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A theoretical study on 1-(thiophen-2-yl-methyl)-2-(thiophen-2-yl)-1*H*-benzimidazole

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Abstract

The molecular geometry and vibrational frequencies of 1-(thiophen-2-yl-methyl)-2-(thiophen-2-yl)-1*H*-benzimidazole ($C_{16}H_{12}N_2S_2$) in the ground state has been calculated using the Hartree–Fock (HF) and density functional method (B3LYP) with 6-31G(d) basis set. The optimized geometric bond lengths and bond angles obtained by using HF and DFT (B3LYP) show the best agreement with the experimental data. Comparison of the observed fundamental vibrational frequencies of 1-(thiophen-2-yl-methyl)-2-(thiophen-2-yl)-1*H*-benzimidazole ($C_{16}H_{12}N_2S_2$) and calculated results by density functional B3LYP and Hartree–Fock methods indicate that B3LYP is superior to the scaled Hartree–Fock approach for molecular vibrational problems.

Keywords: 1-(Thiophen-2-yl-methyl)-2-(thiophen-2-yl)-1*H*-benzimidazole; IR spectra; DFT; HF; Vibrational assignment; Crystal structure

1. Introduction

The benzimidazole ring is a crucial pharmacophore in drug discovery. Benzimidazoles show different biological activities, such as anticancer, antimicrobial, or antihelmintic activities [1]. Bendimizadole derivatives are an unique and broad-spectrum class of antirhino/enteroviral agents. Benzimidazoles exhibit significant activity against several viruses including HIV, herpes (HSV-1), RNA influenza and human cytomegalovirus (HCVM) [2]. The synthesis of benzimidazoles has received much attention owing to the varied biological activity exhibit by a number of these compounds. The synthesis of heteroaryl-substituted 1*H*-benzimidazoles has become of recent interest to medicinal chemists owing to the pharmacophoric properties of the heteroaromatic rings. A number of synthetic methods have been developed in recent years to uncover a variety of new reagents for the synthesis of 2-substituted benzimidazoles [3–6].

Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [7,8]. Rauhut and Pulay calculated the vibrational spectra of 31 molecules by using B3LYP method with 6-31G(d) basis set [9]. In their work, they calculated vibrational frequencies of 20 smaller molecules whose experimental vibrational frequencies are well assigned, and derived transferable scaling factors by using least-square method. The scaling factors are successfully applied to other 11 larger molecules. Thus, vibrational frequencies calculated by using the B3LYP functional with 6-31G(d) basis could be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra [10].

In previous publication, the crystal structure and vibrational spectra of the title compound ($C_{16}H_{12}N_2S_2$) had been studied [11]. However, as far as we know, there are no theoretical results for the title compound ($C_{16}H_{12}N_2S_2$) in the literature. In this study, we have calculated the vibrational frequencies and geometric parameters of the title compound ($C_{16}H_{12}N_2S_2$) in the ground state to distinguish the fundamentals from the experimental vibrational frequencies and geometric parameters, by using the HF and DFT (B3LYP) method. These calculations are

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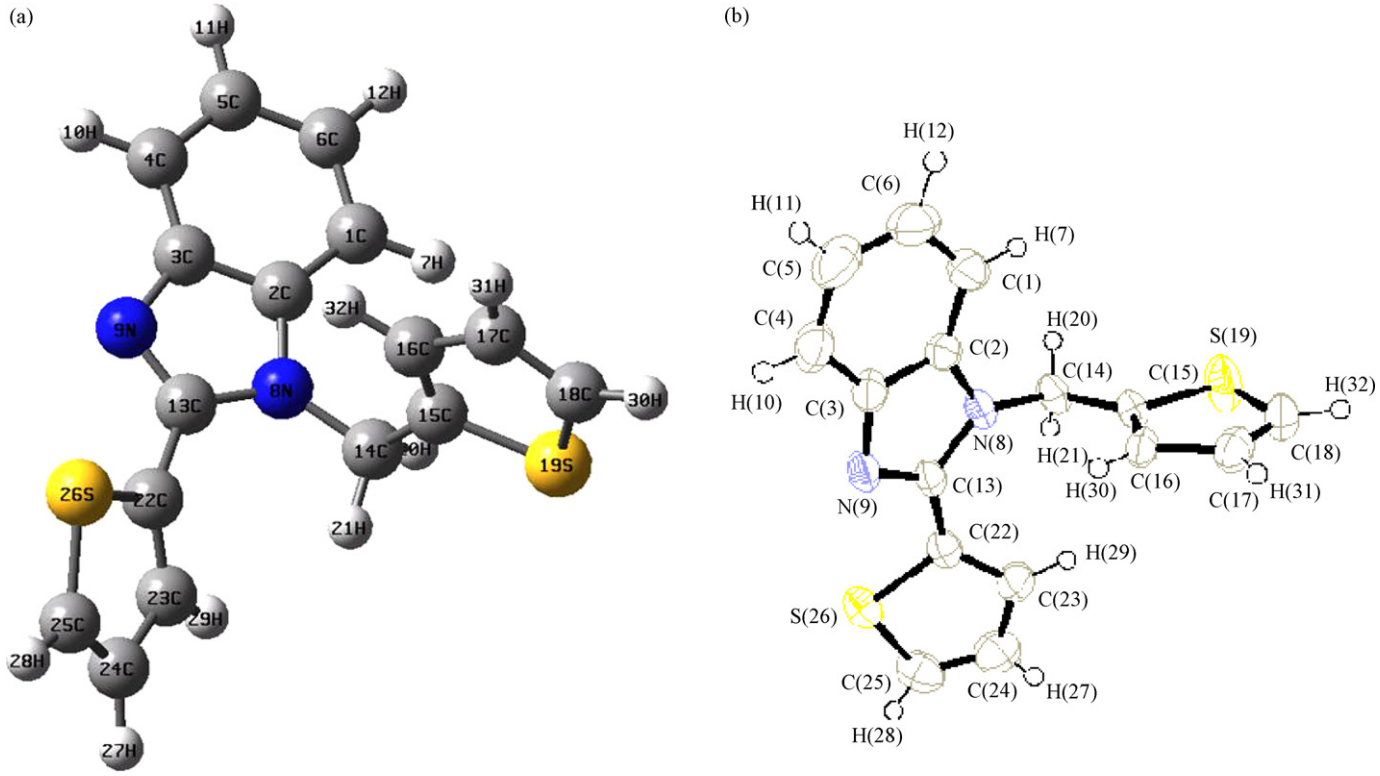

Fig. 1. (a) The theoretical geometric structure of title compound ($C_{16}H_{12}N_2S_2$) and (b) the experimental geometric structure of the title compound (displacement ellipsoids for non-H atoms are drawn at the 50% probability level) taken from reference ($C_{16}H_{12}N_2S_2$) [11].

valuable and providing insight into the vibrational spectrum and molecular parameters.

2. Calculations

The molecular structures of the title compound ($C_{16}H_{12}N_2S_2$) in the ground state (in vacuo) are optimized by HF and B3LYP with the 6-31G(d) basis set. Two sets of vibrational frequencies for these species are calculated with these methods and then scaled by 0.8929 and 0.9613, respectively. Molecular geometry is restricted and all the calculations are performed by using Gauss-View molecular visualisation program [12] and Gaussian 98 program package on personal computer [13].

3. Results and discussions

The features of molecular geometry and vibrational spectra of 1-(thiophen-2-yl-methyl)-2-(thiophen-2-yl)-1*H*-benzimidazole ($C_{16}H_{12}N_2S_2$) have been characterized [11]. Its geometric structure is monoclinic, space group $P2_1/n$, with the cell dimensions $a = 8.950$ Å; $b = 9.141$ Å; $c = 17.429$ Å; $\alpha = \beta = 93.638°$, and $V = 11423.0$ Å^3 [11]. We have shown theoretical and experimental crystal structure of the title compound ($C_{16}H_{12}N_2S_2$) in Fig. 1. The optimized geometric parameters (bond lengths and angles) by HF and B3LYP with 6-31G(d) as the basic set are listed in Table 1 and compared with the experimental crystal geometry for the title compound ($C_{16}H_{12}N_2S_2$). The title compound contains three planar rings. One is the benzimidazole ring (atoms; N8, N9, C1, C2, C3, C4,

Table 1
Optimized and experimental geometries of title compound ($C_{16}H_{12}N_2S_2$) in the ground state

Parameters	Experimental[a]	Calculated	
		HF 6-31G(d)	B3LYP 6-31G(d)
Bond lengths (Å)			
S(26)–C(22)	1.680(3)	1.732	1.716
S(26)–C(25)	1.706(2)	1.719	1.705
S(19)–C(18)	1.686(3)	1.729	1.806
S(19)–C(15)	1.720(2)	1.738	1.820
N(8)–C(2)	1.377(3)	1.383	1.368
N(8)–C(13)	1.387(3)	1.375	1.409
N(8)–C(14)	1.452(3)	1.445	1.459
N(9)–C(3)	1.388(3)	1.378	1.390
N(9)–C(13)	1.315(3)	1.285	1.334
Bond angles (°)			
C(22)–S(26)–C(25)	92.60(13)	91.37	89.50
C(18)–S(19)–C(15)	92.27(13)	91.47	89.51
C(2)–N(8)–C(13)	106.17(18)	105.59	106.48
C(2)–N(8)–C(14)	129.3(2)	125.54	128.48
C(13)–N(8)–C(14)	124.49(19)	128.90	124.63
C(3)–N(9)–C(13)	105.15(19)	105.60	106.05
N(9)–C(13)–N(8)	112.9(2)	113.52	111.86
Dihedral angles (°)			
C(6)–C(1)–C(2)–N(8)	179.5(3)	179.4	179.1
C(13)–C(22)–C(23)–C(24)	−179.0(2)	−177.4	−179.1
C(14)–N(8)–C(13)–N(9)	−178.8(2)	−169.0	−172.1
C(13)–N(8)–C(2)–C(3)	0.7(4)	0.3	0.8

Bond lengths in (Å); bond and dihedral angles in (°).
[a] Taken from Ref. [11].