF/6-311++G (d,p) and B3LYP/6-311G++ (d, p) level is shown Figure 2. The minimum of potential energy curves (PEC) was referred to as zero. Rotational barriers at 0º [ΔE_0 =E (θ =0º)-E (equilibrium)], at 90º [ΔE_{90} =E (ø=90º)-E (equilibrium)] and at 180º [ΔE180 =E (ø=180º)-E (equilibrium)] were calculated by using the energies of the respective optimized structures. The low-energy conformers were obtained at = 0 and 360º conformer. Maxima energy conformer were seen at 180º dihedral angle at HF/6-311++G (d,p) level of theory, but B3LYP/6-311G++ (d, p) level of theory, at 60 and 300º were seen.

Molecular Structure

The equilibrium state structures of 2-Methoxythiophene molecule obtained by the HF/6-311++ G (d,p) and DFT/6-311++G (d,p) methods are compiled The calculated values of the electronic, dipole moment, polarizability, hyperpolarizability, HOMO, LUMO energy and energy gap (ΔEg) at the ground-state equilibrium geometry of studied molecules are listed in Table 1.

Table 1. The electronic, HOMO, LUMO energy, dipole moment, polarizability, hyperpolarizability, and energy gap (ΔEg) of 2-Methoxythiophene molecule

		B3LYP/6-311++G(d. p)				
Electronic Energy (a.u)	μ(D)	α(a.u)	β(a.u)	E_{HOMO}(a.u)	E_{LUMO}(a.u)	$\Delta Eg\,(eV)$
-667.623428555	1.99	79,19	234,66	-0.217313	-0.011980	5,587
		HF/6-311++G(d. p)				
-665.258401234	2.24	72,51	176,01	-0.309299	0.037053	9,425

The X-ray crystal structures for studied molecule is available in the literature and (Blake et al., 1999) and the calculated parameter studied molecule of both at the B3LYP/6-311++G (d, p) and the HF/6-311++ G (d,p) methods in the ground state are tabulated in the Table 2 and findings here.As seen from Table 2, it is found that, in the title molecule, dihedral angle between the thiophene and methoxy group is planar and belong to Cs symmetry group.

Table 2. Selected structural parameters of 2-Methoxythiophene molecule

	Bond length (Å)		
Atoms	Exp[a].	DFT	HF
S-C5	1.715(2)	1.7455	1.7376
S-C2	1.7232(17)	1.7491	1.7349
C2-O	1.350(2)	1.3488	1.3302
C2-C3	1.298(2)	1.3686	1.3478
C3-C4	1.440(3)	1.4342	1.4418
C4-C5	1.353(3)	1.3603	1.3400
O-C6	1.433(2)	1.4262	1.4046
	Bond angle (˚)		
C5-S-C2	91.35(9)	90.7238	90.8151
O-C2-C3	130.79(16)	131.3881	131.1727
O-C2-S	116.20(12)	116.4168	116.3542
C3-C2-S	113.01(13)	112.1951	112.4725
C2-C3-C4	109.11(16)	111.826	111.5949
C5-C4-C3	114.43(17)	113.6329	113.5237
C4-C5-S	112.10(15)	111.6222	111.5938
C2-O-C6	114.42(15)	116.1677	117.5966
	Dihedral angle (˚)		
C3-C2-O-C6	--	0,01	0.00
C1-C2-O-C6	--	-179.99	-179.99

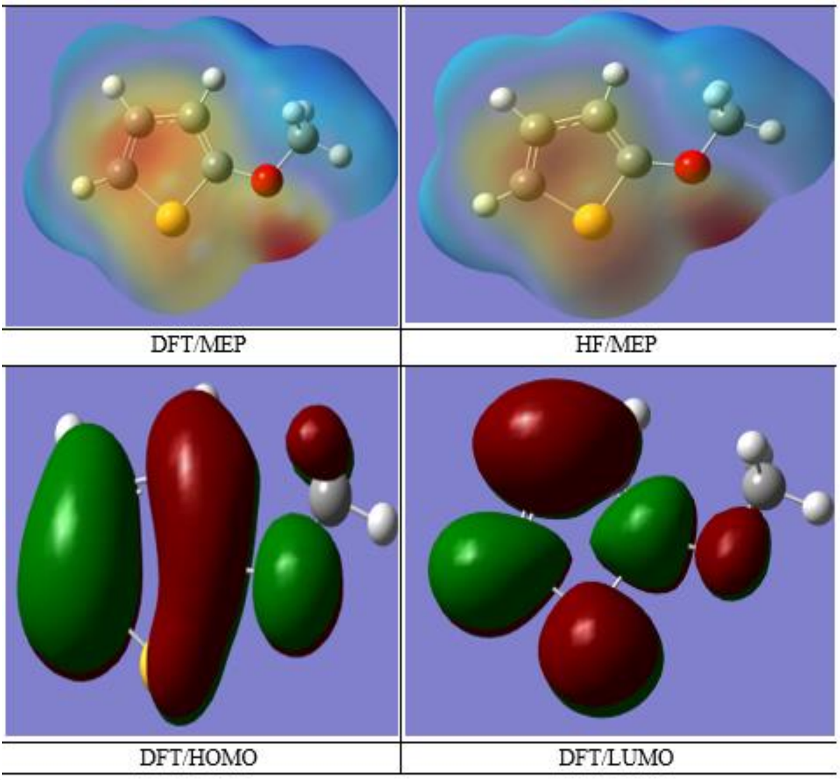
([a] ref. Blake et al., 1999)

The electron affinity (A), global hardness (η)/softness (S), electronegativity (χ), chemical potential (μ), ionization potential (I), chemical potential (Pi) calculated by using HOMO-LUMO energies calculated the B3LYP/6-311++G (d, p) for the compound were given in Table 3.

Table 3. Electronic properties of 2-Methoxythiophene molecule

	property	a.u	eV	kcal/mol	kJ/mol
	LUMO	-0,01198	-0,32598	-7,51749	-31,4535
	HOMO	-0,217313	-5,91324	-136,365	-570,555
A	Electron affinity	0,01198	0,32598	7,51749	31,4535
I	Ionization potential	0,217313	5,91324	136,365	570,555
ΔE	Energy gap	0,205333	5,58725	128,847	539,102
χ	Electronegativity	0,1146465	3,11961	71,941	301,004
Pi	Chemical potential	-0,1146465	-3,11961	-71,941	-301,004
ω	Electrophilic index	0,000674715	0,01836	0,42339	1,77146
IP	Nucleophilic index	-0,01177035	-0,32028	-7,38593	-30,9031
S	Molecular softness	9,7403	265,04	6112,05	25573,1
η	Molecular hardness	0,1026665	2,79363	64,4235	269,551

Molecular electrostatic potential (MEP) surface values of the optimized geometry of 2-Methoxythiophene molecule by the HF/6-311++ G (d,p) and DFT/6-311++G (d,p) methods and the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) obtained B3LYP/6-311++G (d. p) level of theory are presented Figure 3.


DFT/MEP

HF/MEP

DFT/HOMO

DFT/LUMO

Figure 3. (a)The optimized geometry, (b) Molecular electrostatic (MEP) potential surface (PES) and HOMO-LUMO surface of 2-Methoxythiophene molecule

Vibrational Frequencies

2-Methoxythiophene molecule consist of 13 atoms having 33 normal modes of vibrations. The calculated vibrational wavenumbers, FT-IR and FT-Raman intensity of the title compounds are given in Table 4. Also, the calculated vibrational assignments of the normal modes were performed on the basis of the Potential Energy Distribution (PED) and it has been calculated using the Vibrational Energy Distribution Analysis VEDA 4 program (Jamroz, 2004). The molecular structure of the molecule belongs to Cs point group symmetry and It is seen, that the group Cs has two species, A’ and A’’.

Table 4. Electronic properties of 2-Methoxythiophene molecule

Theoretical wavenumbers (cm^{-1})									
	DFT/6-		Intensity		HF/6-		Intensity		
C	Uns	Sc.	IR	Ram.	Uns	Sc.	IR	Ram.	Assignments with PED (≥10 %)
A'	325	311	0,9	139,2	340	308	2,1	123,9	C3H (26)C5H (69)
A'	322	308	3,5	97,7	337	306	5,3	81,8	C3H (70)C4H (21)
A'	319	306	7,8	104,6	335	303	10,2	86,8	C4H (75)C5H (21)
A'	314	301	15,5	103,3	329	298	29,1	99,0	C6H11(46)C6H12(46)
A	307	294	34,2	58,4	323	293	41,9	40,2	C6H11(50)C6H12(50)
A'	301	288	52,2	157,0	317	287	48,8	123,4	C6H13(91)
A'	158	155	110,4	9,7	173	157	118,1	4,3	C2C3(60)OC2(13)HC4C5(17)
A'	151	148	114,8	86,4	166	150	171,1	104,3	C5C4(46)HC6H(12)
A'	150	147	10,1	4,0	162	147	12,7	4,5	OC2(10)HC6H(68)HC6OC2(22
A	148	146	10,4	11,8	161	146	9,0	10,8	HC6H(74)HC6OC2(12)HC6OC2
A'	146	143	60,0	27,4	159	144	79,5	24,3	C5C4(14)HC6H(70)
A'	138	136	4,7	6,2	149	135	4,1	7,2	C4C3(19)C2C3C4(14)HC5S(35)
A'	126	124	7,0	1,5	138	125	12,1	1,3	HC4C5(55)HC5S(12)
A'	122	120	234,2	2,1	135	123	283,7	3,0	C5C4(10)OC2(35) OC6(11)
A'	120	118	1,4	5,2	131	118	9,5	5,2	HC6H(20)HC6OC2(31)HC6OC2
A	116	114	0,7	3,0	128	116	2,5	2,7	HC6H(27)HC6OC2(25)HC6OC2
A'	110	109	15,5	14,2	120	108	13,1	18,3	HC3C4(26)HC5S(47)
A'	106	104	16,6	2,0	113	102	45,2	6,4	C4C3(48)HC3C4(30)
A'	102	100	28,3	3,3	111	101	1,4	2,4	OC6(72)C2C3C4(12)
A	889	874	0,0	1,0	102	931	0,0	2,6	HC3C2C1(47)HC4C5S(28)HC5SC
A'	844	830	18,2	7,2	904	820	21,0	5,5	C1S(29)C2C3C4(21)C5C4C3(30)
A	780	767	20,4	0,8	899	815	24,2	2,0	HC3C2C1(12)HC4C5S(60)C2C3C
A'	745	732	6,4	7,7	811	735	8,3	7,3	C5C4C3(11)SC5C4(33)
A'	724	712	6,5	12,4	778	705	10,0	12,2	C1S(49)C5C4C3(34)
A	674	662	81,4	0,0	770	698	99,7	0,0	HC3C2C1(37)HC5SC2(53)
A	558	548	3,8	1,1	620	562	0,9	1,8	HC5SC2(29)C2C3C4C5(47)OC3S
A'	551	542	7,8	3,0	595	539	7,5	2,8	C1S(18)SC5C4(43)
A	505	496	2,4	0,5	558	506	2,4	0,9	SC5C4C3(49)OC3SC2(31)
A'	401	394	2,5	7,9	433	392	2,2	5,0	C2C3C4(28)OC2S(25)C6OC2(31)
A	278	273	0,3	0,3	304	275	0,2	0,3	C2C3C4C5(21)SC5C4C3(29)OC3S
A'	234	230	3,0	1,0	253	229	3,2	1,0	OC2S(50)C6OC2(42)
A	202	198	0,1	1,3	223	202	0,2	0,8	HC6OC2 (56)OC3SC2(16)
A	82	81	4,7	0,5	93	84	5,5	0,6	C6OC2C3(78)

Conclusion

In this study, the structural parameters, vibrational frequency, the electronic energy, the dipole moment (μ), the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy, the polarizability (α), hyperpolarizability (β) and the potential energy curves (PEC) of 2-methoxythiophene molecule were calculated at Hartree-Fock (HF) and Density Functional Theory (DFT) with B3LYP model using the 6-311++(d,p) basis set in gas phase. The calculated geometric parameters (bond lengths and bond-dihedral angles) of the molecule were compared with the experimental values in the literature (Blake et al., 1999) and they were found to be in good agreement. The vibrational frequencies and spectrums were obtained with the same methods and levels. All vibrational frequencies were found as positive. It is shown that titled compound was stable conclusions here.

The energy band gap, electron affinity (A), global hardness (η)/softness (S), electronegativity (χ), chemical potential (μ), ionization potential (I), chemical potential (Pi) properties of title molecule are calculated by using the highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) energy.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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Author Information

Guventurk UGURLU
Kafkas University
Kars 36100 Turkey
Contact e-mail: *gugurlu@kafkas.edu.tr*

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