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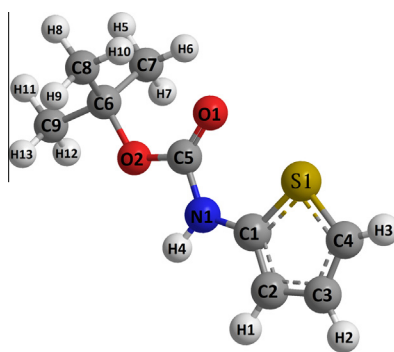
Vibrational frequency analysis, FT-IR, DFT and M06-2X studies on tert-Butyl N-(thiophen-2-yl)carbamate

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HIGHLIGHTS

- The FT-IR spectrum of the title compound were recorded in solid phase.
- The optimized geometry and vibrational frequencies were calculated for the first time.
- The HOMO–LUMO energies and related molecular properties were evaluated.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the experimental and theoretical vibrational frequencies of a newly synthesized tert-Butyl N-(thiophen-2-yl)carbamate have been investigated. The experimental FT-IR (4000–400 cm^{-1}) spectrum of the molecule in the solid phase have been recorded. The theoretical vibrational frequencies and optimized geometric parameters (bond lengths and bond angles) have been calculated by using density functional theory (DFT/B3LYP: Becke, 3-parameter, Lee–Yang–Parr) and DFT/M06-2X (the highly parametrized, empirical exchange correlation function) quantum chemical methods with the 6-311++G(d,p) basis set by Gaussian 09W software, for the first time. The vibrational frequencies have been assigned using potential energy distribution (PED) analysis by using VEDA 4 software. The computational optimized geometric parameters and vibrational frequencies have been found to be in good agreement with the corresponding experimental data, and with related literature results. In addition, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies and the other related molecular energy values have been calculated and are depicted.

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Introduction

The varied use of thiophene-based compounds in applications as wide-ranging as modern drug design [1], opto-electronic and electronic device construction [2], and incorporation into conductive polymers [3] has given rise to extensive investigations. Indeed,

a significant portion of petroleum and other fossil fuels organosulfur contamination arises from condensed forms of thiophene [4]. Thus, there is ongoing interest in assessing, experimentally and theoretically, many of the fundamental properties of even simple thiophene derivatives. A survey of the literature reveals that to the best of our knowledge, the results based on quantum chemical calculations, FT-IR spectroscopy and HOMO–LUMO analysis of the title compound presented in this work have not previously been reported. Herein, we reported detailed interpretation of the infrared and Raman spectra based on the experimental and computational results, which are in excellent agreement. The molecular structure of the title molecule has recently been disclosed based upon studies using single crystal X-ray spectroscopy [5]. In this work, both theoretical and experimental studies have been performed which give a detailed description of the optimized molecular structure and vibrational frequencies of the title molecule.

Experimental details

The FT-IR spectrum (4000–400 cm^{-1}) of the title molecule has been recorded using a Perkin–Elmer Spectrum Two FT-IR Spectrometer with a resolution of 4 cm^{-1} in the solid phase at room temperature. Moreover, the Raman spectrum of tert-Butyl N-(thiophen-2yl)carbamate was recorded using different spectrophotometers with different laser sources. However, fluorescence could not be eliminated in the spectrum. Thus, the recorded Raman spectra were not considered further in this study.

Computational details

Initial atomic coordinates can generally be taken from any database or experimental XRD results. We have used the experimental XRD data and the GaussView software database to determine initial atomic coordinates and to optimize the input structure. After the optimization, we used the most stable optimized structure as a starting point for further theoretical analysis. In this study, initial atomic coordinates that were taken from the GaussView database [6] have produced the most stable structure after optimization. The molecular structure of the title molecule in the ground state (in gas phase) was optimized by using DFT/B3LYP and DFT/M06-2X methods with the 6-311++G(d,p) basis set, and the calculated optimized structure has been used in the vibrational frequency calculations. The calculated harmonic vibrational frequencies have been scaled by 0.9614 (B3LYP) and 0.9489 (M06-2X) for 6-311++G(d,p) levels, respectively [7–9]. The same scale factors were used for the entire spectra. The molecular geometry has not been limited, and all the calculations (vibrational wavenumbers, optimized geometric parameters and other molecular properties) have been performed using the GaussView molecular visualization program [6] and the Gaussian 09W program package [10]. Furthermore, the calculated vibrational frequencies have been clarified by means of the potential energy distribution (PED) analysis of all the fundamental vibration modes by using VEDA 4 program [11,12]. VEDA 4 program has been used in previous studies by many researchers [9,13–16]. All the vibrational assignments have been made at B3LYP/6-311++G(d,p) level for which the molecular structure is more stable. So, some assignments may correspond to its previous or next vibrational frequency value at M06-2X/6-311++G(d,p) level.

Results and discussion

Geometric structure

The single X-ray crystallographic analysis of the tert-Butyl N-(thiophen-2yl)carbamate ($\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$) compound has been previously reported [5]. The theoretical and experimental [5]

structural parameters (bond lengths and bond angles) are shown in Table 1, consistent with the atom numbering scheme (the optimized structure) in Fig. 1. As seen from the figure, the molecule has 26 atoms. A molecule consisting on N atoms has a total of $3N$ degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule. In a nonlinear molecule, 3 of these degrees belong to the rotational, and 3 to the translational motions of the molecule, and so, the remaining motions correspond to vibrational degrees of freedom. The net number of the vibrational modes is $3N-6$. Therefore, for our molecule, three Cartesian displacements of 26 atoms provide 78 internal and 72 normal vibration modes. The molecule has C_1 symmetry. From Table 1 we see that the optimized parameters calculated at both levels of theory are slightly longer or shorter than the experimental values because the theoretical calculations correspond to the molecule in the gas state.

The title compound, $\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$, dihedral angle between the thiophene ring and carbamate group is 15.79° . In the crystal structure, intramolecular C–H \cdots O interactions in tandem with the tert-butyl groups render the packing of adjacent molecules in [001] direction nearly perpendicular. An intermolecular N–H \cdots O hydrogen bond gives rise to a chain extending along [001]. The crystal studied was found to be a racemic twin [5].

We calculated C3–C4, C2–C3 and C1–C2 bond lengths at 1.362(B3LYP)/1.358(M06-2X) Å, 1.425(B3LYP)/1.425(M06-2X) Å and 1.371(B3LYP)/1.366(M06-2X) Å, respectively. These bond lengths were experimentally found to be 1.350, 1.418 and 1.365 Å by Hsu et al. [5], respectively. These bond lengths in different thiophene rings were experimentally found 1.352 [17], 1.440 [18] and 1.370 Å [17], respectively. For 3-ethynylthiophene, these bond lengths were calculated 1.362, 1.439 and 1.378 Å, respectively [19]. The calculated C4–S1 and C1–S1 bond lengths at 1.742(B3LYP)/1.729(M06-2X) Å and 1.747(B3LYP)/1.734(M06-2X) Å, respectively. These bond lengths were observed 1.718 and 1.737 Å, respectively in [5], and for similar structures, these lengths were observed 1.740 by electron diffraction [18] and 1.714 Å by microwave spectra [17]. These lengths for 3-ethynylthiophene [19] have been calculated at 1.735 and 1.724 Å by using B3LYP/6-311++G(d,p) method. For thiophene-2-carbohydrazide bond lengths of C4–S1 and C1–S1 have been found in the range 1.7408–1.7249 Å by Balachandran et al. [20]. Also, in this study within tert-butyl group C–H bond lengths have been calculated in the range 1.089–1.093 Å in B3LYP and 1.088–1.092 Å in M06-2X methods, and observed at 0.980 Å. These results are good agreement with similar tert-butyl groups [21–25]. In carbamate group, C5–O2, C5–O1, C5–N1, N1–H4 bond lengths have been calculated at 1.349(B3LYP)/1.340(M06-2X) Å, 1.212(B3LYP)/1.206(M06-2X) Å, 1.373(B3LYP)/1.368(M06-2X) Å and 1.009(B3LYP)/1.008(M06-2X) Å, respectively. These bond lengths have been found experimentally at 1.337, 1.216, 1.356 and 0.900 Å, respectively. C5–O1, C5–N1 and H1–H4 bond lengths have been calculated at 1.2586, 1.3797 and 1.0210 Å, respectively by using DFT methods by Joseph et al. [22]. Also, C6–O2 and N1–C1 contact points have been calculated at 1.481(B3LYP)/1.461(M06-2X) Å and 1.395(B3LYP)/1.394(M06-2X) Å, respectively. These bond lengths have been reported at 1.484 and 1.396 Å, respectively by Hsu et al. [5].

As to the bond angles of title molecule, C3–C2–C1 bond angle was computed at $112.5(\text{B3LYP})/112.2(\text{M06-2X})^\circ$ and measured at 112.2° by Hsu et al. [5]. For 3-ethynylthiophene by Karabacak et al. [19], this angle was computed at 112.1° and for similar system 112.27° by Bak et al. [17]. C1–S1–C4, C2–C1–S1 bond angles were calculated at 91.7° and 111.8° by Karabacak et al. [19]. These bond angles have been calculated at $90.6(\text{B3LYP})/90.73(\text{M06-2X})^\circ$ and $111.7(\text{B3LYP})/112.0(\text{M06-2X})^\circ$ in this study, and reported at 90.88° and 111.5° Hsu et al. [5].

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