

Theoretical Investigation of Nmr, Conformational, Vibrational and Electronic Structure of 3-Bromo-4-(2-Pyridyl) Thiophene

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Abstract: Compounds containing thiophene and pyridine rings very much attention due to their biological activity. The molecular geometry, vibration frequencies, dipole moment (μ), polarizability (α), hyperpolarizability (β) of 3-Bromo-4-(2-pyridyl) thiophene have been calculated at ab initio Hartree Fock (HF) and Density Functional Theory (DFT / B3LYP) with 6-311++G (d, p) basis set. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) of title molecule has been computed and their respective gap (ΔE_g) have been examined. The gauge independent atomic orbital (GIAO) ^1H - and ^{13}C -NMR chemical shifts values of studied molecule in the ground state in both gas phase and in solution of chloroform and dimethyl sulfoxide have been investigated using the HF and DFT/B3LYP employing different basis sets. In addition, the potential energy curve of the molecule as a function of the dihedral angle (N-C3-C6-C7) have been carried out using the 6-31G basis set in both methods. The results of vibrational parameters were analyzed by VEDA 4 software. The ^1H chemical shifts values of the molecule, which were calculated by both methods, were compared with the data in the literature and there was a good agreement between the structural parameters.

Keywords: 3-Bromo-4-(2-pyridyl) thiophene, HF, DFT, Vibration frequencies, Polarizability (α)

Introduction

Many compounds containing pyridine and thiophene continue to attract the interest of researchers due to their biological properties. Thiophenes with broad spectrum of biological activity and many derivatives has important features such as potential analgesics (Başoğlu et al. 2017), anticonvulsant (Kulandasamy et al. 2009), antiinflammatory (Mohareb et al. 2015), antibacterial (Khalil et al. 2009), antipyretic Amr et al. 2010), antitumor (Abdel-Rahman et al. 2017), antiparasitic (Jose et al. 2007), antimicrobial (Sowmya et al. 2018), antihistaminik (Viswanatha et al. 208). Theoretical study has been played a crucial role in designing and development of novel materials for nonlinear optics. 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, first static hyper polarizability, potential energy scan, the electronic structure and HOMO-LUMO energies of title molecule have been studied. ^1H NMR and ^{13}C NMR chemical shifts calculations have been performed.

Method

Theoretical calculations on the isolated 3-bromo-4-(2-pyridyl) thiophene molecule were 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 geometric parameters of 3-bromo-4-(2-pyridyl) thiophene molecule in the equilibrium state were optimized at HF (Moller et al., 1934) and DFT with Becke's three parameter hybrid functional (B3) (Becke et al., 1988) and combined with gradient corrected correlation functional of Lee–Yang–Parr (LYP) (Lee et al., 1988; Becke, 1993) and employing 6-311++G (d,p) basis set (Francl et al., 1982; Rassolov et al., 2001). After optimization, at all optimized structures of the title compounds obtained B3LYP/6-311++G (d,p) and HF/6-311++G (d,p) level of theory, dipole moment (μ), polarizability (α), hyperpolarizability (β) based on finite field approach and energy differences of ELUMO –EHOMO were

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calculated in the same as level of theory. The ^1H and ^{13}C NMR chemical shifts were calculated by GIAO approach by using B3LYP/6-311+G (2d, p) and HF/6-31G (d) level of theory (McLean et al., 1980; Krishnan et al., 1980).

Results and Discussion

Molecular Structure

The calculated values of the electronic, dipole moment, polarizability, hyperpolarizability, HOMO, LUMO energy and energy gap (ΔE_g) 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 (ΔE_g) of 3-Bromo-4-(2-pyridyl) thiophene

B3LYP/6-311++G (d, p)						
Electronic energy (a.u)	μ (Debye)	α (a.u)	β (a.u)	E_{HOMO} (a.u)	E_{LUMO} (a.u)	ΔE_g
-3373.76496133	1.47	149.86	415.83	-0.243436	-0.055208	5.12
HF /6-311++G(d, p)						
-3368.72657919	1.87	138.14	129.68	-0.323695	0.036273	9.80

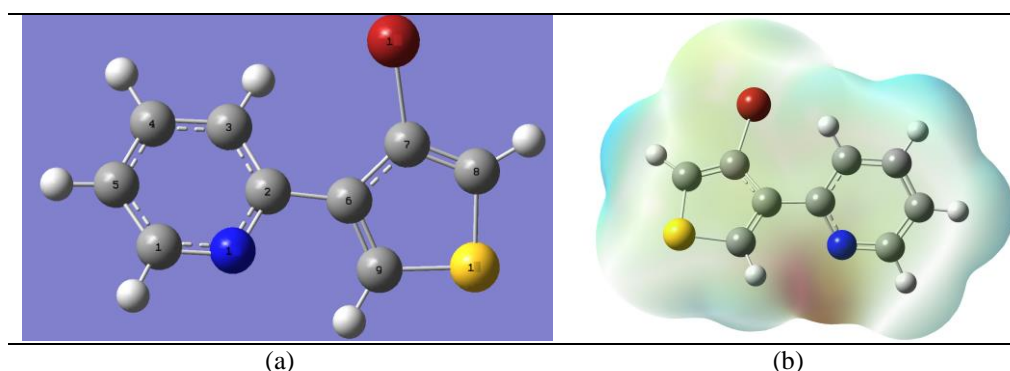


Figure 1. (a)The optimized geometry, (b) Molecular electrostatic (MEP) potential surface (PES) of 3-Bromo-4-(2-pyridyl) thiophene molecule

Table 2. Selected structural parameters of 3-Bromo-4-(2-pyridyl) thiophene

Atoms	DFT	HF	Atoms	DFT	HF
	Bond length/ \AA			Bond angle/($^\circ$)	
C1-N	1.333	1.319	N-C2-C3	121.79	122.12
C1-C5	1.3933	1.383	N-C2-C6	115.58	115.91
N-C2	1.345	1.3234	C3-C2-C6	122.57	121.89
C2-C3	1.4015	1.3908	C2-C6-C7	128.97	128.07
C2-C6	1.4822	1.4884	C2-C6-C9	120.93	121.60
C3-C4	1.3902	1.3811	C7-C6-C9	110.10	110.32
C6-C7	1.4406	1.4462	C6-C7-Br	125.58	125.18
C6-C9	1.3727	1.349	C8-S-C9	91.53	91.34
C7-C8	1.3627	1.342	Dihedral angle /($^\circ$)		
C7-Br	1.9105	1.8925	N-C2-C6-C7	-146.88	-138.42
C8-S	1.7298	1.7194	N-C2-C6-C9	33.23	41.83
C9-S	1.7223	1.7161	C3-C2-C6-C7	36.07	44.64
-	-	-	C3-C2-C6-C9	-143.82	-135.11
-	-	-	C2-C6-C7-Br	4.57	4.27
-	-	-	C9-C6-C7-Br	-175.53	-175.95

The optimized geometry and Molecular electrostatic potential (MEP) surface values of 3-Bromo-4-(2-pyridyl) thiophene molecule obtained B3LYP/6-311++G (d, p) level are presented Figure 1 (a) and (b). The calculated parameter studied molecule of both at the B3LYP/6-311++G (d, p) and HF/6-311++G (d, p) methods in the

ground state are tabulated in the Table 2. The pictures of HOMO and LUMO obtained at the B3LYP/6-311++G (d, p) of 3-Bromo-4-(2-pyridyl) thiophene at the B3LYP/6-311++G (d, p) is given in Figure 2.

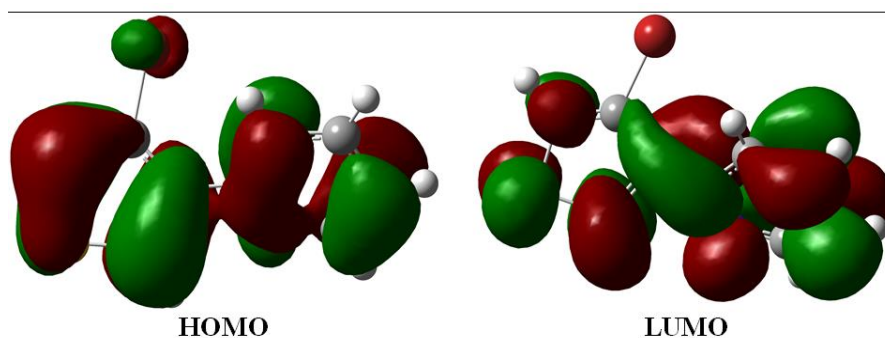


Figure 2. The pictures of HOMO and LUMO of 3-Bromo-4-(2-pyridyl) thiophene

Vibrational Frequencies

The 18 atoms and the number of the normal vibrations is 48. The calculated the IR and Raman spectrums are given in Figure 3.

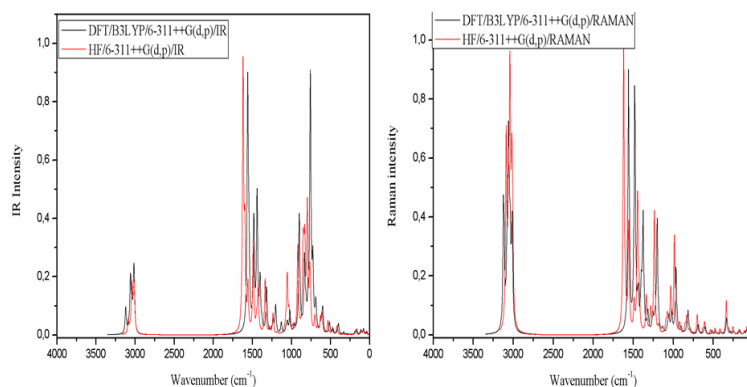


Figure 3. IR and Raman spectrums of 3-Bromo-4-(2-pyridyl) thiophene molecule

NMR Spectral Analysis

Table 3. NMR chemical shifts for 3-Bromo-4-(2-pyridyl) thiophene molecule

Atoms	B3LYP/6-311+G(2d,p)			Exp ^a	B3LYP/6-311++G (d,p)		
	Gas	DMSO	CHCl ₃		Gas	DMSO	CHCl ₃
C2	160.50	161.07	161.10	-	161.38	161.37	161.39
C1	155.52	157.16	156.85	-	156.92	157.98	157.66
C6	148.00	149.06	148.93	-	149.02	149.47	149.34
C4	139.71	143.07	142.17	-	141.04	143.82	142.90
C9	138.83	140.23	140.01	-	141.34	142.11	141.91
C8	133.15	136.77	135.80	-	135.08	138.19	137.19
C7	132.10	132.14	132.27	-	132.98	132.39	132.52
C3	126.46	128.25	127.84	-	128.12	129.33	128.91
C5	125.30	128.25	127.48	-	126.86	129.23	128.45
C1H	8.95	9.00	8.99	8.68	8.90	8.94	8.93
C9H	8.22	8.32	8.29	7.71	8.19	8.28	8.25
C3H	8.20	8.31	8.28	7.77	8.12	8.24	8.19
C4H	7.85	8.15	8.06	7.48	7.82	8.11	8.02
C8H	7.34	7.63	7.52	7.39	7.19	7.49	7.40
C5H	7.30	7.61	7.52	7.27	7.26	7.56	7.46

The calculated values of ^1H - and ^{13}C -NMR chemical shifts values of 3-Bromo-4-(2-pyridyl) thiophene molecule in the ground state in both gas phase and in solution of chloroform and dimethyl sulfoxide were given in Table 3.

Conclusion

In this paper, the ground state geometrical energy dipole moment, polarizability, hyperpolarizability, E_{HOMO} , E_{LUMO} , ΔE_g , ^1H and ^{13}C NMR chemical shifts of 3-Bromo-4-(2-pyridyl) thiophene molecule are examined both HF/6-311++G (d,p) and B3LYP/6-311++G(d,p) level of the theory. Comparison of the calculated and the experimental ^1H and ^{13}C NMR values indicates that results of HF/ 6-31G (d) and B3LYP/6-311++G (d,p) level of the theory are in a good agreement with experimental data for 3-Bromo-4-(2-pyridyl) thiophene molecule.

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