

DFT and AB Initio Study of the Keto-Enol Tautomerism of 2, 4 BIS (Ethoxycarbonyl) -3-Hydroxypyrrole

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Introduction

We decided to theoretically study on two tautomers of 2, 4-Bis (ethoxycarbonyl)-3-hydroxypyrrole because the synthesis and reactivity of these compounds have been mainly studied by Japanese Authors. The X-ray structure of the 2, 4-Bis (ethoxycarbonyl)-3 hydroxypyrrole was reported by Nagatoshi Nishiwaki and Kazuo Matsushima [1]. Also for this compound ¹H and ¹³C-NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz and at 100 MHz with TMS as an internal standard. Coupling constants are given in Hz and without sign. The IR spectra were recorded on a Horiba FT-200 IR spectrometer. The experimental data of this molecule are from the literature [1].

Keywords: ab initio, 2, 4-Bis (ethoxycarbonyl)-3-hydroxypyrrole, DFT, tautomer,

Methods

All the calculations have been carried out with the Gaussian view 3.01, Gaussian 03 [2] using the 6-311G and 6-311G** basis sets at the Hartree-Fock theory (RHF), and Becke's three-parameters exchange functional combined with the LYP correlation functional (B3LYP) [3,4]. The structures of the molecules were completely optimized without any symmetry in all the levels. The harmonic vibrational frequencies and the infrared and Raman intensities were calculated analytically on the resulting ground-state optimized molecular geometries. The calculations are carried out in a Pentium 4 double processor computer.

Results and Discussion

Geometrical structure

The atom numbering on two tautomers of 2, 4-Bis (ethoxycarbonyl)-3 hydroxypyrrole with the B3LYP/6-31G** level are shown in the Fig.1 and experimental (determined by X-ray diffraction) and calculated bond distances and bond angles of two tautomers are listed in Table 1. The smallest difference between the experimental and calculated parameters are observed for the O2-C3-C4 bond angle and C4-C9 bond length; the differences are below 0.06° and 0.0001 respectively obtained with the B₃LYP/6-311G** method and basis set. The B₃LYP/6-311G** calculation results in most bond lengths and bond angles very close to the experimental determined by the X-ray diffraction.

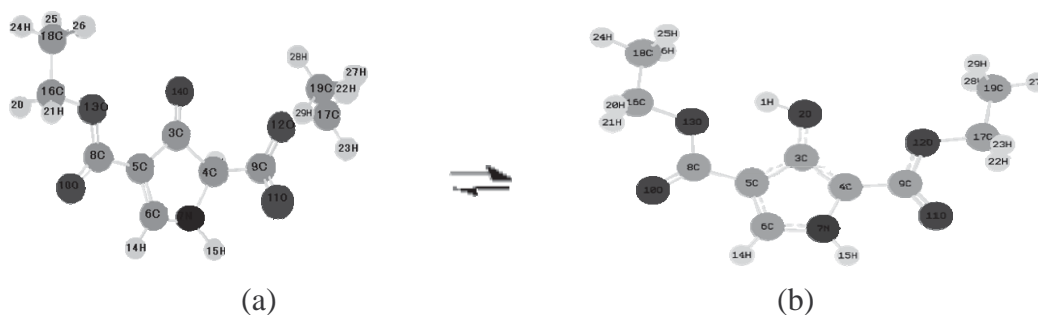


Figure 1. View of the optimized molecular structures on two tautomers of 2, 4-Bis (ethoxycarbonyl)-3-hydroxypyrrole calculated at the B3LYP/6-311G** level.

Table1. Geometry parameters of the two tautomers computed at the HF, B3LYP/ B=6-311G**levels of theory.

Parameter ^a	Tautomer a		Tautomer b		Expt. ^b
	HF/B	B ₃ LYP/B	HF/B	B ₃ LYP/B	
O2-C3	1.1815	1.2044	1.3278	1.3413	1.350
C3-C4	1.5585	1.5867	1.3679	1.3909	1.376
C4-N7	1.4453	1.4529	1.3874	1.3921	1.394
C4-C9	1.5176	1.5195	1.4562	1.4531	1.453
C8-O10	1.1906	1.2139	1.1854	1.2071	1.215
C9-O11	1.1845	1.2080	1.1930	1.2181	1.207
C9-O12	1.3057	1.3328	1.3124	1.3428	1.336
O13-C16	1.4231	1.4463	1.4279	1.4503	1.458
C16-C18	1.5122	1.5149	1.5123	1.5148	1.496
O2-C3-C4	123.52	123.58	126.00	125.76	125.7
O2-C3-C5	131.84	132.13	126.88	126.96	126.4

^a Bond lengths and angles are in Å and degrees. ^b From ref.1.

In agreement with the experiment the calculated tautomer energies showed, that (a) Tautomer is the more stable of (b) tautomer.

Table2. Calculated some characteristics of the two tautomers(b-a)

Parameter	(a) Tautomer		(b) Tautomer		Difference ^a	
	HF/B	B ₃ LYP/B	HF/B	B ₃ LYP/B	HF/B	B ₃ LYP/B
D. Mom ^c	2.813	2.738	1.933	1.410	-0.88	-1.328
Z.P.V ^d	154.31	143.45	154.90	144.05	0.59	0.60
E _{corr}	164.14	153.85	164.65	154.38	0.51	0.53
Z.P _{corr}	154.31	143.45	154.90	144.05	0.59	0.60
H _{corr}	164.73	154.45	164.24	154.97	0.52	0.52
G _{corr}	125.67	114.00	126.97	115.19	1.30	1.20

^a Difference of the two tautomers(3b-3a) (kcal mol⁻¹), ^b Dipole moments(D), ^c Zero-point vibrational energy

Vibrational Spectra

The calculated vibrational spectra of the two tautomers were recorded in the range 500–4000 cm⁻¹ is shown in Fig.2. To minimize the systematic errors of these calculations, scaling factors were applied to the theoretical frequencies.

Computed ¹H-NMR and ¹³C-NMR spectra

Computed B3LYP/ 6-311G** ¹H-NMR and ¹³C-NMR for two tautomers referenced to TMS: ¹H and ¹³C (CH₃)₄Si = 0.00 ppm is compared in Tables 3 and 4.

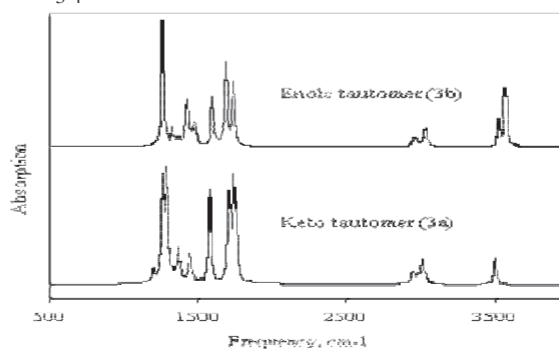


Figure 2. Comparison IR absorption spectra of the two tautomers

Table3. Calculated ^{13}C -NMR chemical shifts (ppm from TMS, $\delta\text{TMS} = 0.00$) for two tautomers

Atomic specific	a Tautomer		b Tautomer		Expt.[7] ^a
	HF/B	B3LYP/B	HF/B	B3LYP/B	
C3	185.74	186.07	154.69	156.43	151.6
C4	61.95	72.92	105.89	113.58	106.7
C5	107.48	114.25	102.75	111.11	104.1
C6	186.71	178.11	139.35	128.62	124.4
C8	162.29	167.76	164.81	167.47	165.9
C9	168.68	170.77	164.11	166.08	161.4
C16	56.22	65.12	56.55	65.09	60.7
C17	57.61	66.53	56.37	65.23	60.8
C18	16.14	15.88	15.92	15.63	14.1
C19	15.67	16.02	16.27	16.00	14.4

^a for b tautomer

Table4. Calculated (B3LYP/ 6-311G**) ^1H , ^{13}C -NMR chemical shifts (ppm from TMS, $\delta\text{TMS} = 0.00$)

Atomic specific	^1H chemical shifts		Expt.[7]
	Tautomer 3a	Tautomer 3b	
H1: (H24,H25,H26)	1.082,1.547, 1.500	1.27 -1.48-1.48	1.36
H2: (H27,H28,H29)	0.871, 1.434, 1.366	1.14 -1.54 -1.54	1.46
H3: (H20,H21)	4.282, 4.141	4.26 - 4.26	4.39
H4: (H22,H23)	3.904, 5.013	4.23- 4.23	4.41
H5: (H14)	8.576	7.19	7.23
H6: (H15)	4.542	7.94	8.4-8.6
H7: (H1)	3.922		
H7: (H1)		7.11	8.9-9.1

^a for 3b tautomer

Conclusions

The geometric parameters, some energy characteristics, vibrational spectroscopic and the ^1H , ^{13}C -NMR data of two tautomers have been calculated at various levels of theory (HF, B3LYP), using basis set from 6-311G to 6-311G**. For structural parameters, the best agreement between experiment and theory was obtained at the B3LYP and HF levels with 6-311G** basis set. In agreement with the experiment the calculated tautomer energies showed, that 3a is the more stable of 3b tautomer.

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