

Structural and computational studies of geometric isomers of 2-(4-methoxystyryl)-1,3-benzothiazole and preparation of their complexes with zinc halides

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ABSTRACT

The 2-(4-methoxystyryl)-1,3-benzothiazole (MeO-sbt) and its complexes with zinc halides of general formula $[ZnX_2(MeO-sbt)_2]$, X = Cl, Br, I, are prepared. Crystal structure of both geometric isomers *cis*-2-(4-methoxystyryl)-1,3-benzothiazole **1a** and *trans*-2-(4-methoxystyryl)-1,3-benzothiazole **1b** are reported. Optimized structures of isomers **1a** and **1b** are consistent with X-ray structures. By comparison of calculated and experimental IR spectra as well as experimental NMR data it has been concluded that *trans*-isomer **1b** was initial product. Quantum-mechanical calculations have shown that thermal isomerization in the singlet ground state is not possible at room temperature, but isomerization could be initiated by high temperature or photochemically which had not been studied in this work.

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1. Introduction

Various natural and synthetic compounds with benzothiazole moiety have versatile pharmaceutical and industrial applications. Benzothiazole and its derivatives exhibit diverse biological properties such as antitumor, antibacterial, antifungal, antiinflammatory and antiallergic activity [1–4]. Some benzothiazole derivatives have interesting photochemical properties due to presence of two different chromophores in their molecule, namely benzothiazole moiety and the substituted aromatic ring [5]. Furthermore, substituted benzothiazoles are of significant interest in design and synthesis of organic luminescent materials [6].

Beside the abovementioned applications, benzothiazole and its derivatives are of substantial coordination interest as well. In addition to π -aromatic systems, these molecules have two endocyclic heteroatoms with pronounced donor abilities, e.g. S and N, and consequently possess significant coordination potential. Coordination polymers have been investigated mostly with respect to their properties and potential technological value in areas of catalysis, chirality, conductivity, luminescence, magnetism [7]. Discovery of the antitumor activity of *cis*-[Pt(NH₃)₂Cl₂] [8] aroused interest in synthesis of new metal(II) complexes which might show improved activity and lowered toxicity. Several platinum(II) complexes with

various derivatives of benzothiazole were investigated in order to find compounds that would be a good enough substitute to *cis*-[Pt(NH₃)₂Cl₂] [9–14].

As a part of our comprehensive investigation of the coordination chemistry of the 12th group metals with various benzothiazole derivatives [15–18] we undertook this investigation. In this paper, we report the synthesis, structural characterization of *cis*- and *trans*-2-(4-methoxystyryl)-1,3-benzothiazole and our results on coordinating ability of MeO-sbt towards zinc(II) ion. In addition we made a computational study on isomers **1a** and **1b** which have included equilibrium geometries optimization, vibrational analysis and consideration of isomerization process possibility.

2. Experimental

2.1. Materials and physical measurements

All reagents were supplied by Aldrich Chemical Co. and were used as received without further purification. The CHNS-microanalyses were performed by the Chemical Analytical Service of the Ruđer Bošković Institute, Zagreb. Infrared spectra were obtained from KBr pellets within the range 4000–400 cm⁻¹ with a Perkin-Elmer FTIR spectrometer 1600 Series. The one-dimensional ¹H and ¹³C spectra were recorded by a Bruker AV 600 spectrometer. Samples were measured in DMSO-*d*₆ solution and chemical shifts (ppm) were referred to TMS.

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2.2. Preparation of compounds

2.2.1. *cis*- and *trans*-2-(4-Metoxystyryl)-1,3-benzothiazole (MeO-sbt)

To a mixture of *p*-anisaldehyde (1.36 g, 10 mmol) and 2-methyl-1,3-benzothiazole (1.49 g, 10 mmol), anhydrous ZnCl₂ (0.5 g, 3.67 mmol) was added in one portion and heated for 3 h at 130 °C (Scheme 1). After cooling, the reaction mixture was triturated with petrol-ether (100 mL) and the obtained yellow solid was filtered off and crystallized from methanol. Yield: 1.9 g (70%), mp 140–142 °C (literature mp 145 °C) [19]. Anal. Calcd. for C₁₆H₁₃NOS (267.34): C, 71.87; H, 4.91; N, 5.24; O, 5.98; S, 11.99%. Found: C, 71.75; H, 4.96; N, 5.22; O, 5.89; S, 12.10%. IR data (KBr pellet, cm⁻¹): 3057(w), 3027(w), 2994(w), 2939(w), 2837(w), 1600(s), 1571(w), 1559(w), 1513(w), 1482(m), 1468(w), 1457(m), 1435(m), 1419(m), 1306(m), 1296(m), 1281(m), 1257(vs), 1233(s), 1219(m), 1192(m), 1174(vs), 1125(w), 1111(m), 1030(s), 1014(m), 963(m), 957(m), 932(w), 872(m), 859(w), 826(s), 809(s), 759(s), 729(s), 686(w), 664(w), 514(w), 466(w). ¹H NMR (300 MHz, DMSO-*d*₆): δ = 3.82 (s, 3H, H-OCH₃), 7.01 (t, 1H, *J* = 8.8 Hz, H-*Ph*), 7.42 (t, 1H, *J* = 8.1 Hz, H-*Bt*), 7.48 (d, 1H, *J* = 16.2 Hz, H-*CH*), 7.51 (t, 1H, *J* = 8.3 Hz, H-*Bt*), 7.62 (d, 1H, *J* = 16.2 Hz, H-*CH*), 7.74 (d, 2H, *J* = 8.7 Hz, H-*Ph*), 7.96 (d, 1H, *J* = 8.1 Hz, H-*Bt*), 8.07 (d, 1H, *J* = 8.1 Hz, H-*Bt*). ¹³C NMR (75 MHz, DMSO-*d*₆): 55.2 (q), 114.4 (d, 2C), 119.4 (d), 121.9 (d), 122.3 (d), 125.1 (d), 126.4 (d), 127.7 (s), 129.3 (d, 2C), 133.9 (s), 137.3 (d), 153.5 (s), 160.4 (s), 166.8 (s).

The recrystallization of the final product from the ethanol gave a few crystals of *cis*-2-(4-methoxystyryl)-1,3-benzothiazole **1a** of suitable quality for the X-ray experiment. Good quality single crystals of *trans*-2-(4-methoxystyryl)-1,3-benzothiazole **1b** were obtained unexpectedly by unsuccessful attempt of hydrothermal complexation of MeO-sbt and ZnBr₂ (see Section 2.2.5).

2.2.2. Preparation of ZnCl₂(MeO-sbt)₂ (**2**)

A solution of MeO-sbt (0.20 g, 0.75 mmol) in chloroform (5 mL) was added slowly to an ethanol solution of zinc chloride (0.05 g, 0.37 mmol in 10 mL). The reaction mixture was stirred and refluxed for 6 h then left at room temperature to evaporate. Obtained pale orange product was washed with small portions of benzene, filtered off and dried. Yield: 0.10 g (40%). Anal. Calcd. for C₃₂H₂₆ZnCl₂N₂O₂S₂ (671.03): C, 57.27; H, 3.91; N, 4.17; S, 9.56%. Found: C, 56.99; H, 3.85; N, 4.11; S, 9.67%. IR data (KBr pellet, cm⁻¹): 2926(w), 2836(w), 1598(vs), 1512(vs), 1466(w), 1455(w), 1436(m), 1308(w), 1287(w), 1255(s), 1202(w), 1172(s), 1111(w), 1027(m), 992(w), 955(m), 934(w), 817(m), 760(s), 728(w), 713(w), 690(w), 511(w).

2.2.3. Preparation of ZnBr₂(MeO-sbt)₂ (**3**)

A solution of MeO-sbt (0.30 g, 1.12 mmol) in chloroform (5 mL) was added slowly to an ethanol solution of zinc bromide (0.11 g, 0.49 mmol in 10 mL). The reaction mixture was stirred and refluxed for 12 h then left at room temperature to evaporate. Obtained orange product was washed with small portions of

benzene, filtered off and dried. Yield: 0.23 g (62%). Anal. Calcd. for C₃₂H₂₆ZnBr₂N₂O₂S₂ (759.93): C, 50.57; H, 3.45; N, 3.69; S, 8.44%. Found: C, 51.04; H, 3.46; N, 3.78; S, 8.30%. IR data (KBr pellet, cm⁻¹): 2927(w), 1622(w), 1596(vs), 1511(vs), 1464(m), 1435(m), 1286(w), 1256(vs), 1201(w), 1173(s), 1027(m), 953(w), 933(w), 816(m), 757(m), 727(m), 690(w), 545(w), 473(w).

2.2.4. Preparation of ZnI₂(MeO-sbt)₂ (**4**)

A solution of MeO-sbt (0.29 g, 1.08 mmol) in chloroform (5 mL) was added slowly to an ethanol solution of zinc iodide (0.16 g, 0.50 mmol in 10 mL). The reaction mixture was stirred and refluxed for 6 h then left at room temperature to evaporate. Obtained pale orange product was washed with small portions of benzene, filtered off and dried. Yield: 0.25 g (59%). Anal. Calcd. for C₃₂H₂₆ZnI₂N₂O₂S₂ (853.93): C, 45.00; H, 3.07; N, 3.34; S, 7.51%. Found: C, 45.37; H, 3.19; N, 3.28; S, 7.85%. IR data (KBr pellet, cm⁻¹): 2920(w), 2833(w), 1620(w), 1596(vs), 1512(vs), 1458(w), 14348(m), 1417(m), 1317(w), 1284(w), 1255(vs), 1203(w), 1171(s), 1111(w), 1031(m), 958(m), 948(m), 930(w), 814(m), 801(m), 756(s), 726(m), 690(m), 505(w).

2.2.5. Reaction of ZnBr₂ with MeO-sbt in hydrothermal conditions

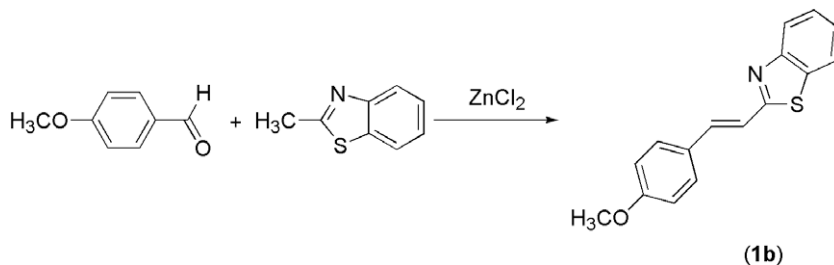
Suspension of zinc bromide (0.06 g, 0.27 mmol) and MeO-sbt (0.15 g, 0.56 mmol) in ethanol (20 mL) was sealed in a Teflon-lined stainless-steel vessel and heated for 5 h at 140 °C. After cooling, the mother liquor was left to stand at room temperature and in a few days pale yellow crystalline product was obtained. The crystals suitable for single crystal X-ray diffraction experiment were filtered off, washed with ethanol and dried. Attempt to obtain metal complex failed. Pale yellow product was proved to be *trans*-MeO-sbt **1b**.

2.3. X-ray crystal structure analysis

The general and crystal data and summary of intensity data collection and structure refinement for isomers **1a** and **1b** are collected in Table 1.

Data were collected at 296 K on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire-3 CCD detector, by applying CrysAlisPro Software system [20]. The compounds were measured with Mo K α radiation generated by a fine-focus sealed tube using a graphite monochromator. Scans were performed in ω and 1° frames were collected. A crystal-detector distance was 50 mm. Data reduction, including absorption correction, was done by CrysAlis RED program [20].

The structures were solved by direct methods implemented in the SHELXS-97 program [21]. The coordinates and the anisotropic thermal parameters for all non-hydrogen atoms were refined by the least-squares methods based on F^2 using SHELXL-97 program [21]. In each structure, the methylene and aromatic hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent C atom at distances of 0.93 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. The methyl H atoms were constrained to an



Scheme 1. Preparation of *trans*-MeO-sbt (**1b**).

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