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Infrared, Raman and temperature-dependent NMR spectra, vibrational assignments, normal coordinate analysis, and DFT calculations of benzoxazoline-2-thione

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ABSTRACT

The tautomerism of benzoxazoline-2-thione (BOT; *thio-keto*) and 2-mercaptobenzoxazole (MBO; *thio-enol*) has been thoroughly investigated by means of Raman (3600–100 cm^{-1}), infrared (4000–200 cm^{-1}), ^{1}H and ^{13}C NMR spectra and X-ray powder diffraction (XRD). In addition, temperature-dependent ^{1}H NMR spectra from −90 to +90 °C were acquired. To complement experimental results with theoretical predictions, we performed Density Functional Theory (DFT) calculations utilizing B3LYP, B3PW91 and SVWN methods at 6-31G(d) basis set. Both computational and spectral results were in favor of *thio-keto* BOT structure with no evidence for the existence of *thio-enol* (MBO) tautomer which firmly eliminates the possibility of an existing equilibrium between *keto* and *enol* forms. Moreover the dimerization percentage of *thio-keto* benzoxazoline-2-thione (BOT) and benzothiazoline-2-thione (BTT) were found to be 11.9% and 2.5%, respectively which favors strong hydrogen bonding interactions in BOT. Aided by normal coordinate analysis, force constants in internal coordinates and potential energy distributions (PEDs), a complete vibrational assignment for all fundamentals was obtained. The results are compared with the sulfur analogue, benzothiazoline-2-thione (BTT) whenever appropriate.

1. Introduction

Benzoxazoline-2-thione (BOT) and benzothiazoline-2-thione (BTT) contain nitrogen, oxygen and sulfur electron donating atoms; therefore they are used as a chelating-type flotation collector [1] and for pre-concentration of silver [2,3], copper, and iron cations. They are also used in re-circulating water systems [4] as an alloy corrosion inhibitor [5–8]. In addition, the *thio-enol* and *thio-keto* moieties can form an adsorptive monolayer on metal and semiconductor substrates [9]. Exchanging carbon for silicon [10,11], oxygen for sulfur [12,13] and fluorine for chlorine [14], may lead to an alteration in the conformational stability towards either C_1 or C_s symmetry. However, the effect of similar atom replacement on tautomerism, does not achieve the same result. Atom exchanges certainly do affect the skeletal vibrational modes and the overall energy as seen in $C_3H_6X_3$ molecules where X is O, S and/or Se [15].

The BOT and BTT conformers were theoretically investigated using AM1 semi-empirical quantum mechanical (QM) calculations [16] along with bonding and anti-bonding molecular orbital interactions [9]. In addition, surface enhanced Raman spectroscopy (SERS) of MBO adsorbed on copper electrodes [17], silver sols [18,19], gold and its complexes [20,21] were studied. To the best of our knowledge, neither conformational stability nor *keto-enol* tautomerism of MBO and BOT were configured yet as well as their dimerization. Thus, we aimed at determining whether the BOT molecule has an equilibrium between *keto* BOT and *enol* MBO, in which a hydrogen moves from a nitrogen atom to the sulfur atom (Fig. 1). Therefore, we initiated the current investigation for BOT using vibrational, mass, ^{1}H and ^{13}C NMR spectral measurements which parallels a recent study on the benzothiazoline-2-thione (BTT) tautomer [22]. To aid in the interpretation of infrared (IR) and

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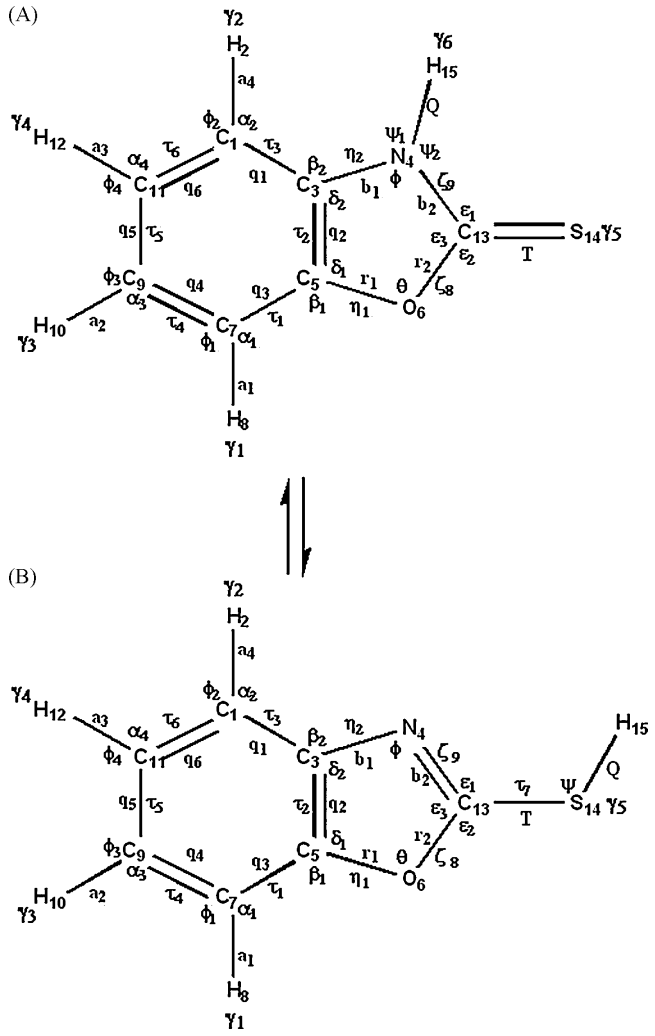

Fig. 1. Atom numbering and internal coordinate definitions for: (A) benzoxazoline-2-thione (BOT) and (B) 2-mercaptobenzoxazole (MBO).

Raman spectral data we performed Gaussian 98 Density Functional Theory (DFT) calculations [23–25] and normal coordinate analysis to estimate the harmonic vibrational frequencies and force constants (FCs) in internal coordinates. The theoretical and experimental results are reported herein and compared with BTT [22,26,27] whenever appropriate.

2. Experimental

2.1. Materials

The solid samples of benzothiazoline-2-thione (99%), benzoxazoline-2-thione (99%), $CDCl_3$ (99.9%), $(CD_3)_2SO$ (99.9%), and CD_2Cl_2 (99.9%) were purchased from Aldrich Chemical Company and used without further purification.

2.2. Spectroscopic measurement

2.2.1. Infrared and Raman spectra

The mid-IR spectra of the solid sample were recorded in the spectral range of 4000–400 cm^{-1} (Fig. 2A) and the difference spectrum dissolved in $CHCl_3$ (Fig. 3) was recorded on Spectrum 100 PerkinElmer FT-IR spectrophotometer using KBr disk technique and IR liquid cells equipped with NaCl windows, respectively. In addition the far-IR spectrum of the solid BOT in CsI disk was recorded using the aforementioned spectrophotometer in the

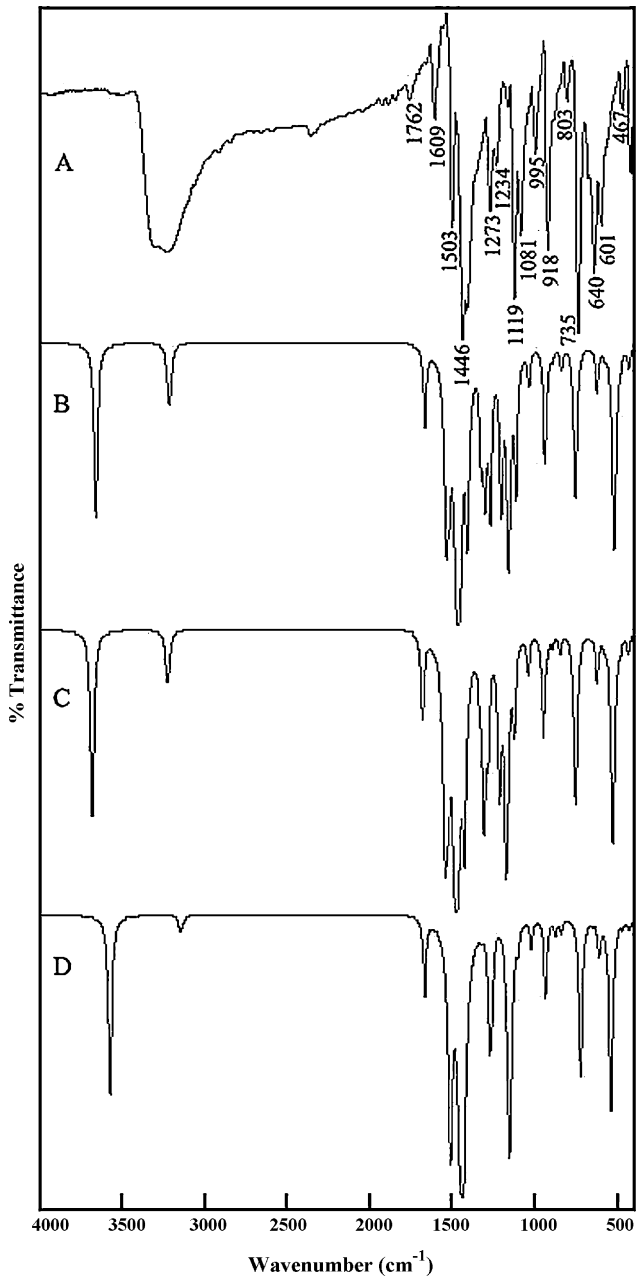

Fig. 2. Infrared spectrum (4000–400 cm^{-1}) of benzoxazoline-2-thione (BOT): (A) Solid and (B) B3LYP/6-31G(d) scaled frequencies; (C) B3PW91/6-31G(d) scaled frequencies; (D) SVWN/6-31G(d) scaled frequencies.

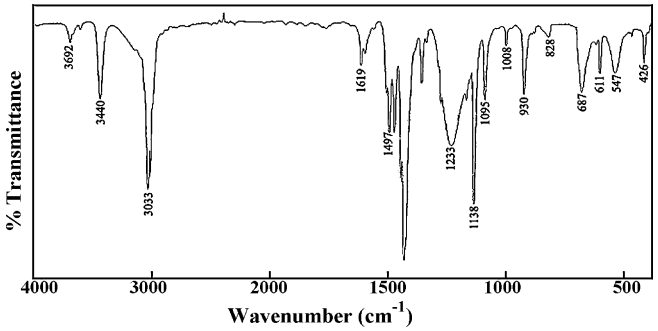

Fig. 3. Infrared difference spectrum (4000–400 cm^{-1}) of benzoxazoline-2-thione (BOT) dissolved in $CHCl_3$.