

X-ray, tautomeric preference, vibrational spectra, and density functional studies on benzoxazole and benzoxazoline derivatives



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ABSTRACT

The solid-state X-ray diffraction, FT-IR, and FT-Raman measurements have been performed on bis(benzoxazole-2-ylthio)methane. Molecular structures and normal vibrations of bis(benzoxazole-2-ylthio)methane have been compared with those of its fragments in thiolic (2-mercaptobenzoxazole and 2-methylthiobenzoxazole) and thionic (benzoxazoline-2-thione and 3-methyl-benzoxazoline-2-thione) forms to elucidate substitutional effects. The observed IR and Raman bands of these molecules have been assigned in the frameworks of calculated mode frequencies as well as the calculated IR and Raman intensities at the B3LYP/6-311++G** level in gas phase. The assignments of all fundamental bands have been expressed in terms of internal coordinates and their percent potential energy distributions. The thionic tautomers are significantly more stable than the thiolic tautomers (by more than 5 kcal/mol) with a keto-enol transition state that lies more than 40 kcal/mol above the most stable thionic tautomers. Therefore, the thionic tautomers are the main species at room temperature. Despite the huge transition barrier, the thiolic tautomers can also exist according to the detailed vibrational spectral analyses. Potential energy surface scans find that the thiolic tautomers have two stable conformations due to the orientation of their SH and SCH₃ moieties.

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1. Introduction

Benzoxazole and benzoxazoline are composed of benzene-fused deprotonated and protonated oxazole ring at the ring nitrogen, respectively. They are found not only in several natural products but also in pharmaceutical drugs such as priaxim [1,2]. Since their thiol (mercapto, or sulfanyl) and thione derivatives are fungicidal and bacteriostatic reagents, they are efficient corrosion inhibitors for many metals and their alloys, and are used in recirculation of water systems and in regulating plant growth [3–10]. They find a great variety of applications in surface science because they form adsorptive monolayers on metal and semiconductor substrates [11–14]. They are chelating agents with the presence of nitrogen, oxygen and sulfur in their contents. This makes them effective collectors in flotation processes for separation of minerals [15,16] and for pre-concentration of transition metal ions [17,18]. As being chelating agents and having

widespread applications in industrial processes, their transition metal complexes attract also considerable attention [19–22].

In this study, we first synthesized bis(benzoxazole-2-ylthio)methane with the chemical formula of C₁₅H₁₀N₂O₂S₂ and abbreviation of bis(BO-NS)Me (see Fig. 1), which emerges as a useful ligand in coordination chemistry as it contains two units of nitrogen, oxygen, and sulfur atoms. We performed its solid-state X-ray diffraction measurement to determine its crystal structure and recorded its solid-state FT-IR and FT-Raman spectra. Vibrational selection rules of the crystalline phase were estimated through factor group analysis. We then investigated thiolic (2-mercaptobenzoxazole abbreviated as BO-NSH and 2-methylthiobenzoxazole abbreviated as BO-NSMe) and thionic (benzoxazoline-2-thione abbreviated as BO-NHS and 3-methyl-benzoxazoline-2-thione abbreviated as BO-NMeS) forms of the fragments of bis(BO-NS)Me (see Fig. 1) to assess the substitutional effects on the structure and vibrational spectra. We calculated gas-phase geometries and vibrational spectra of bis(BO-NS)Me, BO-NSH, BO-NHS, BO-NSMe, and BO-NMeS with density functional theory (DFT) using B3LYP hybrid functional, which has been already proved to be very effective for vibrational studies of analogous compounds by using at least double- ζ Pople basis sets [23–31]. The

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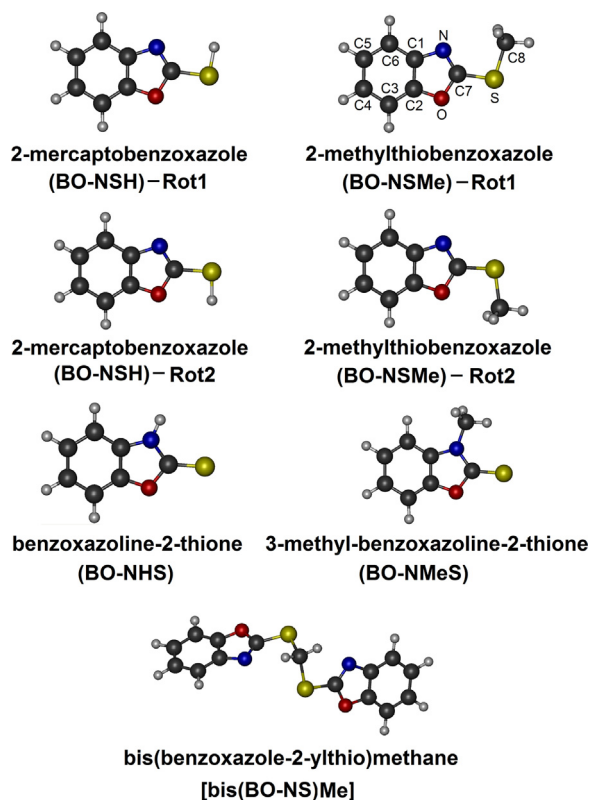


Fig. 1. The investigated compounds and the atom numbering scheme (see at Rot1 of BO-NSMe).

computed vibrational frequencies, and IR/Raman intensities were used to simulate the vibrational spectra and to identify normal modes in the experimental vibrational spectra.

2. Experimental

2.1. Synthesis

All chemicals and solvents used for the synthesis of BO-NSMe/BO-NMeS and bis(BO-NS)Me were reagent grade and processed as purchased without further purification. For synthesizing BO-NSMe/BO-NMeS, a solution of iodomethane (2.84 g, 20 mmol) in EtOH (2 mL) was added dropwise to a solution of BO-NSH/BO-NHS (3.02 g, 20 mmol) in EtOH (10 mL) and H₂O (3 mL) containing KOH (1.18 g, 21 mmol). The mixture was stirred at 75 °C for over-night, cooled to room temperature and poured into 80 mL of ice-cold distilled water. The yellowish oily product was obtained, dissolved in CH₂Cl₂, dried in MgSO₄ and filtered. The filtrate was evaporated to dryness under vacuum obtaining a yellowish oily product (2.50 g, 75%). Found (calculated) [C₈H₇NOS]: C, 58.21 (58.16); H, 4.30 (4.27); N, 8.43 (8.48); S, 19.32 (19.41). ¹H NMR (CDCl₃), δ_H in ppm: 2.74 (s, 3H, CH₃); 7.62–7.59 (m, 1H); 7.43–7.39 (s, 1H); 7.29–7.19 (m, 2H). ¹³C{¹H} NMR (DMSO-d₆), δ_C in ppm: 162.58 (1C); 151.52 (1C); 140.99 (1C); 124.79(1C); 124.68 (1C); 118.53 (1C); 110.37 (1C); 35.45 (CH₃).

Following the method described in literature [32,33], bis(BO-NS)Me was prepared as follows: a solution of CH₂Br₂ (1.74 g, 10 mmol) in EtOH (2 mL, absolute) was added dropwise to a refluxing solution of BO-NSH/BO-NHS (3.02 g, 20 mmol), EtOH (4 mL) containing Na (0.46 g). The mixture was refluxed for two hours, cooled to room temperature and poured into 100 mL of ice-cold distilled water. The brownish product was purified using soxhlet extraction technique by hexane, filling the thimble with celite and charcoal. Creamy white crystalline product was obtained from solution and dried under vacuum (2.39 g, 76%, m.p. 129 °C). ¹H NMR (DMSO-d₆), δ_H in ppm: 5.32 (s, 2H, CH₂); 7.65 (m, 2H); 7.37 (m, 2H). ¹³C{¹H} (DMSO-d₆), δ_C in ppm: 163.08 (1C); 152.01 (1C); 141.48 (1C); 125.29 (1C); 125.18 (1C); 119.02 (1C); 110.87 (1C); 35.95 (CH₂).

Table 1

Crystal data and structure refinement of bis(BO-NS)Me located on a C₂ axis with estimated standard deviations shown in parentheses for the last one or two digits.

Empirical formula	C ₁₅ H ₁₀ N ₂ O ₂ S ₂
Formula weight	314.37
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Hall symbol	–C 2yc
Space group	C2/c (C _{2h} ⁶); no. 15:b1
Point group	2/m (C _{2h})
Unit cell dimensions	<i>a</i> = 21.2229(9) Å; <i>b</i> = 4.14370(10) Å; <i>c</i> = 18.0791(8) Å; α = 90°; β = 121.010(6)°; γ = 90°
Volume	1362.67(9) Å ³
Z; Z ^B	4; 2
Density (calculated)	1.532 g/cm ³
Absorption coefficient	0.395 mm ⁻¹
<i>F</i> (000)	648
Crystal size	0.5 × 0.1 × 0.1 mm ³
Theta range for data collection	3.85°–30.51°
Index ranges	–30 ≤ <i>h</i> ≤ 30; –5 ≤ <i>k</i> ≤ 5; –24 ≤ <i>l</i> ≤ 25
Reflections collected	11189
Independent reflections	2072 [<i>R</i> _{int} = 0.0229]
Completeness to theta = 30.51°	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.95296
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2072/0/116
Goodness-of-fit on <i>F</i> ²	1.059
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0272; <i>wR</i> ₂ = 0.0751
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0335; <i>wR</i> ₂ = 0.0767
Largest diff. peak and hole	0.367 and –0.224 e·Å ⁻³

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