

Contents lists available at ScienceDirect

Journal of Molecular Structure



journal homepage: www.elsevier.com/locate/molstruc

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

Marijana Đaković^a, Helena Čičak^b, Željka Soldin^a, Vesna Tralić-Kulenović^{c,*}

^a Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia ^b Laboratory of Organic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia ^c Department of Applied Chemistry, Faculty of Textile Technology, University of Zagreb, Prilaz baruna Filipovića 30, HR-10000 Zagreb, Croatia

ARTICLE INFO

Article history: Received 18 July 2009 Received in revised form 7 September 2009 Accepted 11 September 2009 Available online 18 September 2009

Keywords: cis- and trans-2-(4-Methoxystyryl)-1,3benzothiazole Zn complexes Crystal structure Weak interactions DFT and HF calculations

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-(4methoxystyryl)-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.

© 2009 Elsevier B.V. All rights reserved.

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

* Corresponding author.
 E-mail address: vtralic@ttf.hr (V. Tralić-Kulenović).

various derivatives of benzothiazole were investigated in order to find compounds that would be a good enough substitute to *cis*- $[Pt(NH_3)_2Cl_2]$ [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.

^{0022-2860/\$ -} see front matter @ 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2009.09.013

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 2methyl-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, / = 16.2 Hz, H-CH), 7.51 (t, 1H, / = 8.3 Hz, H-Bt), 7.62 (d, 1H, *I* = 16.2 Hz, H-CH), 7.74 (d, 2H, *I* = 8.7 Hz, H-Ph), 7.96 (d, 1H, *I* = 8.1 Hz, H-Bt), 8.07 (d, 1H, *I* = 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-metoxystyryl)-1,3-benzothiazole 1b were obtained unexpected by unsuccessful attempt of hydrothermal complexation of MeO-sbt and ZnBr₂ (see Section 2.2.5).

2.2.2. Preparation of $ZnCl_2(MeO-sbt)_2$ (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 $ZnBr_2(MeO-sbt)_2$ (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 $C_{32}H_{26}ZnI_2N_2O_2S_2$ (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 obtained 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 Ka radiation generated by a fine-focus sealed tube using a graphite monochromator. Scans were performed in ω and 1° frames were collected. A crystaldetector distance was 50 mm. Data reduction, including absorption correction, was done by CrysAlice 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).

Table 1

Crystal data and details of the structure refinement for 1a and 1b.

Complex	1a	1b
Empirical formula	C ₁₆ H ₁₃ NOS	C ₁₆ H ₁₃ NOS
Formula weight	267.34	267.34
Temperature [K]	296	296
Wavelength [Å]	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group		
a [Å]	6.6595(2)	9.5492(3)
b [Å]	8.4857(3)	9.9437(3)
c [Å]	12.2033(5)	15.0343(4)
αβ [°]	100.825(3)	106.374(3)
β [°]	101.872(4)	90.881(2)
γ [°]	92.942(3)	99.632(2)
Volume [Å ³]	659.95(4)	1347.41(7)
Ζ	2	4
$\rho_{\text{Calcd}} \left[\text{g/cm}^3 \right]$	1.345	1.318
F(0 0 0)	280	560
Crystal size [mm]	$0.13 \times 0.29 \times 0.41$	$0.31 \times 0.56 \times 0.59$
Reflections collected	14338	17731
Unique reflections	2885	4706
Parameters	173	346
$R_{1,\text{all data}}, R_1^a [I > 2\sigma(I)]$	0.0414; 0.0310	0.0586; 0.0495
$wR_{2,all data}, wR_2^b [I > 2\sigma(I)]$	0.0857; 0.0821	0.1316; 0.1261
g_1, g_2 in w^c	0.0464, 0.0387	0.0619; 0.7799
S ^d on F ²	1.067	1.026
$\Delta \sigma_{ m min/max}$ [e Å ⁻³] ^e	-0.16/0.19	-0.25/0.65

 $\begin{array}{l} {}^{a} \ R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. \\ {}^{b} \ wR = [\sum (F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}. \\ {}^{c} \ w = 1 / [\sigma^{2}(F_{o}^{2}) + (g_{1}P)^{2} + g_{2}P] \ where \ P = (F_{o}^{2} + 2F_{c}^{2})/3 \ . \\ {}^{d} \ S = \sum [w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})]^{1/2}. \end{array}$

ideal geometry [C—H = 0.96Å and $U_{iso}(H) = 1.5U_{eq}(C)$], but were allowed to rotate freely about the C–C bonds.

Graphical work has been performed by the programs ORTEP-3 for Windows [22] and Mercury 1.4.1 [23]. The thermal ellipsoids are drawn at the 50% probability level.

2.4. Computational methods

Density functional theory (DFT) and Hartree-Fock (HF) calculations were performed with the Gaussian 03 program package [24]. B3LYP and mPW1PW91 hybrid DFT methods with standard 6-311++G(d,p) and 6-311+G(2d,p) basis sets and tight convergence criteria were employed for the calculations of geometries of *cis*/ trans-isomers 1a and 1b. B3LYP uses Becke's three-parameter exchange functional and Lee, Yang and Parr's gradient-corrected correlation functional (B3LYP) [25] while mPW1PW91 uses the Perdew-Wang (1991) exchange functional as modified by Adamo and Barone and Perdew and Wang's (1991) gradient-corrected correlation functional [26]. 6-311++G(d,p) and 6-311+G(2d,p) are two valence triple zeta basis sets augmented with additional set(s) of diffuse and polarization functions.

The equilibrium molecular geometries of cis/trans-isomers 1a and 1b were fully optimized in vacuo and the harmonic vibrational analysis was performed at all used levels of theories to verify there are no imaginary vibrational frequencies and to confirm them as minima. In order to compare the calculated and experimental IR spectra, the calculated vibrational wavenumbers have been scaled by the factor 0.96 [27].

Hartree-Fock (HF) ab initio method [28] with 6-311+G(2d,p) basis set was used for the calculation of the transition state of cistrans isomerization. Transition structure was fully optimized in vacuo and the harmonic vibrational analysis gave one imaginary vibrational frequency, which confirms it as the first order saddle point. The intrinsic reaction coordinate (IRC) calculation [29] was also employed at the HF/3-21G level of theory (3-21G is valence double zeta basis sets) to confirm the connection of that transition sate with the two investigated isomers.

3. Results and discussion

3.1. Synthesis

Initially prepared MeO-sbt is *trans*-isomer what was concluded on only nine signals in ¹H NMR spectrum and IHC value of 16.2 Hz which is characteristic for trans spin-spin coupling of olefinic protons. A few crystals of cis-MeO-sbt 1a suitable for X-ray diffraction analysis were obtained by recrystallization from the ethanol solution. Good quality crystals of trans-MeO-sbt 1b were obtained unexpected from the reaction mixture of MeO-sbt and ZnBr₂ in hydrothermal conditions. Generally, zinc complexes were prepared by refluxing of chloroform solutions of corresponding zinc halide and MeO-sbt.

3.2. IR spectra

The IR spectral data for MeO-sbt and its zinc complexes exhibit very similar solid state IR spectra, so we could not unambiguously assign shifts of absorption bands due to metal coordination. Therefore, we can give just general assignation of absorption maxima according to the literature [30,31]. Absorption bands in the range of 1625–1400 cm⁻¹ can only be associated with olefinic double bond and overall ring-skeletal (benzene and thiazole ring) stretching modes. Ring breathing and CH in-plane deformations are observed in the range of $1330-930 \text{ cm}^{-1}$ and CH out-of-plane deformations fall into range 865-720 cm⁻¹. Absorption band at about 680 cm⁻¹ can be associated with C—S stretching frequency.

3.3. Structural description

A survey of the Cambridge Structural Database (CSD) accomplished on version 5.30 (including update 3, May 2009) [32] using ConOuest [33] (version 1.8) has revealed a total of seven entries that contain the 2-styryl-1,3-benzothiazole fragment. Apart from (benzo-15-crown-5)-1,3-benzothiazole [34], structurally characterized are unsubstituted 2-styryl-1,3-benzothiazole [18] and five of its derivatives with one, two and three substituents on phenyl group; 2-(N-carbazolylstyryl)styryl-1,3-benzothiazole [35], 2-(3,4-dimethoxystyryl)-1,3-benzothiazole [36], 2-(3,4-dichlorostyryl)-1,3-benzothiazole [37], 2-(2-bromo-5-nitrostyryl)-1,3-benzothioazole [38] and 2-(2,4-dichloro-5-nitrostyryl)-1,3benzothiazole monohydrate [39]. In all these, trans arrangement of benzothiazolyl and phenyl groups is found. To the best of our knowledge, 1 is the first 2-styryl-1,3-benzothiazole for which both geometric isomers are structurally characterized. The molecular and crystal structures of isomers 1a and 1b are depicted in Figs. 1 and 2 and the pertinent molecular geometry parameters are listed in Table 2.

The main differences in molecular geometries of two isomers, cis 1a and trans 1b, are observed in spatial orientation of the methoxyphenyl moieties. Furthermore, 1b crystallizes with two symmetrically independent molecules, the feature already observed in 2-(3,4-dimethoxystyryl)-1,3-benzothiazole [36] and 2-(2,4-dichloro-5-nitrostyryl)-1,3-benzothiazole monohydrate [39]. Two molecules of 1b (1: S11/N11/O11/C11-C16; 2: S21/N21/ O21/C21–C26) are both reasonably planar, with dihedral angles between the benzothiazolyl and methoxy-containing aryl rings with the olefinic groups of 9.0 (2) and 4.6 (2) $^{\circ}$ in (1), and 7.0 (2) and 6.2 (3)° in (2). Having cis- instead of trans-positioned benzothiazolyl and methoxyphenyl groups, the molecule of 1a is not planar so far. The planarity is retained only in vinyl-benzothiazole



Fig. 1a. The ORTEP-3 drawing of *cis*-2-(4-methoxystyryl)-1,3-benzothiazole **1a** with the atom numbering scheme of the asymmetric unit.



Fig. 1b. Perspective view of crystal packing of **1a**. Hydrogen bonds are presented by dashed lines.

part of molecule [dihedral angle: 7.4 (1)°], while the methoxy-containing aryl ring is turned out of the plane drawn through the rest of the molecule for 71.3 (1)°, probably due to minimization of steric repulsion. The benzothiazole moieties of all three molecules under consideration are almost ideally planar, with the largest deviations from the bt planes being that of the atoms S1 [0.0198(6) Å] in **1a**, C11 [0.043 (2) Å] and C21 [0.024 (2) Å] in **1b**.

In all three molecules, the two C—S bonds of the thiazole rings [e.g. S1—C1 and S1—C2 in **1a**, S11—C11 and S21—C21 in **1b**] differ with respect to each other, but both are within two border cases, single S—C [1.82 Å] and double S=C [1.56 Å] bond [40]. The bond angles around the S atom are within the range found in the five-membered thiazole rings of 2-styryl-1,3-benzothiazole and its



Fig. 2b. Perspective view of crystal packing of 1b. Hydrogen bonds are presented by dashed lines.

derivatives [18,34–39]. The differences in the C–C bonds within benzene ring are usual for such fused rings.

The olefinic C=C bond is somewhat shorter in **1b** [1.314 (4) and 1.303 (4) Å, in **1** and **2**, respectively] than in **1a** [1.325 (2) Å]. Furthermore, the values in both isomers are among the shortest of substituted (1.341 (2) and 1.342 (2) Å in [36]; 1.330 (6) Å in [37], 1.316 (5) Å in [38], 1.341 (8) and 1.340 (8) Å in [39]), but very close to the same in unsubstituted 2-styryl-1,3-benzothiazole (1.314 (4) Å in [18]).

In the crystal structures of both isomers hydrogen bonds are not pronounced. Moreover, no classic hydrogen bonds were found, only weak C–H···O and C–H···N hydrogen bonding and C–H··· π interactions are present. The details of geometries are given in Tables 3 and 4. In 1a, methoxy oxygen and thiazole nitrogen atoms act as hydrogen bond acceptors for vinyl (H9) and benzothiazole (H3) hydrogen atoms, respectively, forming acentric hydrogen bonded rings of the graph-set motif of $R_2^2(17)$. These rings are further fused to each other, thus forming endless supramolecular chains running in [100] direction. The crystal structure is additionally stabilized by only one weak C–H $\cdot \cdot \pi$ interaction between the methoxy-containing phenyl ring hydrogen atom (H14) and benzene π -system of the benzothiazole moiety. In **1b**, two symmetrically related molecules are interconnected by two identical C–H···N interactions forming centrosymmetrical $R_2^2(22)$ dimers [41,42] which are further fused by $R_4^4(16)$ rings forming extended 2D supramolecular sheets in (1-10) plane (Fig. 2c). Interestingly, there are no hydrogen bonds between symmetrically independent molecules. The weak C–H $\cdots \pi$ interactions are, as well, more pronounced in *trans* than in *cis*-isomer. These are mostly established



Fig. 2a. The ORTEP-3 drawing of trans-2-(4-methoxystyryl)-1,3-benzothiazole 1b with the atom numbering scheme of the asymmetric unit.



Fig. 2c. Hydrogen bond motifs of $R_2^2(22)$ and $R_4^4(16)$ formed between symmetrically related molecules.

between aromatic C–H groups and π -systems of fused benzene and phenyl rings.

3.4. Computational studies

Table 2

DFT calculations have been performed for the isomers **1a** and **1b** starting from their X-ray molecular structures. All three used

levels of theory, B3LYP/6-311++G(d,p), B3LYP/6-311+G(2d,p) and mPW1PW91/6-311+G(2d,p), gave geometries which are in good agreement with the X-ray structures. The average absolute deviations (AAD) of the theoretical structural parameters from experimental ones are given in Table 5. The mPW1PW91/6-311+G(2d,p) model gave the best geometries matching with AADs of 0.0090 Å, 0.486° and 4.02° for bond distances, valence angles

Selected bond distances (Å) and angles (°) for isomers 1a and 1b. Theoretical values are calculated at mPW1PW91/6-311+G(2d,p) level of theory.

<table-container>6-9-C31322(2)13400(1-9-19)1313(4)1-313(4)C1-C31.45(2)1.45(2)1.45(2)1.45(2)1.45(2)C1-C31.45(2)1.45(2)1.45(2)1.45(2)1.45(2)C1-C31.47(2)1.466(2)C19-C1101.46(3)1.45(2)S1-C11.75(3)1.72(2)1.72(3)1.72(3)1.72(3)S1-C21.72(1)1.72(2)1.73(2)1.73(2)1.73(2)N1-C11.28(2)1.297N11-C111.28(3)1.71(3)N1-C71.34(2)1.305N11-C171.40(3)1.71(3)N1-C71.34(2)1.352011-C1131.36(3)1.71(3)01-C131.36(1)1.352011-C1131.36(1)1.10(1)01-C141.34(2)1.4102011-C1141.40(2)1.10(2)01-C151.36(1)1.4102011-C1141.41021.10(2)01-C161.237(1)1.4102011-C111.41021.10(2)01-C171.36(1)1.4102011-C111.41021.10(2)01-C161.237(1)1.427(2)1.11021.12(2)1.12(2)01-C171.367(1)1.429(2)1.21(2)1.22(2)1.22(2)01-C171.367(1)1.429(2)1.21(2)1.22(2)1.22(2)01-C161.237(1)1.237(1)1.22(2)1.22(2)1.22(2)01-C171.367(1)1.237(1)1.22(2)1.22(2)1.22(2)01-C161.237(1)1.237(1)1.22(2)<th>Isomer 1a^a</th><th>Experimental</th><th>Theoretical</th><th>Isomer 1b^b</th><th>Experimental</th><th>Theoretical</th></table-container>	Isomer 1a ^a	Experimental	Theoretical	Isomer 1b ^b	Experimental	Theoretical
C1-C3L35(2)L36(2)C1-C381302(4)L3413C9-C10L45(2)L4664C1-C38L45(4)L464C9-C10L46(3)C19-C110L46(3)L4620C9-C10L372(1)L3620C19-C110L467(3)L4520S1-C1L78(1)L78(1)S11-C11T78(3)L4520S1-C2L28(1)L782(1)S11-C12L732(2)T732(2)N1-C1L392(2)L297N11-C11L28(3)L299N1-C7L384(2)L3705N11-C17L38(3)L299O1-C13L361(2)L352O11-C113L36(3)L397(3)O1-C14L42(2)L4102O11-C116L418(4)O1-C15L42(1)L4102O11-C116L418(4)O1-C16L42(1)L4102O11-C116L418(4)O1-C17N134(1)L1785C11-S11-C1282(1)O1-C16L42(1)L4102C11-S11-C1282(1)O1-C17N11,30(1)L4721S11-C11-C11N150(2)11.598S1-C1-C4N1-C1-C42106,12N1-C1N1-C1N1-C1S1-C1-C4L29,91(2)L20,926S11-C11-C11115,6211.499N1-C1-C4L29,91(2)L20,926S11-C11-C18L20,9211.499N1-C1-C4L29,91(2)L20,926S11-C21-C71106,1212.697N1-C1-C4L20,91(2)L20,926S11-C21-C71105,1212.697N1-C1-C4L20,91(2) <td>C8–C9</td> <td>1.325(2)</td> <td>1.3400</td> <td>C18–C19</td> <td>1.313(4)</td> <td></td>	C8–C9	1.325(2)	1.3400	C18–C19	1.313(4)	
C1-C3C1.451(2)1.459(4)(1-C181.454(4)1.444(4) $C9-C10$ 1.445(2)1.465(4)1.446(3)1.446(3)1.446(3) $C9-C10$ 1.467(3)1.467(3)1.450(3)1.50(3) $S1-C1$ 1.75(3)1.76(3)1.76(3)1.76(3) $S1-C2$ 1.75(1)2.162(1)1.73(2)1.73(2)1.73(2) $S1-C2$ 1.78(1)1.72(2)1.73(2)1.73(2)1.73(2) $N-C1$ 2.80(2)2.97(2)N1-C112.86(3)1.57(3) $N-C7$ 1.84(2)1.37(5)N1-C171.408(3)1.77(2) $N-C7$ 1.84(2)1.35(2)1.77(2)1.33(3)1.77(2) $O-C13$ 1.26(2)1.352(2)01-C1131.35(3)1.37(3) $O-C15$ 1.27(2)1.32(2)01-C1131.36(3)1.17(2) $O-C16$ 1.418(4)-01-C1161.418(4)-01-C116 $O-C16$ 1.27(2)1.28(1)1.17(2)1.18(1) $O-C16$ 1.28(1)1.17(2)1.18(1)1.18(1) $O-C1-C16$ 1.28(1)1.28(1)1.18(1)1.18(1) $O-C-C16$ 1.13(1)1.469721-C1-C1821.8(2)1.18(1) $N-C-C-C3$ 1.150(1)1.469721-C1-C181.8(2)1.18(1) $N-C-C-C3$ 1.150(1)1.469721-C1-C181.8(2)1.8(2) $N-C-C-C3$ 1.150(1)1.469721-C1-C181.8(2)1.8(2) $N-C-C-C3$ 1.150(1)1.469721-C2-C31.8(2)1.8(2)				C28–C29	1.302(4)	1.3413
C9-C101.447(2)1.4664C19-C101.46(3)1.462(3)C9-C101.467(3)1.452(3)1.452(3)1.452(3)S1-C11.758(1)1.758(1)1.732(3)1.732(3)1.732(3)S1-C21.728(1)1.732(3)1.732(3)1.732(3)1.732(3)S1-C21.728(1)1.292(2)1.297(3)1.712(3)1.288(3)1.295(3)N1-C11.84(2)1.705(3)N11-C171.488(3)1.295(3)1.718N1-C71.84(2)1.705(3)1.161(2)1.858(3)1.5071.507O1-C161.412(2)1.102011-C161.418(3)1.507O1-C161.412(1)1.102011-C161.418(3)1.109O1-C161.134(11)1.1785C11-N11-C1289.2(1)8.898C1-S1-C289.20(6)8.999C11-S11-C2289.2(1)8.898C1-S1-C21.134(11)1.1785C11-N11-C181.18(2)1.1598S1-C1-C81.237(10)1.14697311-C11-C181.18(2)1.1598S1-C1-C41.2387(10)1.12851.1-C11-C181.18(2)1.1598N1-C1-C61.299(1)1.2385N11-C11-C181.18(2)1.1598N1-C1-C61.299(1)1.293831-C12-C171.81(2)1.1598N1-C1-C61.299(1)1.293831-C12-C171.81(2)1.592N1-C1-C61.299(1)1.5254N11-C12-C181.81(2)1.5263N1-C1-C61.299(1)1.5254N11-C12-C181	C1-C8	1.451(2)	1.4504	C11–C18	1.454(4)	
G-C101.447(2)1.4664C1-C1101.467(3)1.4520S1-C11.758(1)1.7645S1-C111.758(3)1.767S1-C21.728(1)1.7324S1-C121.737(2)1.733N1-C11.288(1)1.732S1-C121.737(3)1.733N1-C11.288(2)1.2977N1-C111.288(3)1.2999N1-C71.384(2)1.705N1-C171.388(3)1.299901-C131.361(2)1.3523011-C1131.357(3)1.50701-C161.412(2)1.4102011-C1161.418(4)1.50901-C161.438(1)1.5071.5071.50901-C161.438(1)1.5091.5091.50901-C161.438(1)1.5091.5091.50901-C161.438(1)1.5091.5091.50901-C161.438(1)1.5091.5091.50901-C161.438(1)1.5091.5091.50901-C161.438(1)1.5091.5091.50901-C161.5091.1291.5191.51901-C161.5091.1291.5291.52901-C161.2091.6291.2291.52901-C161.2091.5291.5291.52901-C161.5091.5291.5291.52901-C161.5291.5291.5291.52901-C161.5291.5291.5291.52901-C161.5291.5291.5291.529				C21-C28	1.465(4)	1.4464
1-C1 $1.75(1)$ 1.764 1.714 $1.758(1)$ $1.758(1)$ $S1-C1$ $1.738(1)$ $1.738(1)$ $1.738(1)$ $1.766(1)$ $1.738(1)$ $S1-C2$ $1.728(1)$ $1.738(1)$ $1.738(1)$ $1.738(1)$ $1.738(1)$ $N1-C1$ $1.298(2)$ $1.297(2)$ $1.278(1)$ $1.278(1)$ $1.738(1)$ $N1-C1$ $1.384(2)$ $1.297(2)$ $1.278(1)$ $1.278(1)$ $1.278(1)$ $N1-C7$ $1.384(2)$ 1.3705 $N1-C1$ $1.48(3)$ $1.259(3)$ $O1-C16$ $1.381(2)$ 1.3207 $01-C13$ $1.389(3)$ 1.3718 $O1-C16$ $1.421(2)$ 1.402 $01-C16$ $1.418(3)$ 1.102 $O1-C16$ $9.206(1)$ 1.102 $01-C1-C2$ $802(1)$ 88.989 $C1-N1-C7$ $11.34(11)$ 11.785 $C1-N1-C7$ $10.6(2)$ 11.598 $S1-C1-N1$ $11.56(10)$ 11.4697 $S1-C1-N1$ $11.58(1)$ 11.598 $S1-C2-C3$ 2	C9–C10	1.447(2)	1.4664	C19–C110	1.466(3)	
S1-C11.78(1)1.7645S1-C11.78(3)1.7676S1-C21.78(1)1.73241.76121.73781.7732S1-C21.7371.73781.73781.7378N1-C11.289(2)1.2977N1-C11.286(3)1.2998N1-C71.384(2)1.3705N1-C11.286(3)1.299901-C131.361(2)1.3523011-C1131.35731.371801-C161.421(2)1.4102011-C1161.418(3)1.410201-C161.421(2)1.4102011-C1161.418(3)1.410901-C171.3523011-C1161.418(3)1.410901-C161.421(2)1.4102011-C1161.418(3)1.410901-C161.418(1)1.1785C11-S11-C128.32(1)8.99901-C1711.34(11)11.785C11-S11-C128.32(1)8.99901-C1711.34(11)11.785C11-S11-C128.32(1)8.99901-C1711.34(11)11.785C11-S11-C128.32(1)8.99901-C1711.34(11)11.785C11-S11-C128.32(1)8.99901-C1711.34(11)11.785C11-S11-C128.32(1)8.99901-C1711.34(11)11.785C11-S11-C128.32(1)8.99901-C1711.34(11)11.599S11-C12-C131.512(3)1.512(3)01-C1711.599S11-C12-C131.512(2)1.512(3)1.512(3)01-C1711.599S11-C12-C131.52(2)1.512(C29–C210	1.467(3)	1.4520
$\begin{array}{ c c c c c } & 1.728(1) & 1.7324 & 1.712(2) & 1.733(2) & 1.737(2) & 1.733(3) & 1.777(2) & 1.733(3) & 1.777(2) & 1.737(3) & 1.777(3) & 1.737(3) & 1.7777(3) & 1.777(3) & 1.777(3) & 1.777(3) & $	S1-C1	1.758(1)	1.7645	S11-C11	1.758(3)	
S1-C21.728(1)1.73241.1-C11.732(2)1.7338N1-C11.289(2)1.29771.73781.73841.7384N1-C11.289(2)1.3705N1-C11.286(3)1.2899N1-C71.384(2)1.3705N1-C171.380(3)1.271801-C131.361(2)1.3523011-C1131.357(3)1.571801-C161.421(2)1.4102011-C1161.418(3)1.410901-C161.421(2)1.4102011-C1161.418(3)1.410901-C1711.34(11)11.785C11-S11-C128.2(1)8.2(1)C1-S1-C28.920(6)8.9090C11-S11-C128.2(1)8.2(1)C1-N1-C711.34(11)11.785C11-N11-C1710.9721.565S1-C1-C812.387(10)12.4721S11-C11-C1812.12(2)1.251S1-C1-C812.98(10)11.4697S11-C12-C1812.12(2)1.251S1-C1-C812.99(12)12.0385S11-C12-C1312.02(2)1.251N1-C7-C312.90(1)12.328S11-C12-C1312.02(2)1.252S1-C2-C312.91(1)12.524N11-C17-C1210.51(2)1.25.02N1-C7-C411.49(1)11.5254N11-C17-C1211.51(2)1.25.02N1-C7-C512.57(1)12.5217N11-C17-C1211.52(2)1.5.62N1-C7-C612.57(1)15.521N11-C17-C1211.52(2)1.5.62N1-C7-C613.64(1)11.5951.21-C2-C2011.61(2)1.5.62 <td></td> <td></td> <td></td> <td>S21-C21</td> <td>1.766(3)</td> <td>1.7676</td>				S21-C21	1.766(3)	1.7676
N1-C1 1.737(2) 1.737(2) 1.738 N1-C1 1.298(2) 1.2977 N1-C1 1.298(3) 1.258(3) N1-C7 1.384(2) 1.3705 N1-C17 1.286(3) 1.258(3) 01-C13 1.361(2) 1.3523 01-C13 1.357(3) 1.357(3) 01-C16 1.421(2) 1.4102 011-C116 1.418(3) 1.359(3) 1.359(3) 01-C16 1.421(2) 1.4102 011-C116 1.418(3) 1.019(2) C1-S1-C2 8.920(6) 89.090 C1-S1-C12 89.2(1) 89.991 C1-S1-C2 8.920(6) 1.1785 C1-N1-C17 109.7(2) 100(2) 11.891 S1-C1-C8 1.36010 1.4697 S1-C1-C18 12.18(2) 12.25(2) 12.492 S1-C1-R1 1.506(10) 1.4697 S1-C1-C18 12.18(2) 12.25(2) 12.493 S1-C2-C3 1.205(10) 1.4697 S1-C1-C18 12.18(2) 12.267 S1-C2-C4 1.209.991 1.20.385 S1-C1-C18	S1-C2	1.728(1)	1.7324	S11-C12	1.723(2)	
N1-C11298(2)1297N11-C111278(3)1295N1-C11384(2)13705N11-C171408(3)125901-C131361(2)1352301-C1731350(3)1371801-C131361(2)1352301-C1131357(3)1357(3)01-C161412(2)1410201-C1161418(4)100001-C1789.20(6)89.090C1-S1-I-C1289.2(1)88.99C1-S1-C289.20(6)89.090C1-S1-I-C1289.2(1)88.99S1-C1-C81133(1)11.785C1-N1-C17109.7(2)11.598S1-C1-C8123.87(10)124.721S1-C1-I-C18121.8(2)122.432S1-C1-C8123.97(10)124.721S1-C1-N11116.5(2)14.893N1-C1-C8120.99(12)120.385S1-C1-2-R13126.2(2)124.921S1-C2-C3120.99(12)129.386S1-C1-2-C17109.(2)12.99(2)S1-C2-C41490(11)15254N1-C1-C16125.7(2)12.92(2)N1-C7-C618.4(1)17.993C13-C1-C17109.(2)15.2(2)N1-C7-C618.4(1)17.993C13-C1-C16128.7(2)11.52(2)C13-O1-C1618.4(1)17.993C13-C1-C1618.2(2)11.52(2)C13-O1-C1618.4(1)17.993C13-C1-C1611.8(2)11.52(2)C14-C13-O115.2(1)11.52(2)C14-C13-O111.52(2)11.52(2)C14-C13-O115.2(1)11.52(2)C14-C13-O111.52(2)11.52(2)<				S21-C22	1.737(2)	1.7338
Ni-C7 1.384(2) 1.3705 Ni-C77 1.286(3) 1.2959 0i-C13 1.36(2) 1.3523 01-C13 1.3573) 1.3507 0i-C16 1.42(12) 1.4102 01-C16 1.418(3) 1.4109 0i-C16 1.42(12) 1.4102 01-C16 1.418(3) 1.4109 C1-S1-C2 89.090 C11-S11-C12 89.2(1) 89.899 C1-NI-C7 11.33(1) 11.785 C1-N1-C17 109.7(2) 115.89 S1-C1-C3 2.87(10) 124.721 S1-C1-C18 124.8(2) 124.82 S1-C1-C4 2.98(1) 14.697 S1-C1-C18 124.8(2) 144.83 S1-C1-C3 1.99.0(1) 124.627 116.6(2) 144.83 S1-C1-C4 2.99.8(12) 20.385 Ni-C1-C18 124.8(2) 124.82 S1-C2-C3 1.99.9(12) 1.99.169 S11-C12-C18 124.8(2) 124.82 S1-C2-C4 1.99.4(9) 1.99.169 S11-C12-C18 124.8(2) 124.82 S1-C2-C4	N1-C1	1.298(2)	1.2977	N11-C11	1.278(3)	
NI-C7138(2)13705NII-C171408(3)01-C13136(2)13523011-C1131389(3)1371601-C16142(2)14102011-C1131357301-C16142(2)14102011-C1161418(4)C1-S1-C289.20(6)89.090C1-S1I-C1289.2(1)88.989C1-NI-C7111.34(11)11.785C1-NI-C17109.7(2)51-C1-C8123.87(10)124.721S11-C11-C18121.8(2)11.58851-C1-C8123.87(10)14.697S11-C11-C18121.8(2)14.893S1-C1-C8123.87(10)124.721S11-C11-C18121.8(2)14.893S1-C1-C8123.87(10)124.92111.56214.89312.675S1-C2-C3109.0(2)124.92111.56212.82712.675S1-C2-C3109.9(2)12.0385N11-C11-C1812.8(2)12.875S1-C2-C4109.0(2)12.939S11-C12-C1813.1(2)12.827S1-C2-C7109.4(9)12.938S11-C12-C1313.1(2)12.827S1-C2-C7109.4(9)12.524N11-C17-C1215.6(2)14.819N1-C7-C612.57/1212.5217N11-C17-C1215.6(2)15.2(2)N1-C7-C613.8(1)17.993C113-011-C12618.2(2)15.82C13-01-C1613.8(1)17.993C113-011-C12618.2(2)15.82C1-C3-C9-C1015.52C113-011-C12618.2(2)15.82				N21-C21	1.286(3)	1.2959
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-C7	1.384(2)	1.3705	N11-C17	1.408(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				N21-C27	1.389(3)	1.3718
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	01–C13	1.361(2)	1.3523	011–C113	1.357(3)	
01-C161421(2)1410201-C1161418(4)021-C2161418(3)14109021-C2289.20(6)89.090C11-S11-C1289.20(1)01-C171005(2)21-S21-C2289.20(1)89.89801-C171005(2)11.58821-S21-C221106(2)11.58851-C1-C8123.87(10)124.721S11-C11-C18121.8(2)122.43251-C1-R4123.87(10)14.697S11-C11-N111105(2)14.893N1-C1-C8123.87(10)120.385N11-C11-C18121.8(2)122.432S1-C1-R4129.9(2)129.308S11-C12-C13129.0(2)129.287S1-C2-C319.9(1)129.308S11-C12-C13129.0(2)129.287S1-C2-C7109.49(9)109.169S11-C12-C13129.0(2)129.287S1-C2-C7109.49(9)109.169S11-C12-C17100.1(2)159.202N1-C7-C6125.77(12)152.517N11-C17-C12115.1(2)115.426N1-C7-C6125.77(12)15.51C113-C11-C18128.(2)115.426C13-O1-C16125.77(12)12.517C113-C11-C18115.(2)115.426C14-C13-O115.3(1)11.993C113-O21-C226118.8(2)116.02C14-C13-O115.2(1)11.551C113-C11-C18115.2(1)115.2(1)115.2(1)C1-C13-O115.3(1)12.517C113-O21-C226118.8(2)116.02116.02C14-C13-O115.3(1)12.517C113-O11-C18115.2(1)115.2(1) </td <td></td> <td></td> <td></td> <td>021–C213</td> <td>1.356(3)</td> <td>1.3507</td>				021–C213	1.356(3)	1.3507
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	01–C16	1.421(2)	1.4102	011–C116	1.418(4)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				021–C216	1.418(3)	1.4109
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C1-S1-C2	89.20(6)	89.090	C11-S11-C12	89.2(1)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				C21-S21-C22	89.2(1)	88.989
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C1-N1-C7	111.34(11)	111.785	C11-N11-C17	109.7(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				C21-N21-C27	110.6(2)	111.598
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	S1-C1-C8	123.87(10)	124.721	S11-C11-C18	121.8(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				S21-C21-C28	122.5(2)	122.432
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	S1-C1-N1	115.06(10)	114.697	S11-C11-N11	116.5(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				S21-C21-N21	115.6(2)	114.893
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	N1-C1-C8	120.98(12)	120.385	N11-C11-C18	121.7(3)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				N21-C21-C28	121.8(2)	122.675
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	S1-C2-C3	129.17(10)	129.308	S11-C12-C13	129.0(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				S21-C22-C23	130.1(2)	129.287
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	S1-C2-C7	109.49(9)	109.169	S11-C12-C17	109.1(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				S21-C22-C27	108.5(2)	109.094
$\begin{array}{cccccccccccccc} & & & & & & & & & & & & $	N1-C7-C2	114.90(11)	115.254	N11-C17-C12	115.5(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				N21-C27-C22	116.1(2)	115.426
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-C7-C6	125.77(12)	125.217	N11-C17-C16	125.7(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				N21-C27-C26	124.6(2)	125.202
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C13-01-C16	118.4(1)	117.993	C113-011-C126	118.8(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				C213-021-C226	118.2(2)	118.164
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C12-C13-01	115.3(1)	115.951	C112-C113-011	115.5(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				C212-C213-021	115.8(2)	116.025
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C14-C13-01	125.2(1)	124.573	C114-C113-011	125.3(2)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				C214-C213-021	124.9(2)	124.577
C21-C28-C29-C210 -176.3(2) 180.000 S1-C1-C8-C9 -4.3(2) -11.951 S11-C11-C18-C19 5.3(4) S21-C21-C28-C29 -4.7(4) 0.000 C8-C9-C10-C11 116.7(2) 133.645 C18-C19-C110-C111 177.5(2) C14-C13-01-C16 1.4(2) 0.515 C114-C113-011-C116 0.7(3) C214-C213-021-C216 -6.1(3) 0.000	C1-C8-C9-C10	-5.7(3)	-7.952	C11-C18-C19-C110	177.1(2)	
S1-C1-C8-C9 -4.3(2) -11.951 S11-C11-C18-C19 5.3(4) S21-C21-C28-C29 -4.7(4) 0.000 C8-C9-C10-C11 116.7(2) 133.645 C18-C19-C110-C111 177.5(2) C14-C13-01-C16 1.4(2) 0.515 C114-C113-011-C116 0.7(3) C214-C213-021-C216 -6.1(3) 0.000				C21-C28-C29-C210	-176.3(2)	180.000
S21-C21-C28-C29 -4.7(4) 0.000 C8-C9-C10-C11 116.7(2) 133.645 C18-C19-C110-C111 177.5(2) C14-C13-O1-C16 1.4(2) 0.515 C114-C113-O11-C116 0.7(3) C14-C13-O21-C216 -6.1(3) 0.000	S1-C1-C8-C9	-4.3(2)	-11.951	S11-C11-C18-C19	5.3(4)	
C8-C9-C10-C11 116.7(2) 133.645 C18-C19-C110-C111 177.5(2) C14-C13-O1-C16 1.4(2) 0.515 C114-C113-O11-C116 0.7(3) C214-C213-O21-C216 -6.1(3) 0.000		. ,		S21-C21-C28-C29	-4.7(4)	0.000
C14-C13-O1-C16 1.4(2) 0.515 C28-C29-C210-C211 -175.4(3) 180.000 C114-C113-O11-C116 0.7(3) C214-C213-O21-C216 -6.1(3) 0.000	C8-C9-C10-C11	116.7(2)	133.645	C18-C19-C110-C111	177.5(2)	
C14-C13-O1-C16 1.4(2) 0.515 C114-C113-O11-C116 0.7(3) C214-C213-O21-C216 -6.1(3) 0.000				C28-C29-C210-C211	-175.4(3)	180.000
C214–C213–O21–C216 –6.1(3) 0.000	C14-C13-O1-C16	1.4(2)	0.515	C114-C113-011-C116	0.7(3)	
				C214-C213-O21-C216	-6.1(3)	0.000

 $^{^{}a}$ The average absolute deviations of the theoretical bond distances of benzene ring in methoxyphenyl moiety is 0.0099 Å and in benzothiazole moiety is 0.0060 Å.

^b The average absolute deviations of the theoretical bond distances of benzene ring in methoxyphenyl moiety is 0.0073 Å and in benzothiazole moiety is 0.0079 Å.

 Table 3

 Hydrogen-bonding (Å and °) for isomers 1a and 1b.

D—H···A	D—H	Н…А	D…A	∠DHA	Symmetry code
Isomer 1a C3−H3…N1 C9−H9…O1	0.93	2.64 2.71	3.534(2) 3.395(2)	165 131	x + 1, y, z x - 1, y, z
<i>Isomer</i> 1b C19–H19…S11 C29–H29…S21 C15–H15…O11 C25–H25…O21 C116–H16A…N11	0.93 0.93 0.93 0.93 0.93 0.96	2.69 2.75 2.65 2.57 2.64	3.148(3) 3.195(3) 3.445(3) 3.426(3) 3.549(3)	112 110 144 153 158	x = 1, y, z $-$ $-$ $x, y, -1 + z$ $x, y, -1 + z$ $-x - y, 1 - z$
C216—H21B···N21	0.96	2.58	3.428(4)	148	1 - x, -y, 1 - z

and dihedral angles, respectively. These structures and selected structural parameters are shown in Fig. 3 and Table 2, respectively. The small differences between X-ray and calculated structures are consequence of different states of matter: during the theoretical calculation single isolated molecule is considered *in vacuo*, while many molecules are treated in solid state during X-ray diffraction. However, all the calculated geometric parameters, obtained by three used models, represent good approximations and they can be applied as groundwork for prediction and exploring the other properties of the isomers.

Trans-isomer **1b** is planar (C_s point group), while *cis*-isomer **1a** has no symmetry (C_1 point group). The energy difference between

Table 4

C–H··· π interactions for isomers **1a** and **1b**.

the two isomers is within 24.0 and 25.6 kJ/mol depending on the calculation model, whereas the *trans*-isomer **1b** is more stable one. The thermal *cis-trans* isomerization in the singlet ground state does not occur at the room temperature. The energy barrier for rotation around the olefinic double C-C bond is very high (296.2 kJ/mol at HF/6-311+G(2d,p) level of theory related to the *trans*-isomer **1b**) mostly due to the π -bond breaking. Earlier investigations showed that such torsional pathway in stilbene derivatives was the only possible thermal isomerization mechanism [43]. The corresponding transition structure is shown in Fig. 4. The dihedral angle amounts 106.49°. The harmonic normal mode calculation of transition structure gave imaginary frequency of 1440i cm⁻¹. The π -bonds of both isomers and frontier orbitals (HOMO and LUMO) of transition state for rotation process are shown in Fig. 5. The possibility of photochemical isomerization was not considered in this study.

The theoretical IR spectra of two isomers and the comparison with the experimental FTIR spectrum of initial reaction product MeO-sbt are shown in Fig. 6(a-c). Generally, calculated spectra of both isomers are very similar. In the region above 1700 cm⁻¹ spectra are simple and only C—H bond stretching bands around 3000 cm^{-1} are present. The region below 1700 cm^{-1} is much more complicated because it consists of stretching and bending vibrations bands. Bands around the 1600 cm^{-1} correspond to the C=C stretching vibrations. In the region below 1600 cm^{-1} , which is mostly fingerprint region, calculated spectra show only few differ-

C—H····Cg ^a	H···Cg	γ ^b (°)	C—H···Cg (°)	C···Cg (Å)	Symmetry operation on Cg
<i>lsomer</i> 1a C14–H14····Cg(C2 → C7)	2.97	9.11	144	3.765(2)	<i>x</i> , −1 + <i>y</i> , <i>z</i>
Isomer 1b					
C116—H12B····Cg(S21, N21, C21, C22, C27)	2.98	17.11	154	3.861(3)	1 - x, -y, 1 - z
$C13-H13\cdots Cg(C210 \rightarrow C215)$	2.98	20.93	126	3.609(3)	1 - x, 1 - y, 1 - z
$C23-H23\cdots Cg(C12 \rightarrow C17)$	2.68	7.97	136	3.410(3)	1 + x, y, z
$C26-H26\cdots Cg(C12 \rightarrow C17)$	2.96	12.31	135	3.681(3)	x, y, z
C111—H111····Cg(S21, N21, C21, C22, C27)	2.82	11.36	130	3.488(2)	1 - x, 1 - y, 1 - z
$C112-H112\cdots Cg(C22 \rightarrow C27)$	2.98	6.49	126	3.605(2)	1 - x, $1 - y$, $1 - z$
$C211 - H211 \cdots Cg(C110 \rightarrow C115)$	2.85	5.27	130	3.519(2)	1 + x, y, z

^a Centre of gravity of the aromatic ring. C–H··· π interactions are selected on criteria H···Cg < 3.4 and γ < 30°.

^b γ = angle defined by a line connecting centre of gravity of the aromatic ring with H atom and the normal to the aromatic ring.

Table 5

Average absolute deviations of theoretical structural parameters from the experimental ones.

	B3LYP/6-311++G(d,p)	B3LYP/6-311+G(2d,p)	mPW1PW91/6-311+G(2d,p)
Bonds/Å	0.0137	0.0121	0.0090
Valence angles/°	0.564	0.552	0.486
Dihedral angles/°	4.58	4.43	4.02



Fig. 3. Optimized structures at mPW1PW91/6-311+G(2d,p) level of theory of isomers 1a (a) and 1b (b).



Fig. 4. Optimized structure of transition state at HF/6-311+G(2d,p) level of theory (two different views).



Fig. 5. π-Bonds (HOMO) of isomer 1a (a) and isomer 1b (b). Frontier orbitals of transition state (HOMO (c) and LUMO (d)) for rotation around central C–C bond. (MO surface isovalue = 0.02).

ences each other (marked by small orange circles in Fig. 6(c)) and most of the corresponding bands are present in the experimental spectrum. The only exception is band at 1370 cm^{-1} in *cis*-isomer **1a** which is not found in experimental spectrum. This band corresponds to the H–C=C–H synchronous in-plane bending (wag-ging). Analogous band in *trans*-isomer **1b** is observed at 1215 cm^{-1} (also marked in Fig. 6(c). The rest of the marked bands at 995, 677, 648 and 474 cm⁻¹ correspond to the in-plane bendings involving *trans*-olefinic double bond.

By calculated IR spectra and their comparison with experimental FTIR, it has been confirmed that experimental spectrum belongs to *trans*-isomer **1b**.

4. Conclusion

The crystal structures of two isomorphs **1a** and **1b** are determined by X-ray diffraction analysis at room temperature and their molecular structures are confirmed by DFT calculations. Apart from being only *cis* and *trans*, main difference between two isomers is observed in spatial orientation of methoxyphenyl moieties. While *trans* **1b** is essentially planar, in *cis* **1a** methoxy-containing aryl ring closes the dihedral angle of 71° with the rest of the molecule. In both, **1a** and **1b**, weak C—H···O, C—H···N and C—H··· π interactions are found to be main supramolecular tool in crystal formation. Transition state for thermal *cis*–*trans* isomerization in the singlet ground state was calculated. Calculations showed that barrier for that interconversion is too high to occur at the room temperature, mostly due to the π -bond breaking. Comparison of calculated and experimental IR spectra was also made, which gave confirmation that *trans*-isomer **1b** was initially synthesized. *Cis*-isomer **1a** was prepared by recrystallization of **1b** from ethanol.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 739225 for complex **1a** and 739226 for complex **1b**. Copies of this information may be obtained from the Director, CCDC, 12



Fig. 6a. Unscaled calculated IR spectra of isomers 1a (cis-calc) and 1b (trans-calc).



Fig. 6b. Experimental FTIR spectrum of MeO-sbt (exp).



Fig. 6c. Scaled calculated IR spectra of isomers 1a (cis-calc) and 1b (trans-calc) and experimental FTIR spectrum of MeO-sbt (exp) in the 1750-450 cm⁻¹ region. (Larger differences between cis-calc and trans-calc are marked by small orange circles.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or website: http://www.ccdc. cam.ac.uk).

Acknowledgements

This research was supported by Ministry of Science, Education and Sports of the Republic of Croatia (Grant Nos. 119-1193079-1332, 119-1191342-1339 and 117-0000000-3283).

References

- [1] R.H. Goldfarb, R.P. Kitson, K.W. Yoshino, N. Horohita, Y. Kotera, Y. Inoue, M. Ohashi, Anticancer Res. 19 (1999) 1663.
- E.A. Sener, O.T. Arpaci, I. Yalcin, N. Altanlar, Farmaco 55 (2000) 397.
- A.B. Nadkarn, R.V. Kamath, G.B. Khadse, Indian J. Heterocycl. Chem. 9 (2000) [3] 309
- L. Racané, V. Tralić-Kulenović, L. Fišer-Jakić, D.W. Boykin, G. Karminski-Zamola, [4] Heterocycles 55 (2001) 2085.
- [5] I. Petkov, T. Deligeorgiev, I. Timtcheva, Dyes Pigments 35 (1997) 171.
 [6] H.Y. Fu, X.Y. Sun, X.D. Gao, F. Xiao, B.X. Shao, Synthetic Metals 159 (2009) 254. C. Janiak, Dalton Trans. (2003) 2781.
- B. Rosenberg, L. Van Camp, J.E. Trosko, V.H. Mansour, Nature 222 (1969) 385.
- [9] J.A. Muir, G.M. Gomez, M.M. Muir, O. Cox, M.E. Cadiz, Acta Crystallogr. C43 (1987) 1258
- [10] J.A. Muir, G.M. Gomez, M.M. Muir, M.E. Cadiz, O. Cox, Acta Crystallogr. C44 (1988) 803.
- G.M. Gomez, M.M. Muir, J.A. Muir, O. Cox, Acta Crystallogr. C44 (1988) 1554. [11]
- [12] M.M. Muir, G.M. Gomez, M.E. Cadiz, J.A. Muir, Inorg. Chim. Acta 168 (1990) 47.
- [13] C.M. Lozano, M.M. Muir, X. Tang, Y. Li, J. Chem. Crystallogr. 24 (1994) 639. C.M. Lozano, O. Cox, M.M. Muir, J.D. Morales, J.L. Rodríguez-Cabán, P.E. Vivas-[14]
- Mejía, F.A. Gonzales, Inorg. Chim. Acta 271 (1998) 137.
- [15] Z. Popović, D. Mrvoš-Sermek, Ž. Soldin, V. Tralić-Kulenović, Acta Crystallogr. C57 (2001) 20.
- [16] Z. Popović, Ž. Soldin, G. Pavlović, D. Matković-Čalogović, D. Mrvoš-Sermek, M. Rajić-Linarić, Struct. Chem. 13 (5/6) (2002) 425. [17] Z. Popović, G. Pavlović, Ž. Soldin, V. Tralić-Kulenović, L. Racané, Acta
- Crystallogr. C59 (2003) m4.
- [18] G. Pavlović, Ž. Soldin, Z. Popović, V. Tralić-Kulenović, Polyhedron 26 (2007) 5162.
- [19] S. Ried, J.L. Hinschung, Ann. Chem. 600 (1956) 47.
- [20] Oxford Diffraction, CrysAlisPro Version 171.32, Oxford Diffraction Ltd., Abingdon, Oxfordshire, England, 2007.
- G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
- [22] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
- [23] I.J. Bruno, J.C. Cole, P.R. Edgington, M.K. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr. B58 (2002) 389.
- [24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al., Gaussian 03, Revision C02, Gaussian Inc., Pittsburgh, PA, 2004.
- [25] R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989.
- [26] (a) C. Adamo, V. Barone, J. Chem. Phys. 108 (1998) 664;
- (b) B.J. Lynch, Y. Zhao, D.G. Truhlar, J. Phys. Chem. A 107 (2003) 1384.
- [27] Available from: http://cccbdb.nist.gov/
- [28] C.C.J. Roothaan, Rev. Mod. Phys. 23 (1951) 69.
- [29] K. Fukui, Acc. Chem. Res. 14 (1981) 363.
- [30] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1964.
- [31] C.N.R. Rao, R. Venkataraghavan, Can. J. Chem. 42 (1964) 43.
- [32] H.F. Allen, W.D.S. Motherwell, Acta Crystallogr. B58 (2002) 380.
- [33] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kesser, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr. B58 (2002) 389.
- [34] S.P. Fedorov, O.A. Fedorova, E.N. Andryukhina, S.P. Gromov, M.V. Alfimov, L.G. Kuzmina, J.A.K. Howard, J.-J. Aaron, New J. Chem. 27 (2003) 280.
- [35] D.-X. Cao, Q. Fang, D. Wang, Z.-Q. Liu, G. Xue, G.-B. Xu, W.-T. Yu, Eur. J. Org. Chem. (2003) 3625.
- [36] L.G. Kuzma, O.A. Fedorova, E.N. Andryukhina, M.M. Mashura, S.P. Gromov, M.V. Alfimov, Kristallographiya (Russ.) (Crystallogr. Rep.) 51 (2006) 467.
- [37] J. Yin, P. Kumar, J.R. Dimmock, J.W. Quail, Acta Crystallogr. C51 (1995) 2700. [38] J.A. Muir, O. Cox, L.A. Bernerd, M.M. Muir, J. Crystallogr. Specrtrosc. Res. 22
- (1992) 695.
- [39] O. Cox, M. Cordero, S. Pineiro, S.D. Huang, Acta Crystallogr. C53 (1997) 310.
- [40] N. Trinajstić, Tetrahedron Lett. 12 (1968) 1529.
- [41] J. Bernstein, R.E. Davies, L. Shimoni, N.-L. Chang, Angew. Chem. Int. Ed. Engl. 34 (1995) 1555.
- [42] M.C. Etter, Acc. Chem. Res. 23 (1990) 120.
- [43] A. Cembran, F. Bernardi, M. Garavelli, L. Gagliardi, G. Orlandi, J. Am. Chem. Soc. 126 (2004) 3234.