error in the statistical evaluation of the characteristics and the specific description of the molecular structures in matrix form [4].

However, on the whole, the results obtained provide evidence for the usefulness of the new method: first, for a comparative evaluation of the level of antimicrobial activity of diverse structural variants of semisynthetic penicillins; second, for a preliminary evaluation of the prospects of inclusion in the side chain of antibiotics of new structural systems that makes it possible in advance to exclude genuinely known unpromising modifications from the plan of the experimental research.

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POLYFUNCTIONAL MACROHETEROCYCLES.

3.* SYNTHESIS OF NITROGEN- AND SULFUR-CONTAINING CROWN-COMPOUNDS WITH EXOCYCLIC METHOXYCARBONYL- AND PHENETHYL GROUPS

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Reaction of 1-methoxycarbonylethyl- and 1-phenethylaziridines with hydrogen sulfide leads to the corresponding diaminosulfides which with formaldehyde form the derivatives 1,9-dithia-4,6,12,14-tetraazacyclohexadecanes. 7,9,18,20-Tetrakis(2-phenethyl)-1,4,12,15-tetrathia-7,9,18,20-tetraazacyclodocosane, which forms a stable crystalline complex with chloroform, is produced upon reaction of 1,8-bis(2-phenethylamino)-3,6-dithiaoctane with formaldehyde.

Nitrogen- and sulfur-containing macroheterocyclic compounds are used as complexing agents for transition metal ions [2, p. 158; 3, p. 86; 4]. They are effective extractants for silver(I), copper(II), mercury(II), platinum(II), palladium(II), and gold(III) [5]. The extractive properties of the crown-compounds are enhanced upon introduction of exocyclic functional groups into the macrocycle molecule.

The method developed earlier by us for synthesis of macroheterocycles with methoxycarbonyl-, cyan-, and phenethyl groups on the nitrogen atoms of the macrocycle is based on the reaction of functionally 1-substituted aziridine with α,ω-dithiols and subsequently cyclocondensation of the heterochains which form with diamines [6, 7]. In order to develop further the method and to prepare new types of macroheterocycles which contain exocyclic functional groups, and to study their complexation properties, we studied the reaction of N-substituted diaminosulfides with formaldehyde.

1,5-Bis(2-methoxycarbonylethylamino)-3-thiapentane (I) and 1,5-bis(phenethylamino)-3-thiapentane (II) were prepared by a known synthetic scheme for diaminosulfides [8] by reaction of 1-(2-methoxycarbonylethyl)- and 1-phenethylaziridines with hydrogen sulfide in methanol at 20°C with ∿80% yield.

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*For Communication 2, see [1].

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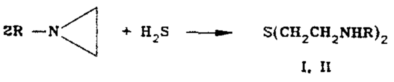
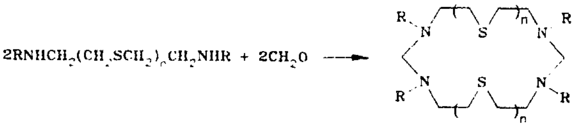


I, II

I $R=CH_2CH_2COOCH_3$; II $R=CH_2CH_2C_6H_5$

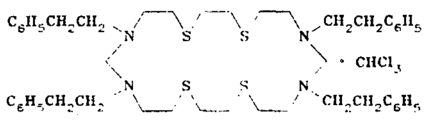
Cyclocondensation of the diaminosulfides I and II and 1,8-bis(2-phenethylamino)-3,6-dithiaoctane (III) [7] with formaldehyde under high dilution conditions forms primarily the "dimeric" macrocyclic compounds IV-VI with 60-70% yield.



IV-VI

IV $R=CH_2CH_2COOCH_3$, V, VI $R=CH_2CH_2C_6H_5$; IV, V $n=1$, VI $n=2$

The 22-membered macroheterocycle VI forms a stable crystalline solvate VII with chloroform. Complexes of macroheterocycles with chloroform of the "host-guest" type are known [9]. The complex VII obtained us us is a light-yellow crystalline compound with mp 209-210°C and is stable upon storage and heating.



VII

Compounds I, II, and IV-VII are thick oils or crystalline compounds which are very soluble in benzene, methanol, chloroform, acetone, DMSO, and DMF. Absorption bands near 3300 cm^{-1} which are characteristic of NH group vibrations of secondary amines are present in the IR spectra of diamines I and II. These bands are absent in the spectra of macroheterocycles IV-VII. Vibrations of the ester group are located in the 1730 cm^{-1} region in the spectra of I and IV. Absorption frequencies of the aromatic rings in the spectra of II and V-VI appear in three regions: the C—H stretching is observed as three absorption bands at 3010, 3050, and 3070 cm^{-1}; absorptions at 1590, 1480, and 1450 cm^{-1} are related to skeletal vibrations of the aromatic C—C bonds; and absorptions at 720 and 680 cm^{-1} are explained by deformations of the C—H bonds.

EXPERIMENTAL

IR spectra were obtained on a UR-20 instrument. PMR spectra were taken on a Tesla BS-497 (100 MHz) spectrometer in $CDCl_3$ with HMDS internal standard. The mass spectrum of I was obtained on a MAT-212 instrument (70 eV); the molecular weights of IV and V were determined cryoscopically in benzene. Elemental analyses and the molecular weights found agreed with those calculated.

1,5-Bis(2-methoxycarbonylethylamino)-3-thiapentane (I, $C_{12}H_{24}N_2O_4S$). A solution of 12.9 g (0.1 mmole) 1-(2-methoxycarbonylethyl) aziridine in 100 ml methanol was saturated with H_2S for 2 h at room temperature. The solvent was removed. The residue was dissolved in chloroform and precipitated by petroleum ether and cooling. Yield 11.7 g (80%). Oil. PMR spectrum: 4.46 (s, $COCH_3$), 3.65 (s, OCH_3), 2.86 (m, NCH_2), 2.59-2.52 ppm (m, SCH_2).

1,5-Bis(2-phenethylamino)-3-thiapentane (II, $C_{20}H_{28}N_2S$) was prepared analogously from 1-phenethylaziridine with 82% yield. Oil. PMR spectrum: 7.25 (m, C_6H_5), 2.84 ppm (m, NCH_2, SCH_2).

4,6,12,14-Tetrakis(2-methoxycarbonylethyl)-1,9-dithia-4,6,12,14-tetraazacyclohexadecane (IV, $C_{26}H_{48}N_4O_8S_2$). A solution of 2.92 g (0.01 mole) diamine I in 300 ml methanol and 4 ml 40% formaldehyde solution in 300 ml methanol were added synchronously over 6 h at 60°C to 1 liter methanol with vigorous stirring. The solvent was removed under reduced pressure. The residue was purified chromatographically on aluminum oxide with a mixture of benzene and methanol (2:1) as eluent. The solvent was removed, the residue was washed thrice with petroleum ether, and dried in vacuum. Yield 2.13 g (70%). Oil. PMR spectrum: 4.61 (s, $COCH_2$), 3.66 (s, OCH_3), 3.22 (g, NCH_2N), 2.78 (m, NCH_2), 2.51-2.45 ppm (m, SCH_2).

4,6,12,14-Tetrakis (2-phenethyl)-1,9-dithia-4,6,12,14-tetraazacyclohexadecane (V, $C_{42}H_{56}N_4S_2$) was prepared analogously from 3.28 g (0.01 mole) diamine II and 4 ml 40% formaldehyde solution with 2.3 g (68% yield. Oil.

7,9,18,20-Tetrakis(2-phenethyl)-1,4,12,15-tetrathia-7,9,18,20-tetraazacyclodocosane (VI, $C_{46}H_{64}N_4S_4$) was prepared analogously from 3.88 g (0.01 mole) 1,8-bis(2-phenethylamino)-3,6-dithiaoctane and 4 ml 40% formaldehyde solution. Yield 2.52 g (63%). Oil. PMR spectrum: 7.21 (m, C_6H_5), 4.20 (m, $C_6H_5CH_2$), 3.37-3.14 (q, NCH_2N), 2.76 (m, NCH_2), 2.68 ppm (m, SCH_2).

Complex 7,9,18,20-Tetrakis(2-phenethyl)-1,4,12,15-tetrathia-7,9,18,20-tetrazacyclodocosane with Chloroform (VII, $C_{46}H_{64}N_4S_4 \cdot CHCl_3$). A solution of 1.0 g macroheterocycle VI in 20 m. chloroform was heated to boiling. After cooling, VII was precipitated by petroleum ether or by removal of chloroform and the residue was recrystallized from methanol. Yield 0.9 g (82%). mp 209-210°C. PMR spectrum: 8.61 (s, $CHCl_3$), 7.29 (m, C_6H_5), 5.36 (m, $C_6H_5CH_2$), 3.42 (s, NCH_2N), 2.93 ppm (m, NCH_2, SCH_2).

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REACTIONS OF 10-TELLURONIAANTHRACENE PERCHLORATES WITH NUCLEOPHILES

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10-Telluroniaanthracene perchlorates react with nucleophiles (X^- = halide, hydroxide, methoxide) via intermediate free telluroxanthyl radicals. With 9-aryl-10-telluroniaanthracene perchlorates, high yields of 9-aryl-9-X-telluroxanthenes are obtained, but with 10-telluroniaanthracene the principal product is 9,9'-bis(telluroxathenyl) as a result of rapid competitive dimerization.

The first 10-telluroniaanthracene perchlorates (I) were reported in 1980 [1]. Other than reduction with aluminohydride to give 9-aryltelluroxanthenes, however, no reactions of these compounds have been described. We have now examined the reactions of (I), exemplified by 9-(p-tolyl)-10-telluroniaanthracene perchlorate (Ia, R = p-$CH_3C_6H_4$) and 10-telluroniaanthracene perchlorate (Ib, R = H), with some nucleophiles. The nucleophiles used water, sodium hydroxide, sodium methoxide, and ammonium halides. The latter were chosen in view of their adequate solubility in the solvent used for the reactions. All the reactions were carried out in dry THF under argon, at ambient temperature.

The perchlorate (Ia) reacted with ammonium halides to give, ultimately, 9-(p-tolyl)-9-halotelluroxanthenes (IIa-c) in satisfactory yields. The formation of the latter compounds,

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