

Two Isomeric Fourteen-Membered Bis-dithioacetals Derived from (*Z*)- and (*E*)-But-2-ene-1,4-dithiols

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Abstract—(*Z*)-But-2-ene-1,4-dithiol was found to undergo isomerization into the *E* isomer. Condensation of (*Z*)- and (*E*)-but-2-ene-1,4-dithiols with acetaldehyde gave isomeric fourteen-membered bis-dithioacetals whose structure was determined by X-ray analysis.

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The formation of monomeric and dimeric cyclic dithio acetals, as well as of polymeric products, is determined by the nature of initial α,ω -dithiol and carbonyl compound [1], and macrocyclic compounds with short hydrocarbon bridges between sulfur atoms are difficultly accessible [2]. While studying seven-membered unsaturated dithioacetals [3], we found that the condensation of but-2-ene-1,4-dithiol with acetaldehyde, apart from previously reported 2-methyl-1,3-dithiacyclohept-5-ene (**I**) [4], gives two minor products **II** and **III** which were isolated in low yields (2 and 3%, respectively; Scheme 1). The ¹H and ¹³C NMR spectra of compounds **I–III**, recorded at low temperature, are fairly similar; the spectra indicated the presence of CH₂CH=CHCH₂ and CH₃CH fragments in their molecules. According to the X-ray diffraction data, com-

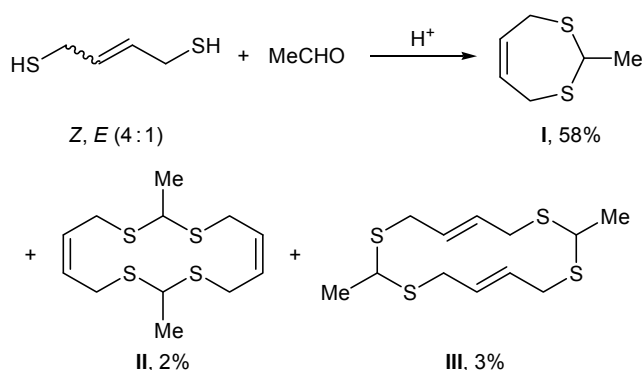
pounds **II** and **III** are fourteen-membered bis-dithioacetals [5]. The formation of macrocyclic compound **II** might be expected [1], while the presence in the reaction mixture of its isomer **III** with *E* configuration at the double bond is difficult to predict and therefore special comment is necessary.

Obviously, bis-dithioacetal **III** could be formed only as a result of condensation of (*E*)-but-2-ene-1,4-dithiol with acetaldehyde. Stereochemical ¹H NMR analysis [6] showed that the source of (*E*)-but-2-ene-1,4-dithiol is the corresponding *Z* isomer (which undergoes isomerization on storage as neat liquid) rather than (*Z*)-but-2-ene-1,4-diol, (*Z*)-1,4-dichlorobut-2-ene, and the corresponding dithioacetate [7].

Molecule **II** is oriented along the 2₁ axis, so that only a half of the molecule is independent (Fig. 1). The bond lengths and bond angles therein are within the corresponding standard values. According to [8], the heteroring conformation should be represented as [2525] with equatorial orientation of the methyl groups. Comparison of the molecular structures of compound **II** and isomeric tetrathiadiene with sulfur atoms at the double bonds [9] shows their essential similarity. An exception is the transannular distance between the *sp*²-carbon atoms, which is longer by 0.48 Å in molecule **II**.

Analysis of intermolecular interactions revealed neither shortened contacts nor hydrogen bonds in the crystalline structure of *cis*-tetrathiadiene **II**. However,

Scheme 1.



weaker interactions (as in its isomer [9]) give rise to cylindrical structures oriented along the *b* crystallographic axis (Fig. 2).

Isomer **III** with *trans*-configured double bonds was found to exist in crystal as three independent molecules with insignificantly differing geometric parameters in a unit cell. Each independent molecule has [124124] ring conformation (Fig. 3) with equatorial orientation of the methyl groups. The mode of crystal packing of compound **III** radically differs from that found for *cis* isomer **II**. Due to differences in geometric parameters, the three molecules in a unit cell are not parallel to each other, which leads to reduced symmetry, and no cylindrical structures are formed. On the other hand, all independent molecules give rise to a zigzag layer along the *ac* plane (Fig. 4), and the crystal packing of **III** is characterized by the presence of 14.4-Å³ cavities.

Analysis of intermolecular interactions revealed shortened S...S contacts with an interatomic distance of 3.40 Å which is considerably shorter than the sum of the van der Waals radii (3.70 Å). In addition, C-H...S contacts exist in crystal. It should be noted that short sulfur-sulfur contacts in the crystalline structure of sulfur-containing heterocycles constitute a necessary but insufficient condition for conducting properties [9, 10].

Undoubtedly, the transformation of (*Z*)-but-2-ene-1,4-dithiol into the *E* isomer attracts particular interest. According to our preliminary data, fourteen-membered unsaturated bis-dithioacetals with *E* configuration of the olefinic fragments are also formed from benzaldehyde and pivalaldehyde.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400.13 and 100.61 MHz, respectively, using hexamethyldisiloxane as reference. The mass spectrum (electron impact, 70 eV) was obtained on a Finnigan MAT-212 instrument with direct sample admission into the ion source.

X-Ray analysis of single crystals of **II** and **III** was performed at the Collective Use Center (Spectral Analytical Center at the Diffraction Methods Laboratory, Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences) on a Smart Apex II CCD diffractometer (λMoK_α irradiation). The structures were solved by the direct method using SIR program [11] and were refined first in isotropic and then in anisotropic approximation

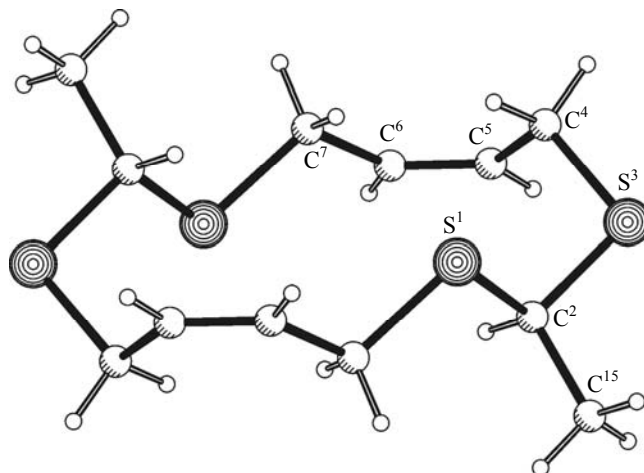


Fig. 1. Structure of the molecule of *trans*-2,9-dimethyl-(5*Z*,12*Z*)-1,3,8,10-tetrathiacyclotetradeca-5,12-diene (**II**) in crystal according to the X-ray diffraction data.

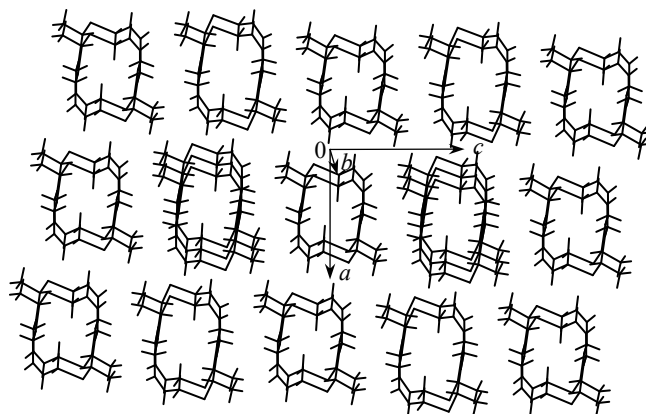


Fig. 2. Crystal packing of *trans*-2,9-dimethyl-(5*Z*,12*Z*)-1,3,8,10-tetrathiacyclotetradeca-5,12-diene (**II**).

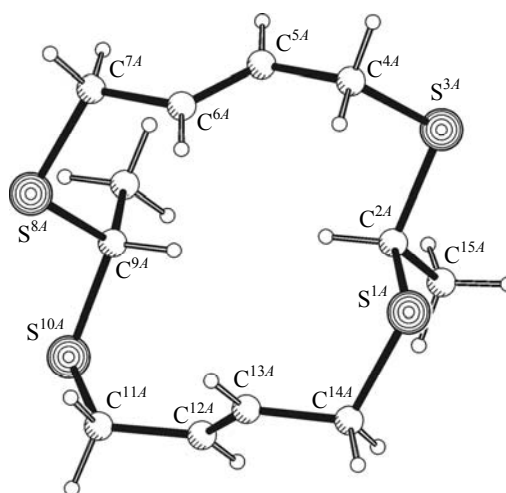


Fig. 3. Structure of the molecule of *trans*-2,9-dimethyl-(5*E*,12*E*)-1,3,8,10-tetrathiacyclotetradeca-5,12-diene (**III**) in crystal according to the X-ray diffraction data. Only one of three independent molecules is shown.

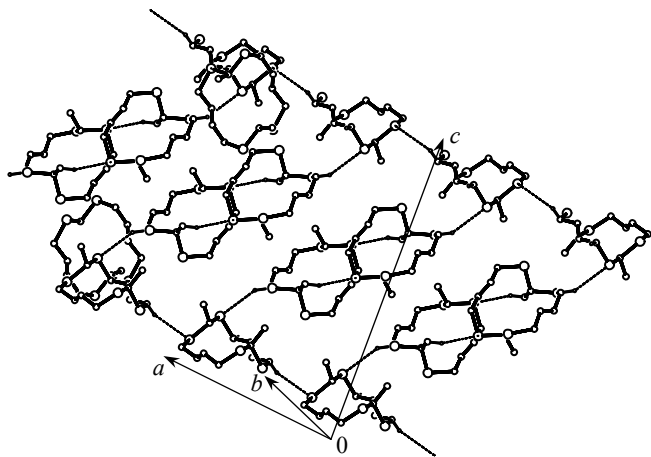


Fig. 4. Crystal packing of *trans*-2,9-dimethyl-(5*E*,12*E*)-1,3,8,10-tetrathia-cyclotetradeca-5,12-diene (**III**) via short S...S and C-H...S contacts. Only hydrogen atoms involved in intermolecular interactions are shown.

using SHELXL97 [12] and WinGX [13]. Intermolecular contacts were analyzed with the aid of PLATON software [14].

Compound II: colorless prisms, monoclinic crystal system, $C_{12}H_{20}S_4$, M 292.56; $a = 8.695(2)$, $b = 5.3967(13)$, $c = 16.097(4)$ Å; $\beta = 96.330(5)^\circ$; $V = 750.7(3)$ Å³; $d_{\text{calc}} = 1.294$ g/cm³; $Z = 2$; space group $P2_1/n$; φ - and ω -scanning; 5633 independent reflections were measured, 1230 of which were characterized by $I > 2\sigma(I)$.

Compound III: colorless prisms, triclinic crystal system, $C_{12}H_{20}S_4$, M 292.56; $a = 9.2411(7)$, $b = 12.812(1)$, $c = 21.5619(16)$ Å; $\alpha = 74.964(1)$, $\beta = 88.291(1)$, $\gamma = 78.874(1)^\circ$; $V = 2418.6(3)$ Å³; $d_{\text{calc}} = 1.205$ g/cm³; $Z = 6$; space group $P-1$; φ - and ω -scanning; 19929 independent reflections were measured, 5800 of which were characterized by $I > 2\sigma(I)$. The coordinates of hydrogen atoms were calculated on the basis of stereochemical considerations and were refined according to riding model. The crystallographic data for compounds **II** and **III** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 713524 and CCDC 713525, respectively).

***trans*-2,9-Dimethyl-(5*Z*,12*Z*)-1,3,8,10-tetrathia-cyclotetradeca-5,12-diene (II).** A solution of 1.54 g (12.8 mmol) of a mixture of isomeric (*Z*)- and (*E*)-but-2-ene-1,4-dithiols (4:1), 2.82 g (64 mmol) of acetaldehyde, and a catalytic amount of *p*-toluenesulfonic acid in 50 ml of benzene was heated under reflux in a flask equipped with a Dean–Stark trap. The mixture was washed with a 10% aqueous solution of sodium hydroxide and water and dried over MgSO₄. Yield 0.03 g (2%). Colorless crystals, mp 184–186°C (from

ethanol). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.61 d (6H, CH₃, ³ $J = 6.7$ Hz), 3.47 m (8H, CH₂), 3.95 q (2H, CH, ³ $J = 6.7$ Hz), 5.58 m (4H, CH=). ¹³C NMR spectrum (CDCl₃), δ_c , ppm: 21.52 (CH₃), 28.11 (CH₂), 43.77 (CH), 126.88 (=CH). Found: m/z 292 [M]⁺. $C_{12}H_{20}S_4$. Calculated: M 292.7

***trans*-2,9-Dimethyl-(5*E*,12*E*)-1,3,8,10-tetrathia-cyclotetradeca-5,12-diene (III).** The mother liquor was concentrated, and the residue was recrystallized from ethanol. Yield 0.05 g (3%). Colorless crystals, mp 94–96°C. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.52 d (6H, CH₃, ³ $J = 8.0$ Hz), 3.26 m (8H, CH₂), 3.69 q (2H, CH, ³ $J = 8.0$ Hz), 5.46 m (4H, CH=). ¹³C NMR spectrum (CDCl₃), δ , ppm: 21.14 (CH₃), 33.81 (CH₂), 38.93 (CH), 129.72 (=CH). Found, %: C 48.72; H 6.79. $C_{12}H_{20}S_4$. Calculated, %: C 49.27; H 6.89.

The subsequent recrystallization from ethanol gave 1.08 g (58%) of dithioacetal **I**. Its ¹H NMR spectrum was identical to that reported in [4]; mp 35–36°C [4].

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