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Experimental and theoretical study of a novel synthesized thiophene compound

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ABSTRACT

The structural of dibenzo[*b*,*d*]thiophene-2,8-diamine ($C_{12}H_{10}N_2S$) has been characterized using single-crystal X-ray diffraction (XRD), FT-IR and ^{1}H NMR techniques. The molecular geometric parameters, normal mode frequencies and the corresponding vibrational assignments, gauge-including atomic orbital (GIAO) ^{1}H chemical shift values of the title compound in the ground state have been calculated using the Hartree-Fock (HF) and density functional (B3LYP) methods with 6-31G(d,p) basis set. Vibrational assignments have been made by the potential energy distribution (PED) analyses. The compound crystallizes in Orthorhombic space group $P2_12_12_1$ with the unit cell dimensions a = 5.8347 (1) Å, b = 10.0895 (4) Å, c = 17.1142 (8) Å, V = 1007.50 (6) Å^3. The calculated results reveal that the optimized geometries can well reproduce the crystal structure. The theoretical vibrational frequencies and ^{1}H NMR chemical shift values show good agreement with the experimental data.

1. Introduction

Thiophene belongs to the class of heterocyclic compounds with a five-membered ring containing one sulfur heteroatom bearing the formula C_4H_4S. It is regarded as an aromatic compound due to its extensive substitution reactions obeying 4n + 2π electron rule [1,2]. The word "thiophene" is derived from the Greek word "theion" for sulfur, and another Greek word "phaino" which means shining. Elemental sulfur has been well known to act as an antifungal agent for a long time [2]. Thiophene derivatives are important heterocyclic compounds that are used in technology as a constructing unit for the synthesis of a charge transporting molecules in transistors, organic solar cells and organic light-emitting diodes [3–7]. On the other hand, the dibenzothiophene-amine derivatives have attracted the researchers for the synthesis of Schiff base compounds. Some Schiff bases containing thiophene rings have been reported as effective corrosion inhibitors for various metals in acid media [8–10]. Quantum chemical calculation is one of the modern emerging tools in unraveling physical and chemical properties of molecules. The availability of software packages makes the quantum chemical computation is a simple task. The molecular structure, harmonic force fields, vibrational wavenumbers, electronic transitions as well as IR intensities and Raman activities of organic molecules have been studied by using density functional theory (DFT) and Hartree-Fock (HF) calculations.

In this study, we present results of a detailed investigation of the structural characterization of dibenzo[*b*,*d*]thiophene-2,8-diamine using single crystal X-ray, FT-IR and ^{1}H NMR and quantum chemical calculations. The geometrical parameters, fundamental frequencies and GIAO 1H NMR chemical shift values of the title compound in the ground state were calculated using the DFT (B3LYP) and Hartree-Fock (HF) methods with the 6–31G (d,p) basis set. These calculations are valuable for providing insight into molecular parameters and the vibrational and NMR spectra. The aim of this work is to explore the molecular dynamics and the structural parameters that govern the chemical behavior and to compare the predictions made from theory with experimental observations.

2. Experimental and computational method

2.1. Instrumentation

The melting point was determined by system Kofler: type WME, Nr 6865. The FT-IR spectrum of the title compound has been recorded by JASCO-FT/IR-4200 Spectrometer with MCT detector

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from the range of 4000-600 cm^{-1} in a solid phase at room temperature, number of scans 8, resolution 4 cm^{-1}. The ^1H NMR spectra were recorded on a Bruker Avance 300 mHz spectrometer using Acetonitrile-d_3 (UPAC name 2,2,2-trideuterioacetonitrile, CD_3CN) as a solvent with chemical shifts being reported as δ (ppm) from TMS.

2.2. Synthesis and growth

Dibenzo[*b*,*d*]thiophene-2,8-diamine (DBTDA) was prepared by a condensation in ethanol (800 ml) of 2, 8-dinitrodibenzothiophene (2.70 g, 9.8 m mol) with 2.0 g of carbon (10% palladium) at 60 °C. Then we added 50 ml of hydrazine hydrate solution in 200 ml of ethanol and heated to reflux for 6 h. The yellow precipitate was filtered, washed with an amount of Cold ethanol and dried in a vacuum. A single-crystal suitable for an X-ray structural analysis was obtained by slow evaporation from ethanol-dichloromethane (1:1) solution at room temperature. Yield: 49%; M.P = 201 °C.

2.3. Single crystal X-ray diffraction

The Intensity data for dibenzo[*b*,*d*]thiophene-2,8-diamine were collected using a Bruker AXS Kappa CCD single crystal X-ray diffractometer equipped with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at room temperature with a crystal dimension of 0.12 mm × 0.06 mm × 0.06 mm. No absorption corrections applied to the data sets. The structure was solved by direct methods by using the SHELXS86 program [11] and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXL-97 program [12]. The MERCURY package and ORTEP-3 for Windows programs were used for generating molecular structures [13,14]. All hydrogen atoms were included using a riding model and refined isotropically with CH = 0.93 Å and NH_2 = 0.86 Å U_{iso} (H) = 1.2 U_{eq}. Relevant crystal data and details of the structure determinations are given in Tables 1 and 2.

2.4. Computational procedures

All Geometric optimizations of investigating compound and quantum chemical calculations were performed using the Gauss View Molecular Visualization program [15] and standard Gaussian-03 software package [16] on an Intel (R) core (TM) i5-3470 CPU (3.2 GHz and 4 GB RAM) personal computer. Geometry optimization of the title compound in the ground state (in vacuo) was carried out by two different methods: ab initio methods at the Hartree–Fock (HF) level with the 6-31G(d,p) basis sets and at the density functional theory (DFT) level with the non-local hybrid density functional B3LYP [17], combining Becke's three-parameter hybrid exchange functional with the correlation functional of Lee et al. [18] at basis sets 6-31G(d,p) [19]. ^1H Nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated using the standard GIAO/TMS B3LYP/6-311 + G (2d,p) (Gauge-Independent Atomic Orbital) approach [20,21] with the Gaussian 03 program package. Furthermore, the calculated vibrational frequencies were clarified by means of the potential energy distribution (PED) analysis and assignments of all the fundamental vibrational modes using VEDA4 program [22].

3. Results and discussion

3.1. Description of the crystal structure

Single crystal X-ray diffraction study revealed that the title

Table 1
Crystal data and structure refinement parameters of dibenzo[*b*,*d*]thiophene-2,8-diamine.

Compound	dibenzo[*b*,*d*]thiophene-2,8-diamine
Empirical formula	$C_{12}H_{10}N_2S$
Formula weight	214.28
Temperature (K)	293
Wavelength (Mo kα) (Å)	0.71073
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	
a, *b*, *c* (Å)	5.8347 (1), 10.0895 (4), 17.1142 (8)
α, *β*, *γ* (°)	90.00, 90.00, 90.00
Melting point (K)	474
Volume (Å^3)	1007.50 (6)
Z	4
Density (calculated) (Mg/m^3)	1.413
Adsorption coefficient (mm^{-1})	0.28
F(000)	448
Crystal size (mm)	0.12 × 0.06 × 0.06
Crystal color/form	Yellow/Plate
θ Range for data collection (°)	3.1–26.4
hkl range	$-6 \le h \le 6$ $-12 \le k \le 12$ $-21 \le l \le 21$
Reflections	
Number of reflections with $I > 2\sigma(I)$	1751
Number of independent reflections/R_{int}	1953/0
Number of data/restraints/parameters	1953/0/137
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit (GOF) on F^2 (S)	1.08
R [$F^2 > 2\sigma(F^2)$]	0.043
w$R(F^2)$	0.123
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0822P)^2 + 0.1425P]$ where $P = (F_o^2+2F_c^2)/3$
Max/min $\delta\rho$ (e/Å^3)	0.26/−0.28
Extinction coefficient	0.056(10)
Flack parameter	0.04 (11)