NATURE OF THE ISOMERIZATION AND STRUCTURE OF THE ISOMERS OF 4-BENZYL-2,3-5,6-BIS(TETRAMETHYLENE)-4H-THIOPYRAN AND 3,4-BENZO-5,9-7,8-BIS(TETRAMETHYLENE)-6-THIATRICYCLO-[1.3.3]NON-7-ENE

A. A. Shcherbakov, G. G. Aleksandrov,
Ya. T. Struchkov, and V. G. Kharchenko

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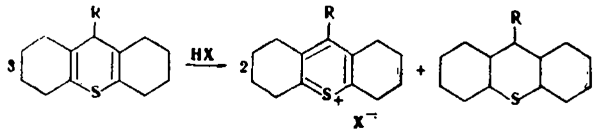
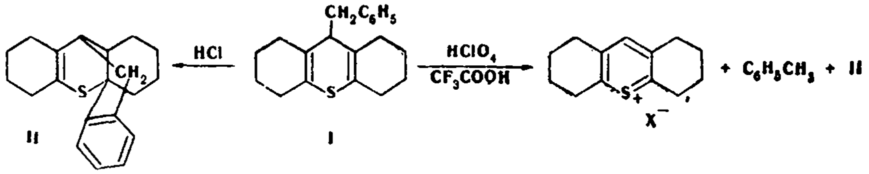
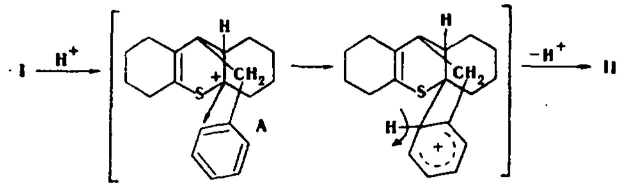
It is known that 4-R-2,3-5,6-bis(tetramethylene)-4H-thiopyrans are disproportionated by protic acids forming 9-R-sym-octahydrothioxanthylium salts and perhydrothioxanthenes [1]:



However, no disproportionation is observed if a benzyl group is located at C_4. In this case isomerization or the simultaneous occurrence of isomerization and the elimination of the benzyl group takes place from the effect of hydrogen chloride, perchloric, trifluoroacetic, and other acids. In the latter case the formation of a sym-octahydrothioxanthylium salt, toluene, and isomer II is observed:



The nature of the isomerization presented is evidently due to the formation of a stable carbocation (A) during the protonation of the double bond in the heteroring and its electrophilic interaction with the aromatic ring:



The isomerization of this nature has been confirmed by an x-ray diffraction analysis of substances I and II, as a result of which it was established that the starting compound I is 4-benzyl-2,3-5,6-bis(tetramethylene)-4H-thiopyran and that isomer II is 3,4-benzo-5,9-7,8-bis-(tetramethylene)-6-thiatricyclo[1.3.3]non-7-ene, in contrast to the conclusion arrived at in [2] concerning its structure, which was based on the IR and UV spectra.

The stereochemistry of molecule I with the torsional angles is shown in Fig. 1a; the bond lengths and valence angles are given in Fig. 1b. The torsional angles, bond lengths, and valence angles of molecule II are given in Fig. 2a, b, and c, respectively.

The compounds investigated, I and II, are isologs of thioxanthenes, which have been structurally well investigated [3-7]. The S—C (sp^2) bond lengths in thioxanthenes have been found to be in the 1.746(5)-1.773(4) Å range, where the values found for structures I and II also fall: S—C(12) 1.772(1) and 1.762(3), S—C(13) 1.748(1) and 1.844(3) Å, respectively. The small difference in the S—C bond lengths in compound I cannot be simply explained, but

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N. G. Chernyshevskii Saratov State University, Saratov 410601. Institute of Hetero-organic Compounds, Academy of Sciences of the USSR, Moscow 117312. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1470-1473, November, 1979. Original article submitted January 31, 1979.

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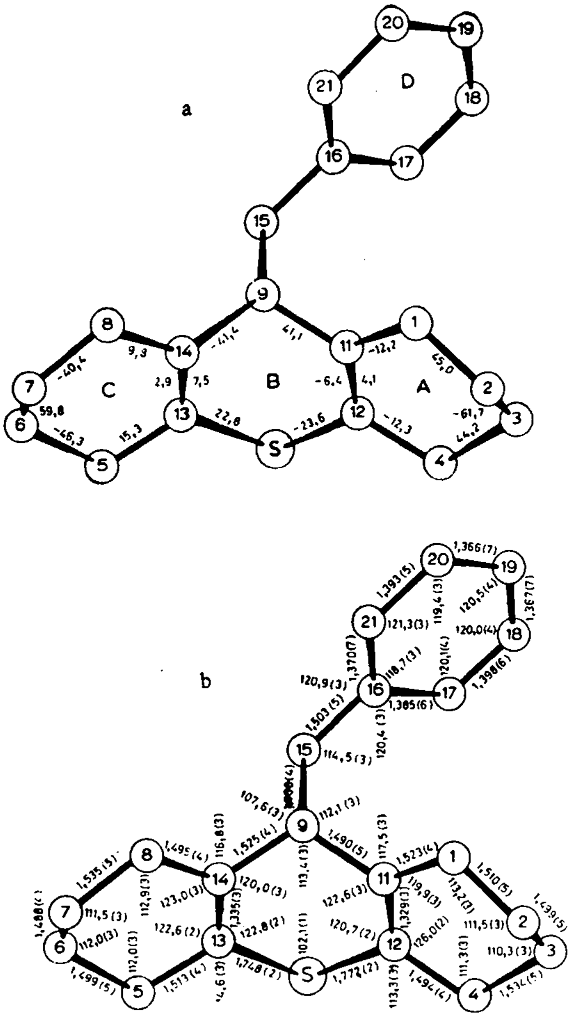

Fig. 1. Geometry of molecule I: a) torsional angles; b) bond lengths and valence angles.

the substantial difference for substance II is completely understandable since S—C(13) is a bond with an sp^3-hybridized carbon and its length almost coincides with the standard value. The endocyclic angle C(12)SC(13) in molecules I and II is the same and equals 102.1(2)°, i.e., it is close to that found in the p-bromobenzyl ester of 2H-thiopyrancarboxylic acid (100.4°) [8]. Note that the lengths of the endocyclic S—C bonds [1.759(2) and 1.827(3) Å] in this molecule practically coincide with those found in compound II. The lengths of the ordinary, double, and aromatic C—C bonds in molecules I and II coincide with the corresponding standard values [9].

The thiopyran ring B in molecule I has the conformation of a flattened (especially at the S atom) and somewhat distorted boat (in the ideal boat of cyclohexane τ = 0, 60, —60, 0, 60, —60°). The ring being discussed is also a boat in the more rigid thioxanthene molecules, but a less distorted one.

In accordance with the boat conformation of the central heteroring B side rings A and C in molecule I are bent back to one side of the plane of the bottom of the boat so that the tricyclic system has on the whole a cissoidal configuration and approximate C_S symmetry (Fig. 1). The benzyl substituent has an axial orientation and is found on the opposite side of ring B relative to the A and C rings; this decreases the steric interactions between benzene ring D and the side rings A and C.

According to the torsional angles (Fig. 2a), the dihydrothiopyran ring B in molecule II has a half-chair conformation which is noticeably distorted because of the linkage with the adjoining rings and the presence of an S atom with a smaller valence angle than for the carbon atoms. The cyclohexene rings in both structures (A and C in I and C and D in II) have a

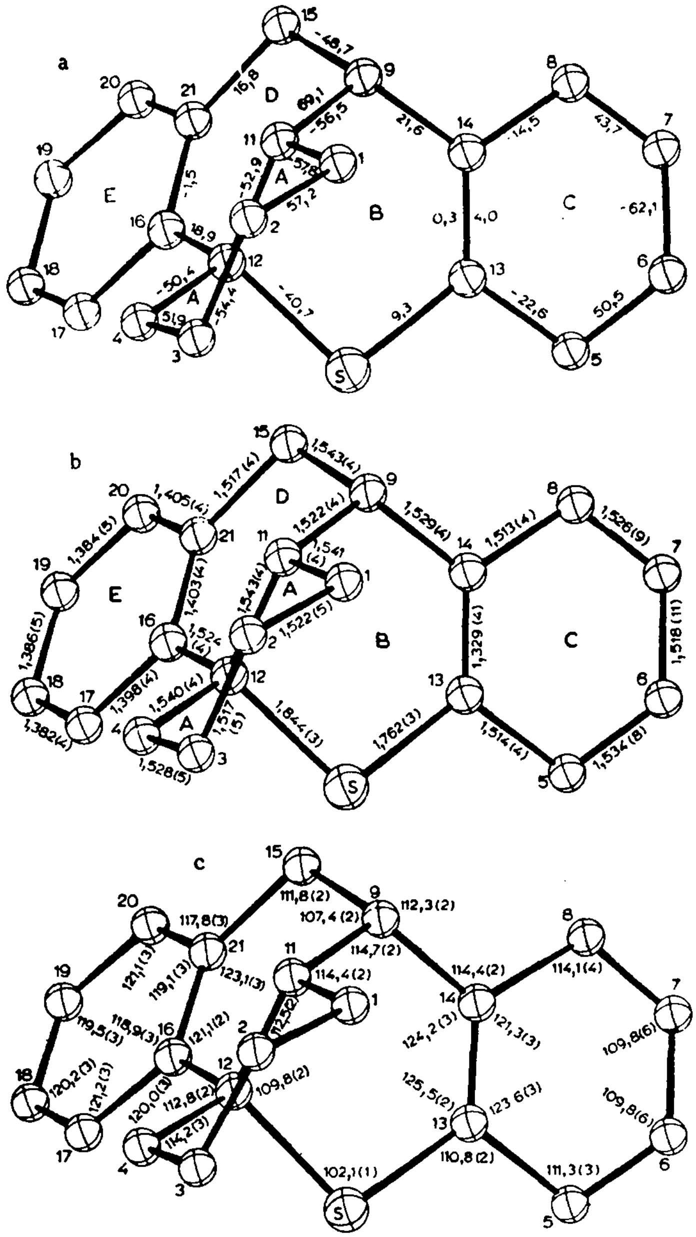

Fig. 2. Geometry of molecule II: a) torsional angles; b) bond lengths; c) valence angles. The torsional angles not shown in the figure are: in ring A: C(1)C(11)C(12)C(4), 53.5°; in ring B: C(9)C(11)C(12)S 66.0°. The valence angles not shown in the figure are: C(2)C(1)C(11), 110.3(3)°; C(2)C(3)C(4), 112.1(3)°; C(9)C(11)C(12), 110.5(2)°; C(4)C(12)C(11), 109.5(2)°; C(4)-C(12)S, 106.3(2)°; C(11)C(12)C(16), 110.1(2)°; and C(12)C(16)S, 108.3(2)°.

distorted half-chair conformation. According to the electron diffraction data [10], the cyclohexene itself has an ideal half-chair conformation with torsional angles τ = 0, 15.2, −48.5, 66.6, −48.5, and 15.2°.*

Cyclohexane ring A in molecule II has a conformation of an almost undistorted chair (Fig. 2a). The bond to the S atom is axial, and to the C(9) and C(16) atoms equatorial, i.e., rings A and B have a trans linkage.

The orientation of the exocyclic bonds relative to ring B in molecule II is as follows: axial with C(1) and C(16), equatorial with C(4), and pseudoequatorial with C(15). The

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*Calculated by us.

orientation of the exocyclic bonds relative to ring D is axial with C(14), equatorial with C(1) and H(9), pseudoaxial with S, and pseudoequatorial with C(4). Ring D has a trans linkage (the linkage of rings B and C can be called "pseudocis") with cyclohexane ring A. The benzene rings (D in I and C in II) are planar.

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HETEROATOMIC AZIRIDINE DERIVATIVES.

10*. NEW MACROHETEROCYCLIC SYSTEMS — DERIVATIVES OF 1,2-BENZO-4,13-DIAZA-7,10-DITHIACYCLOTETRADECA-1-ENE AND 1,4-DIAZA-7,10,11,14-TETRATHIACYCLOHEXADECANE

M. G. Voronkov, V. I. Knutov, V. A. Usov,
M. K. Butin, and O. B. Bannikova

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Recently the chemistry of macrocyclic compounds has produced a new development. The synthesis of catenanes and rotaxanes, the invention of crown ethers, the syntheses of cyclophanes, ansa compounds, etc. [2-5] are broadly well-known results in this field.

The cyclization of linear bifunctional compounds is one of the methods of synthesizing macrocycles. In order to obtain linear diamines we reacted aziridine and N-(carbomethoxyethyl)aziridine with 1,2-ethanedithiol in various solvents. 1,2-Ethanedithiol in methanol at 60°C reacts with 2 moles of aziridine or N-(carbomethoxyethyl)aziridine forming the diamino-3,6-dithiaoctanes I, II. In an aprotic solvent (benzene) 1,2-ethanedithiol yields sulfide III with aziridine, which is easily oxidized by atmospheric oxygen to disulfide IV (see Scheme 1).

Diamines I and II easily react with phthalic dichloroanhydride in dry benzene or toluene at 5°C in the presence of triethylamine under conditions of high dilution [6]. The yields of the derivatives of 1,2-benzo-4,13-diaza-7,10-dithiacyclotetradeca-1-ene V, VI come to 66 and 70%, respectively.

The reaction of disulfide IV with oxalyl chloride proceeds similarly in dry benzene forming 1,2-dioxo-3,16-diaza-6,9,10,13-tetrathiacyclohexadecane (VII) with an 80% yield.

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*See [1] for Communication 9.

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