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Effect of intermolecular hydrogen bonding, vibrational analysis and molecular structure of 4-chlorobenzothioamide

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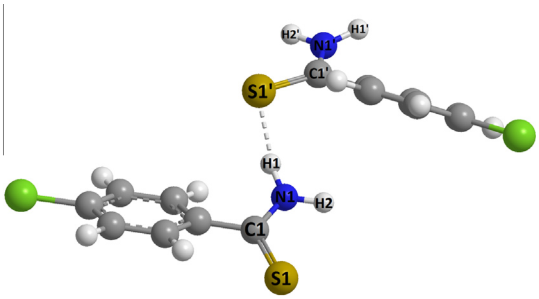
HIGHLIGHTS

- The FT-IR and μ-Raman spectra of 4-chlorobenzothioamide are recorded in solid phase.
- Theoretical vibrational modes and molecular structure are given for the first time.
- The dimeric form of 4-chlorobenzothioamide are simulated.
- Effect of intermolecular hydrogen bonding to vibrational modes are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, the experimental and theoretical vibrational spectra of 4-chlorobenzothioamide were investigated. The FT-IR (400–4000 cm^{-1}) and μ-Raman spectra (100–4000 cm^{-1}) of 4-chlorobenzothioamide in the solid phase were recorded. The geometric parameters (bond lengths and bond angles), vibrational frequencies, Infrared and Raman intensities of the title molecule in the ground state were calculated using ab initio Hartree–Fock and density functional theory (B3LYP) methods with the 6-311++G(d,p) basis set for the first time. The optimized geometric parameters and the theoretical vibrational frequencies were found to be in good agreement with the corresponding experimental data and with the results found in the literature. The vibrational frequencies were assigned based on the potential energy distribution using the VEDA 4 program. The dimeric form of 4-chlorobenzothioamide was also simulated to evaluate the effect of intermolecular hydrogen bonding on the vibrational frequencies. It was observed that the N—H stretching modes shifted to lower frequencies, while the in-plane and out-of-plane bending modes shifted to higher frequencies due to the intermolecular N—H···S hydrogen bond. Also, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and diagrams were presented.

Introduction

Thioamides are biologically active compounds, possessing a wide spectrum of activities. Their derivatives are widely used as fungicides, herbicides and important synthetic intermediates for thiazoles and amidines. They have enormous practical and synthetic applicability and their importance and impact as synthetic intermediates is continuously growing. Thioamides are generally synthesized using Lawesson's reagent or phosphorus penta sulfide. Aromatic thioamide derivatives are generally synthesized by treatment of the corresponding nitrile with gaseous hydrogen sulfide in the presence of alkali metal sulfide or ammonium sulfide in alcohols, triethylamine in pyridine, sodium sulfide and phase transfer catalyst in benzene and water or anion exchange resin in alcohols [1–13].

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The thioamide group is present in a number of biologically active compounds; therefore, a detailed vibrational assignment of infrared (IR) and Raman (R) spectra of the title compound is important for further spectroscopic studies of structurally related molecules. In an earlier paper have been reported FT-IR and FT-Raman spectra of thioamides and selenoamides. [14]. Experimental single-crystal XRD studies have also been performed on benzothioamide molecule [1,2]. Intermolecular hydrogen bonding is a key to the formation of crystal structure of matter. However, hydrogen bonding causes significant shifts in the vibrational frequencies of some characteristic modes, so vibrational spectroscopy is very important tool for understanding the effect of hydrogen bonding. Also, the dynamics of hydrogen bonding in an excited state are very different. Indeed, hydrogen bonding in excited states is particularly important in photophysical processes and photochemical reactions. Excited-state hydrogen-bonding dynamics are mainly determined by vibrations of hydrogen donor and acceptor groups [15]. Zhao and Han have made significant contributions to the literature regarding the effect of hydrogen bonding on vibrational spectra in excited state [16,17], internal conversion and intersystem crossing [18,19], and intramolecular charge transfer in excited state [20].

To our best knowledge, no computational vibrational study on monomeric and dimeric 4-chlorobenzothioamide (4-CBTA) has been published in the literature. Hence, in the work described in this paper a theoretical study were performed to obtain a detailed description of the molecular structure and vibrational spectra of 4-CBTA, utilizing Hartree–Fock (HF) and density functional theory (DFT/B3LYP) methods with the 6-311++G(d,p) basis set. Experimental FT-IR and μ-Raman spectra of the molecule were also recorded and compared with the results of the theoretical studies. In addition, we have determined the shifts in the vibrational frequencies relative to the dimeric 4-CBTA in order to investigate the effects of intermolecular hydrogen bonding in the ground state.

Experimental details

4-CBTA was purchased from Sigma–Aldrich (St. Louis, MO, USA) and, used (i.e., its spectra were recorded) with no further purification. The FT-IR spectrum (400–4000 cm^{-1}) of a KBr disk of 4-CBTA was recorded using a Pelkin Elmer (Waltham, MA, USA) Spectrum One FT-IR spectrometer with a resolution of 4 cm^{-1} at room temperature. The μ-Raman spectrum (100–4000 cm^{-1}) of the molecule was recorded using a Jasco (Easton, MD, USA) NRS-3100 laser Raman spectrophotometer at room temperature. The 785 nm line of a green diode laser was used as the exciting light, and 25 scans were accumulated.

Computational details

The optimized structure parameters, harmonic vibrational frequencies, IR intensities and Raman scattering activities of 4-CBTA were calculated using ab initio HF and DFT/B3LYP methods with the 6-311++G(d,p) basis set. All computations were performed using the Gaussian 09 program package [21]. The calculated harmonic frequencies were scaled by 0.9051 and 0.9614 for the HF and B3LYP levels of theory with the 6-311++G(d,p) basis set [22], respectively. Additionally, the calculated vibrational frequencies were clarified by performing a potential energy distribution (PED) analysis of all the fundamental vibration modes using the VEDA 4 program [23]. VEDA 4 has been used in previous studies by many researchers to realize PED analysis of vibrational modes [24–26].

Table 2
Experimental and calculated geometric parameters of 4CBTA with 6-311++G(d,p).

Geometric parameters	Calculated values		Experimental values	
	B3LYP	HF	Ref. [1]	Ref. [2]
Bond lengths (Å)				
S1—C1	1.664	1.654	1.671	1.675
Cl1—C4	1.755	1.741	1.737	
N1—H1	1.009	0.993	0.860	0.860
N1—H2	1.009	0.994	0.860	0.860
N1—C1	1.354	1.333	1.320	1.316
C1—C2	1.489	1.493	1.483	1.486
C2—C3	1.401	1.390	1.393	1.380
C2—C6	1.403	1.391	1.391	1.388
C3—H3	1.083	1.073	0.930	0.930
C3—C5	1.389	1.381	1.383	1.381
C4—C5	1.393	1.383	1.376	1.364
C4—C7	1.391	1.381	1.375	1.373
C5—H4	1.082	1.073	0.930	0.930
C6—H5	1.084	1.075	0.930	0.930
C6—C7	1.392	1.384	1.386	1.384
C7—H6	1.082	1.073	0.930	0.930
R^2	0.9883	0.9883		
Bond angles (°)				
H1—N1—H2	118.3	118.6	120.0	120.0
H1—N1—C1	121.5	121.6	120.0	120.0
H2—N1—C1	118.1	118.5	120.0	120.0
S1—C1—N1	121.6	121.9	121.0	120.9
S1—C1—C2	123.2	123.1	122.4	121.0
N1—C1—C2	115.2	115.1	116.6	118.1
C1—C2—C3	120.2	120.3	120.4	120.0
C1—C2—C6	121.2	120.8	120.9	122.0
C3—C2—C6	118.5	119.0	118.7	118.0
C2—C3—H3	118.9	119.4	119.6	119.2
C2—C3—C5	121.0	120.7	120.7	121.5
H3—C3—C5	120.2	119.9	119.6	119.2
Cl1—C4—C5	119.5	119.5	119.2	
Cl1—C4—C7	119.5	119.4	119.3	
C5—C4—C7	121.0	121.1	121.6	120.8
C3—C5—C4	119.3	119.4	119.2	119.3
C3—C5—H4	120.6	120.5	120.4	120.3
C4—C5—H4	120.1	120.2	120.4	120.3
C2—C6—H5	120.3	120.5	119.6	119.6
C2—C6—C7	121.0	120.9	120.9	120.8
H5—C6—C7	118.6	118.7	119.6	119.6
C4—C7—C6	119.1	119.1	119.0	119.5
C4—C7—H6	120.2	120.3	120.5	120.3
C6—C7—H6	120.7	120.6	120.5	120.3
R^2	0.7658	0.7825		

Results and discussion

The optimized monomer (a) and dimer (b) molecular structures of 4-CBTA are shown in Fig. S1 (Supplementary information) along with the atom numbering scheme. 4-CBTA is a molecule that has 16 atoms. Three Cartesian displacements of 16 atoms provide 48 internal and 42 normal vibration modes. The total energies (corrected for the zero point energy) for the molecule, calculated using HF and B3LYP with the 6-311++G(d,p) basis set, are given in

Table 1
Sum of electronic and zero point energies (hartree/particle), dipole moments (debye), HOMO (a.u), LUMO (a.u) and HOMO–LUMO gap values of 4-CBTA.

Methods	6-311++G(d,p)				
	Energies	Dipole moment	HOMO energies	LUMO energies	HOMO–LUMO gap value energies
B3LYP	−1183.647210	3.7654	−0.22359	−0.0808	−0.14279
HF	−1180.146198	4.2724	−0.32404	0.02875	−0.35279