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AB INITIO HF AND DFT STUDIES ON MOLECULAR STRUCTURE AND VIBRATIONAL ANALYSIS OF 2,5-DIBROMOPYRIDINE

2,5-DIBROMOPIRIDIN'IN MOLEKÜLER YAPISI VE TITREŞIM FIREKANSLARI ÜZERINE AB INITIO HF VE DFT ÇALIŞMALARI

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ABSTRACT

Theoretical study on molecular structure and vibrational spectra of 2,5-dibromopyridine (2,5-DBP) have been investigated. The optimized geometry, theoretical vibration frequencies and intensities were calculated by using ab initio Hartree-Fock and density functional B3LYP method with 6-31G(d,p) basis sets. The vibrational analysis of title molecule was done and its optimized geometry parameters (bond lengths and bond angles) were given. Scaled theoretical frequencies have been compared with experimental spectra. Observed and calculated frequencies have been shown good agreement. Furthermore, from the comparison it was concluded that the B3LYP method is superior to the HF method for molecular structure and vibrational frequencies.

Keywords: 2,5-dibromopyridine; Hartree-Fock; DFT; IR spectra, Raman spectra.

ÖZET

Bu çalışmada, 2,5-dibromopiridin'in (2,5-DBP) moleküler yapısı ve titreşim firekansları teorik olarak incelenmiştir. Optimize geometri, teorik titreşim frekansları ve şiddetleri ab initio Hartree-Fock ve yoğunluk fonksiyonu teorisi (B3LYP) kullanılarak 6-31G(d,p) temel seti ile hesaplatılmıştır. 2,5-DBP'in titreşimsel analizi ve optimize geometric parametleri (bağ uzunlukları ve bağ açıları) sunulmuştur. Skala çarpanı ile

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düzeltilmiş teorik frekanslar, deneysel olarak elde edilmiş FT-IR ve Raman spektrumları ile karşılaştırılmıştır. Deneysel ve teorik frekansların iyi uyum göstermiştir. Ayrıca, teorik ve deneysel verilerin karşılaştırılmasında, B3LYP yönteminin HF yöntemine göre daha üstün olduğu sonucuna varılmıştır.

***Anahtar Kelimeler*:** 2,5-dibromopiridin; Hartree-Fock; DFT; IR spektrumu; Raman Spektrumu

1. INTRODUCTION

2,5-DBP is pyridine derivative molecule, having a chemical formula of [$C_5H_3Br_2N$]. Halogen substituted pyridine derivates have been extensively studied molecules due to their presence in many chemical structures of biomedical and industrial fields. As very similar molecules, the experimental and theoretical studies of Brome substituted pyridines have been studied by some authors (Krishnakumar and Xavier, 2005; Chiret et. al., 2009).

Al-Far and Ali (2009) have been reported the geometric structure of 2,5-DBP by using single crystal X-Ray Diffraction (XRD) at 90 °K and found that planar sheets connected with C — H ··· N hydrogen bonding and Br ··· Br interactions.

In this present study, the optimized molecular geometries and vibrational spectra of 2,5-DBP have been calculated by using ab initio Hartree-Fock (HF) and density functional theory (B3LYP) methods with 6-31G(d,p) basis set level. The calculated optimized geometric parameters and vibrational frequencies have been compared with the corresponding experimental data.

2. COMPUTATIONAL METHODS

The vibrational frequencies and optimized structure parameters of 2,5-DBP have been calculated by using ab initio Hartree-Fock (HF) and density function theory (B3LYP) methods at 6-31G(d,p) basis set level. All computations have been performed using Gaussian 03 program package on high performance computing system (Frisch et.al., 2003). To close the calculated frequencies to the experimental ones the scale factors of 0.8929 and 0.9613 are used for HF and B3LYP with 6-31G(d,p) basis set, respectively (Foresman and Frisch, 1996). Additionally, the calculated vibrational frequencies were clarified by means of the potential energy distribution (PED) analysis of all the fundamental vibrations modes by using VEDA 4 program (Jamróz, 2004).

3. RESULTS And DISCUSSION

2,5-DBP is a molecule having 11 atoms, which belongs to the point group C_1. The three Cartesian displacements of the 11 atoms provide 33 internal modes and 27 normal modes.

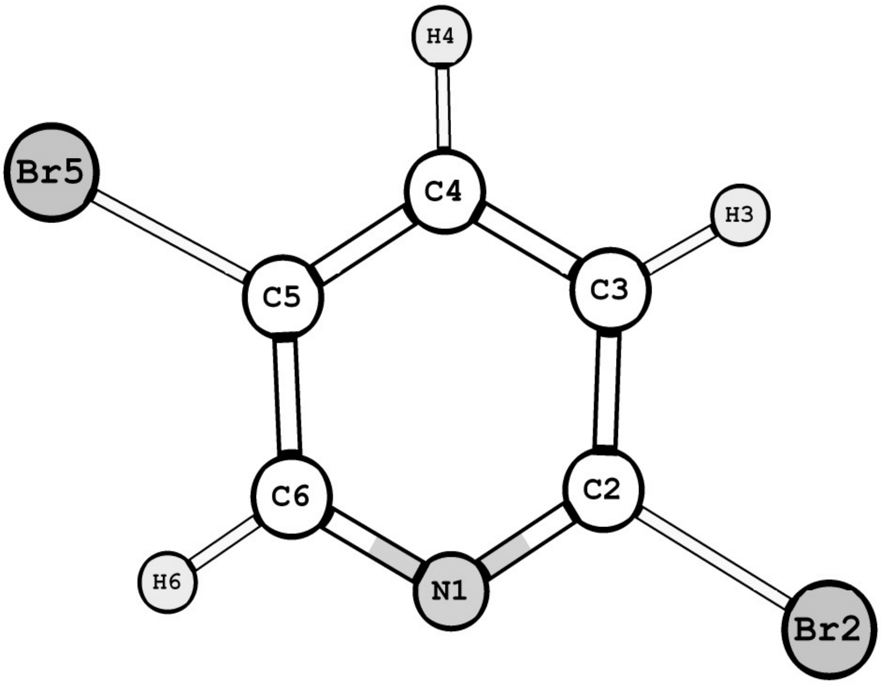


Figure 1. Calculated optimized molecular structure of 2,5-DBP.

The calculated optimized geometry of 2,5-DBP is given in Figure 1. Calculated total energies (corrected with zero point energy) of optimized molecule for HF and B3LYP are -5385.2378 and -5390.4290 Hartree/Particle, respectively. The relative energies between the HF and B3LYP calculations is 3257.6 kcal/mol. Therefore, B3LYP calculation has minimum energy for title molecule.

The resulting scaled vibrational frequencies and proposed vibrational assignments with PED's analysis of optimized molecule are given in Table 1. The tables also show the experimental vibrational frequencies of the compounds. The experimental (IR or Raman) vibrational frequency values have been found from the spectra obtained by the web pages of Acros Organics and Sigma-Aldrich Cooperations (Acros Organics, 2009; Sigma-Aldrich, 2009). The calculated vibrational frequencies in the tables are scaled and their symmetry species are written in the first column of the tables. As seen form from Table 1, the calculated frequencies are in good agreement with the experimental ones. Additionally, correlation graphics of vibrational frequencies are given Figure 2. It has been clearly seen that the B3LYP method gives better correlation values than the HF method for the vibrational frequencies. The calculated C – H stretching modes are in nearly 3050 cm^{-1} for HF and 3100 cm^{-1} for B3LYP, the C – C ring stretching modes are calculated in interval between 1448 – 623 cm^{-1} for HF and 1426 – 605 cm^{-1} for B3LYP. Br – C stretching and bending vibrations are observed in fingerprint region. Br – C stretching mode is observed as strong and sharp peak at 409 cm^{-1} in experimental FT-IR spectra. This mode is calculated at 410 cm^{-1} for HF and 402 cm^{-1} for B3LYP. Vibrational assignments in the Table 1 are shown good agreement with related literature (Krishnakumar and Xavier, 2005; Chiret et. al., 2009). The theoretical infrared intensities and Raman activities can also be seen in the tables.

Table 1. Experimental and calculated vibrational frequencies of the 2,5-DBP.

		Experimental frequencies		Calculated 6-31G(d.p)					
				HF			B3LYP		
No	Assignments (%PED^a)	IR^b	Raman^c	IR	IR int.	R act.	IR	IR int.	R act.
1	$\nu_{CH}(95)$	3102	3108	3045	0.1	99.7	3111	0.3	115.2
2	$\nu_{CH}(99)$	-	3086	3024	5.0	64.1	3094	0.3	57.8
3	$\nu_{CH}(97)$	3025	3053	3023	1.1	66.6	3076	5.5	82.9
4	$\nu_{CH}(53)+\delta_{HCC}(11)$	1549	1548	1584	36.3	38.6	1547	15.5	25.6
5	$\nu_{CH}(42)+\delta_{CCC}(11)$	1511	-	1570	34.1	3.3	1538	19.1	15.7
6	$\delta_{HCH}(63)+\nu_{CC}(11)$	1441	-	1448	163.7	0.5	1426	148.2	0.7
7	$\nu_{NC}(14)+\delta_{HCC}(14)+\delta_{HCN}(10)$	1357	-	1350	45.7	1.5	1340	35.1	2.8
8	$\delta_{HCN}(41)+\nu_{NC}(15)+\delta_{HCC}(22)$	1276	1276	1271	2.7	3.7	1264	0.7	3.2
9	$\nu_{NC}(48)+\nu_{CC}(37)$	-	1232	1129	2.9	4.6	1248	0.1	2.7
10	$\delta_{HCC}(59)+\nu_{CC}(20)$	1118	1135	1089	137.6	0.6	1113	5.6	1.5
11	$\nu_{CC}(19)+\delta_{HCC}(17)+\delta_{CCC}(11)$	1095	1084	1068	0.7	22.3	1073	152.9	0.3
12	$\nu_{CC}(42)+\nu_{NC}(22)+\delta_{CNC}(13)+\nu_{BrC}(10)$	1079	-	1049	33.1	3.9	1061	21.8	36.2
13	$\delta_{CCN}(26)+\delta_{CCC}(13)+\delta_{CNC}(13)$	998	-	999	0.0	0.5	973	71.0	1.2
14	$\tau_{CCCN}(20)+\tau_{HCNC}(10)$	-	-	986	75.1	1.0	956	0.2	0.5

Contiuned Table 1

		Experimental frequencies		Calculated 6-31G(d.p)					
				HF			B3LYP		
No	Assignments (%PED[a])	IR[b]	Raman[c]	IR	IR int.	R act.	IR	IR int.	R act.
15	τ_{HCNC}(67)+τ_{CCCN}(16)	917	-	961	2.3	1.9	916	2.4	2.6
16	τ_{HCNC}(76)	833	-	846	30.1	0.9	818	22.3	1.8
17	τ_{CNCC}(50)+τ_{HCNC}(21)+γ_{BrCCC}(14)	736	745	738	6.7	0.2	721	3.1	0.2
18	δ_{CCC}(48)+ν_{BrC}(21)+ν_{CC}(10)	717	-	721	1.6	21.4	718	1.4	13.9
19	δ_{CNC}(27)+δ_{CCC}(26)+δ_{CNC}(18)+ν_{CC}(10)	625	632	613	4.1	5.2	605	4.2	5.2
20	γ_{BrCCC}(49)+τ_{HCNC}(38)	482	-	495	6.6	0.1	480	4.0	0.2
21	τ_{CCCC}(48)+τ_{CNCC}(25)+τ_{HCNC}(21)	420	-	419	4.8	0.3	411	4.0	0.3
22	ν_{BrC}(82)	409	-	410	16.8	0.0	402	24.8	0.0
23	δ_{NCBr}(45)+δ_{CCBr}(45)	-	322	311	2.1	1.2	308	1.3	1.4
24	τ_{CCCN}(13)+δ_{BrCC}(13)	-	295	277	0.3	1.5	271	0.2	1.3
25	ν_{BrC}(67)+δ_{CNC}(17)	-	220	209	0.1	8.3	206	0.2	7.8
26	δ_{CCBr}(49)+δ_{BrCN}(40)	-	-	161	0.3	0.1	159	0.2	0.1
27	τ_{CCCN}(57)+γ_{BrCCC}(35)	-	-	77	0.2	0.0	72	0.2	0.0
Scaling factor 0.9613							0.8929		

[a] Potential Energy Distribution (PED). less then 10% are not shown.
[b] Taken from (Acros, 2009).
[c] Taken from (Sigma-Aldrich, 2009).
□: stretching; □: bending; □: out of plane bending; □: torsion.

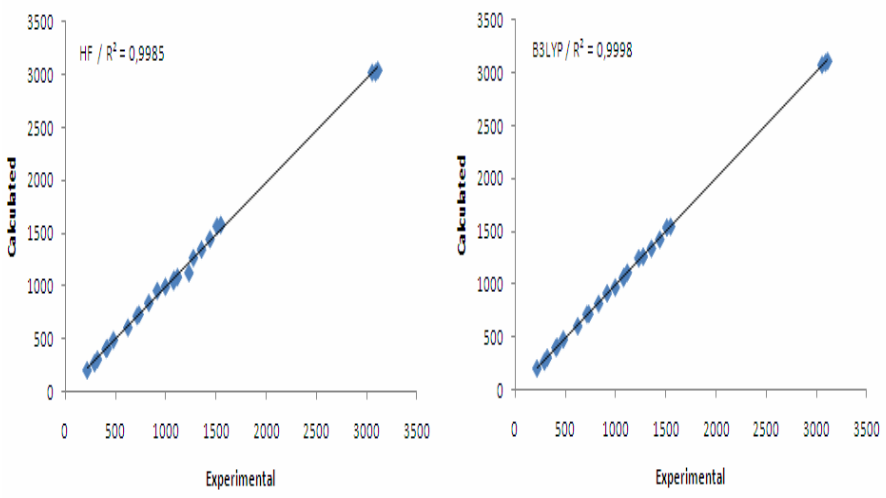


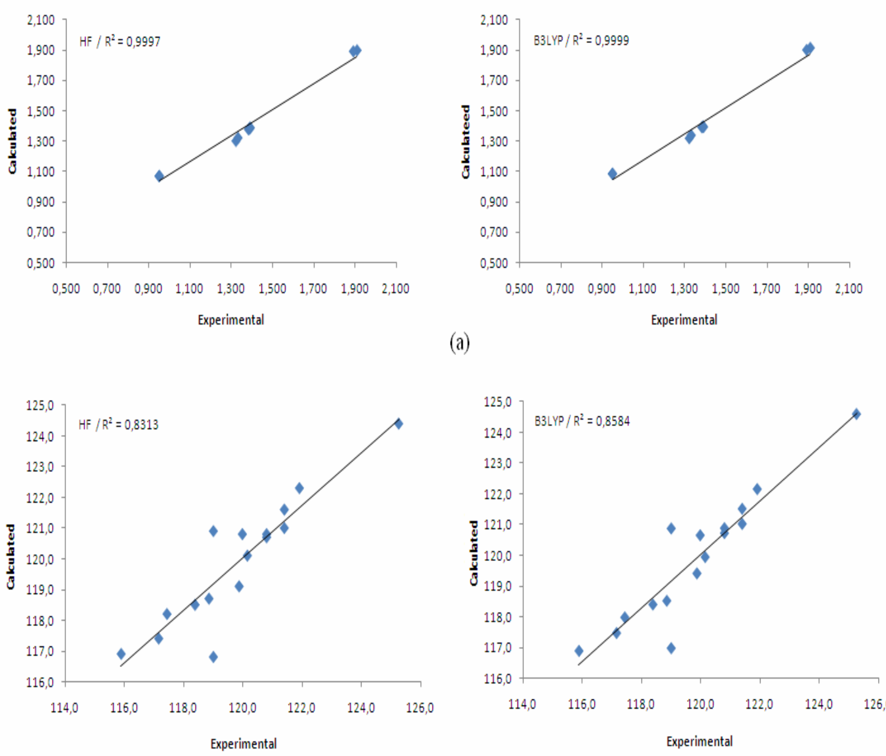
Figure 2. Correlation graphics between experimental and calculated vibrational frequencies for 2,5-DBP.

Table 2. Experimental and calculated geometric parameters of 2,5-DBP.

Bond lenghts	**Exp.**[a]	**HF**	**B3LYP**	**Bond angles**	**Exp.**[a]	**HF**	**B3LYP**
Br2-C2	1.909	1.896	1.917	C2-N1-C6	117.4	118.2	118.0
N1-C2	1.322	1.303	1.319	N1-C2-C3	125.3	124.4	124.6
N1-C6	1.332	1.323	1.339	N1-C2-Br2	115.9	116.9	116.9
Br5-C5	1.891	1.889	1.903	C3-C2-Br2	118.9	118.7	118.5
C2-C3	1.389	1.387	1.398	C4-C3-C2	117.2	117.4	117.5
C3-C4	1.383	1.379	1.391	C4-C3-H3	121.4	121.6	121.5
C3-H3	0.950	1.072	1.083	C2-C3-H3	121.4	121.0	121.0
C4-C5	1.389	1.384	1.395	C3-C4-C5	118.4	118.5	118.4
C4-H4	0.950	1.074	1.084	C3-C4-H4	120.8	120.8	120.9
C5-C6	1.391	1.391	1.393	C5-C4-H4	120.8	120.7	120.7
C6-H6	0.950	1.074	1.086	C4-C5-C6	119.9	119.1	119.4
				C4-C5-Br5	120.0	120.8	120.7
				C6-C5-Br5	120.2	120.1	119.9
				N1-C6-C5	121.9	122.3	122.2
				N1-C6-H6	119.0	116.8	117.0
				C5-C6-H6	119.0	120.9	120.9

[a] Taken from (Al-Far, 2009)

In Table 2, calculated optimized structure parameters (bond lengths and bond angles) are given for the title molecule in accordance with the atom numbers in Figure 1. The table also compares the calculated structure parameters with those obtained experimentally from X-ray data for the geometric structure of 2,5-DBP (Al-Far and Ali, 2009). The correlation graphics between the experimental and calculated geometric parameters are given Figure 3. From the correlation values in Figure 3, we can say that there is also a good agreement between them, and furthermore, the B3LYP method is superior to the HF method as it was in the vibrational frequencies.



(a)

(b)

Figure 3. Correlation graphics between experimental and calculated (a) bond lengths and (b) bond angles for 2,5-DBP.

4. CONCLUSION

The ground state optimized structure and vibrational analysis of 2,5-DBP have been calculated by using ab initio Hartree-Fock (HF) and density functional theory (B3LYP) methods with 6-31G(d,p) basis set level. The vibrational frequencies and optimized geometry parameters (bond lengths and bond angles) of 2,5-DBP were obtained and compared to the corresponding experimental data. It was also seen that the B3LYP method is superior to the HF method for both the vibrational frequencies and geometric parameters. Also, detailed assignments with PED% analysis for vibrational frequencies of title molecule have been presented.

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