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Synthesis of 1-Alkyl 3,5-Bis(ω-mercaptoacetoalkyl) Isocyanurates and Macrocyclic Disulfides Derived Thereof

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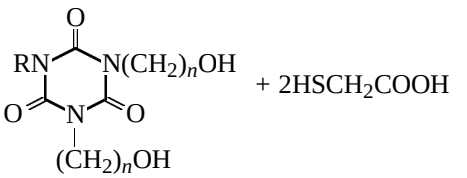
Abstract — 1-Alkyl 3,5-bis(ω-hydroxyalkyl) isocyanurates were reacted with mercaptoacetic acid to obtain 3,5-bis(ω-mercaptoacetoxyalkyl) isocyanurates whose oxidation gives rise to macrocyclic disulfides.

Earlier [1, 2] we reported on the synthesis of 1-alkyl 3,5-bis(ω-mercaptoalkyl) isocyanurates by reaction of 1-alkyl 3,5-bis(ω-haloalkyl) isocyanurates with thiourea followed by hydrolysis of the resulting isothiuronium salts. The present work deals with the synthesis of new podands on the basis of 1-alkyl isocyanurates containing in the *N*-alkyl chain a mercaptoacetyl group whose oxidation gives rise to macrocyclic disulfides.

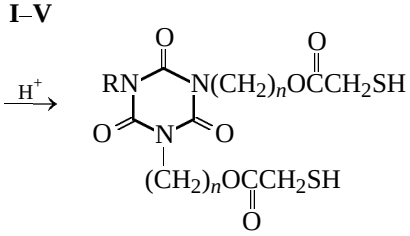
The interest in such structures is motivated, first, by their potential biological activity. It is known that thiols and their derivatives (cystine, cysteine, glutathione, lipoic acid, etc.) play an exceptionally important role in biochemical processes. Such processes as energy accumulation, electron transport, acyl and alkyl transfer, structure stabilization, and detoxication all involve CH groups [3]. The proposed structures can be used as building blocks for designing sulfur-containing macrocycles with azine fragments (pyrimdine, 1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*-trione), which makes possible modeling biological systems and processes involving SH groups.

On the other hand, sulfur-containing podands and crown ethers occupy an important place in supramolecular chemistry, since they are capable of selectively binding transition and heavy metal ions. Moreover, such compounds hold promise as active components of membranes of ion-selective electrodes and molecular receptors [4, 5], as well as potential redox-switched and electrochemically switched systems [6–8].

1-Alkyl 3,5-bis(ω-mercaptoacetoxyalkyl) isocyanurates **VI**–**X** were obtained by esterification of 1-alkyl 3,5-bis(ω-hydroxyalkyl) isocyanurates **I**–**V** with mercaptoacetic acid.



I–**V**



VI–**X**

R = CH_3, *n* = 2 (**I, VI**), 3 (**II, VII**); R = $C_6H_5CH_2$, *n* = 2 (**II, VIII**), 3 (**IV, IX**); R = *o*-$CH_3OC_6H_4O(CH_2)_2$, *n* = 2 (**V, X**).

The starting isocyanurates **II**, **IV**, and **V** were prepared by alkylation of disodium salts of the corresponding isocyanurates with 3-chloropropanol and ethylene chlorohydrin similarly to the synthesis of 1-alkyl 3,5-bis(3-hydroxyethyl) isocyanurates **I** and **III**, described in [2]. The synthesis of compounds **XVI** and **XVII** used as starting materials for preparing compound **V** is described in Experimental.

Thiols **VI**–**X** are transparent thick oily substances with a characteristic odor. They are spontaneously oxidized on handling, forming oligomeric disulfides. The IR spectra of compounds **VI**–**X** contain a medium-intensity ν(SH) band at 2560 cm^{-1}, which is no longer observed in the spectra of oligomeric oxidation products.

Oxidative cyclization of thiols **VI**–**X** in the conditions described in [9] gave macrocyclic compounds **XI**–**XV**.

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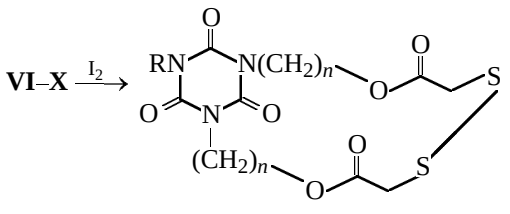

XI–**XV**

R = CH_3, *n* = 2 (**XI**), 3 (**XII**); R = $C_6H_5CH_2$, *n* = 2 (**XIII**), 3 (**XIV**); R = *o*-$CH_3OC_6H_4O(CH_2)_2$, *n* = 2 (**XV**).

Compounds **XI**–**XV** are colorless crystalline substances readily soluble in chloroform. Compounds **XII** and **XIV** that have three methylene groups in the macrocyclic moiety are soluble in ethyl acetate, acetone, and methanol. The composition and structure of macrocycles **XI**–**XV** were proved by X-ray diffraction, elemental analysis, and NMR and IR spectroscopy. The yields of macrocycles **XI**, **XIII**, and **XV** with two methylene groups (Figs. 1a, 1b, and 2) are 50–60%, whereas the yields of macrocycles **XII** and **XIV** with three methylene groups (Figs. 3a and 3b) are much lower (10–12%). It should be noted that thiols **VI**–**X** were oxidized into disulfides **XI**–**XV** in air, and, therefore, oxidation into oligomeric disulfides is highly probable, especially in the case of relatively unstable thiols **VII** and **IX**.

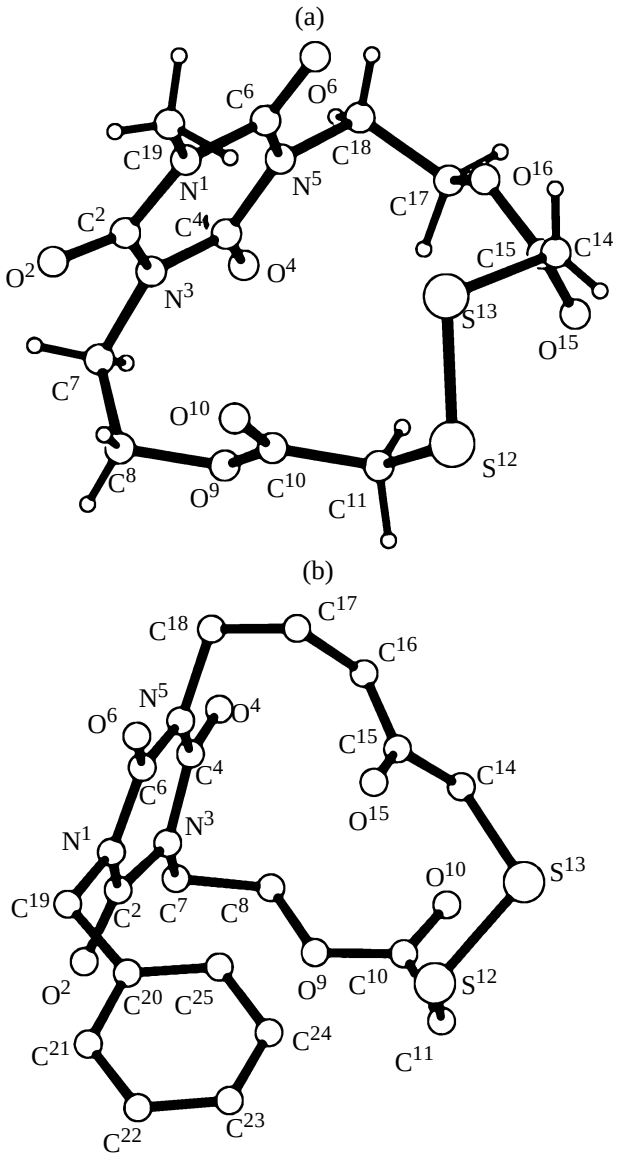

Fig. 1. Molecular geometry of compounds (a) **XI** and (b) **XIII** in crystals. For compound **XIII**, hydrogen atoms are not shown.

As seen from the figures, the conformation of the macrocycle radically changes both in going from compounds containing two methylene groups in the chain to compounds containing three methylene groups and with change of 1-substituent. It should be noted that in crystals of the compounds we observe differences in the type of intermolecular contacts and in molecular packing, which, too, may affect macroring conformation. The X-ray diffraction results for these compounds will be considered in more detail in a separate publication.

It should be noted that similar dilactone structures derived from pyridine have been prepared in yields of 15–80% by template condensation with bis(triphenylstannyloxymethyl)pyridine of dicarboxylic acid difluorides containing sulfide and disulfide bridges [10], and their ability to complexation with $Eu(fod)_3$ has been studied [11]. Compounds containing two uracil moieties and a disulfide bridge incorporated in the macrocycle, 3,4-dithia[6.6](1,3)- and 3,4-dithia[6.1](1,5)-pyrimidinophanes, have also been described [12, 13].

EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 instrument in thin films or suspensions in Vaseline. The ^1H NMR spectra of compounds **II**, **IV**–**X**, **XVI**, and **XVII** were obtained on a Varian T-60 spectrometer at 60 MHz, and the ^1H and ^{13}C NMR spectra of compounds **X**–**XV** were obtained on a WM-250 instrument at 250 MHz, internal reference TMS. Thin-layer chromatography was performed on Silufol, developer iodine vapor. Single-crystal X-ray diffraction analysis was performed on an Enraf–Nonius CAD-4 automatic four-circle diffractometer.

1-Benzyl-3,5-bis(3-hydroxypropyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (IV). Benzyl isocyanurate, 6.6 g, was added with stirring to sodium butylate obtained from 1.4 g of sodium in 100 ml of

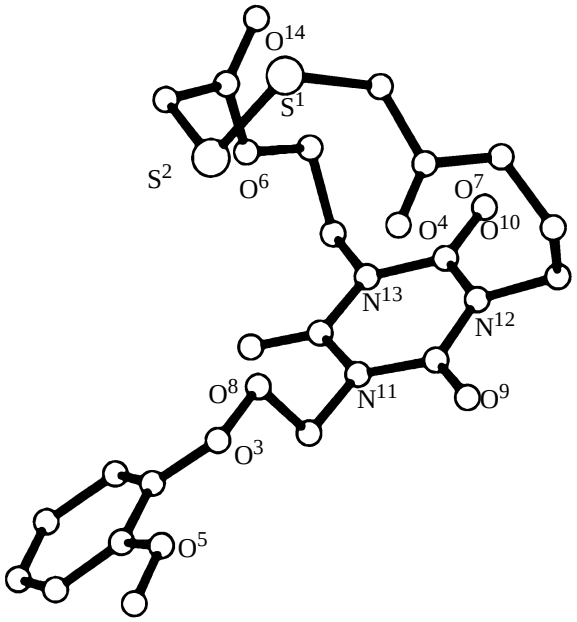

Fig. 2. Molecular geometry of compound **XV** in crystal (hydrogen atoms are not shown).

absolute methanol, and the mixture was heated under reflux for 6 h. Butanol was distilled off in a vacuum, the residual butanol was removed by azeotropic distillation with toluene, and the residual toluene was distilled off in a vacuum. Absolute DMF, 200 ml, and 6.3 g of 3-chloropropanol were added, and the mixture was heated at 80–90°C for 4–6 h (to pH 7). After cooling, the precipitate was filtered off, and DMF was distilled off in a vacuum. The residue was subjected to column chromatography on silica gel in benzene–methanol (20 : 1) to isolate 8.4 g (84%) of compound **IV** as a transparent thick oily substance. R_f 0.435 (benzene–methanol, 10 : 1). IR spectrum (thin film), cm^{-1}: 3400 v.s (OH), 3080–3025 m (several bands, C_6H_5), 1670 v.s (C=O), 1045 s (C–O), 755 s (isocyanurate ring), 690, 673 m (C_6H_5). ^1H NMR spectrum (CD_3OD), δ, ppm ($^3J_{HH}$, Hz): 1.82 m (4H, CH_2), 3.57 m (4H, CH_2O, 5.8), 3.97 m (4H, CH_2N, 6.4), 4.97 s (2H, CH_2Ph), 7.28 m (5H, C_6H_5). Found, %: C 57.14; H 6.48; N 12.58. $C_{16}H_{21}N_3O_5$. Calculated, %: C 57.30; H 6.31; N 12.53.

Compounds **II** and **V** were prepared in a similar way.

3,5-Bis(3-hydroxypropyl)-1-methyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (II). Yield 61%, thick nontransparent oily substance, crystallizes on standing. R_f 0.46 (ethyl acetate–methanol, 10 : 1). IR spectrum (thin film), cm^{-1}: 3450 v.s (OH), 1670 v.s (C=O), 1045 s (C–O), 755 s (isocyanurate ring). ^1H NMR

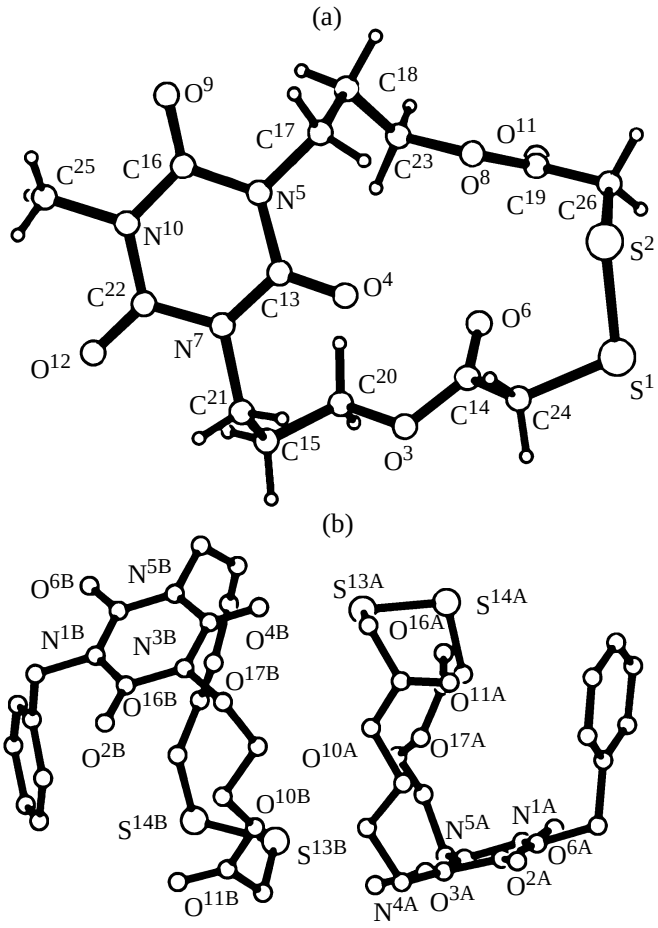

Fig. 3. Conformations of macrocycles with three methylene groups in the chain. (a) Compound **XII** and (b) compound **XIV**. The crystal of compound **XIV** contains two independent molecules A and B (hydrogen atoms are not shown).

spectrum (CD_3OD), δ, ppm ($^3J_{HH}$, Hz): 1.88 m (4H, CH_2), 3.34 s (3H, CH_3), 3.67 m (4H, CH_2O, 6.0), 4.03 m (4H, CH_2N, 7.0). Found, %: C 46.62; H 6.27; N 16.33. $C_{10}H_{17}N_3O_5$. Calculated, %: C 46.33; H 6.61; N 16.21.

3,5-Bis(2-hydroxyethyl)-1-[2-(*o*-methoxyphenoxy)ethyl]-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (V) was prepared by alkylation of 1,3-disodium 5-[2-(*o*-methoxyphenoxy)ethyl isocyanurate (**XVI**) with 2-chloroethanol. Yield 84%, thick transparent oily substance, crystallizes on standing. R_f 0.43 (ethyl acetate–methanol, 10 : 1). IR spectrum (thin film), cm^{-1}: 3500–3300 v.s (OH), 1710, 1670 v.s (C=O), 1590 m (C_6H_4), 1245, 1212 s (C_{arom}–O), 1120, 1020 s (C_{alif}–O), 1045 s (C–O alc.), 755 s (isocyanurate ring), 740 s (C_6H_4). ^1H NMR spectrum (CD_3OD), δ, ppm: 3.75 m (4H, CH_2O), 3.80 s (3H, CH_3O), 3.99 m (2H,

OCH_2), 4.25 m (6H, CH_2N), 6.87 m (4H, C_6H_4). Found, %: C 52.15; H 5.71; N 11.44. $C_{16}H_{21}N_3O_7$. Calculated, %: C 52.31; H 5.76; N 11.44.

1-Benzyl-3,5-bis(2-mercaptoacetoxyethyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (VIII). 1-Benzyl 3,5-bis(2-hydroxyethyl) isocyanurate (**III**) and 5 g of mercaptoacetic acid were heated under reflux in absolute toluene in the presence of 0.6 g of *p*-toluenesulfonic acid (or sulfosalicylic acid) with a Dean–Stark trap for 4–5 h. Toluene was removed by distillation, the residue was subjected to column chromatography on silica gel, eluent benzene–ethyl acetate, 10 : 1. Yield 8.5 g (84%), colorless transparent oily substance. R_f 0.50 (benzene–ethyl acetate, 5 : 1). IR spectrum (thin film), cm^{-1}: 3070–3015 m–w (several bonds, C_6H_5), 2560 w (SH), 1725 v.s (C=O ester), 1670 v.s (isocyanurate C=O), 1280 s, 1150 s (C–O), 752 s (isocyanurate ring), 698 m (C_6H_5). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 1.85 t (2H, SH, 8.0), 3.04 d (4H, CH_2S, 8.0), 4.07–4.38 m (*AA'BB'*, 8H, NCH_2CH_2O), 5.00 s (2H, CH_2Ph), 7.32 m (5H, C_6H_5). Found, %: C 47.28; H 4.32; N 9.08; S 13.93. $C_{18}H_{21}N_3O_7S_2$. Calculated, %: C 47.46; H 4.65; N 9.23; S 14.08.

Compounds **VI**, **VII**, and **IX**–**XI** were prepared in a similar way.

3,5-Bis(2-mercaptoacetoxyethyl)-1-methyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (VI). Yield 47%, colorless transparent oily substance. R_f 0.31 (benzene–ethyl acetate, 5 : 1). IR spectrum (thin film), cm^{-1}: 2560 m (SH), 1730 v.s (C=O ef.), 1670 v.s (isocyanurate C=O), 1285–1270 s, 1142 s (C–O), 752 s (isocyanurate ring). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 2.03 t (2H, SH, 8.0), 3.23 d (4H, CH_2S, 8.0), 3.33 s (3H, CH_3), 4.08–4.43 m (*AA'BB'*, 8H, NCH_2CH_2O). Found, %: C 37.67; H 4.38; N 10.94; S 16.53. $C_{12}H_{17}N_3O_7S_2$. Calculated, %: C 37.99; H 4.52; N 11.08; S 16.53.

3,5-Bis(3-mercaptoacetoxypropyl)-1-methyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (VII). Yield 47%, colorless transparent oily substance. R_f 0.35 (benzene–ethyl acetate, 3 : 1). IR spectrum (thin film), cm^{-1}: 2560 m (SH), 1740 v.s (ester C=O), 1670 v.s (isocyanurate C=O), 1278 s, 1160–1145 s (C–O), 760 s (isocyanurate ring). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 2.05 t (2H, SH, 8.0), 3.26 d (4H, CH_2S, 8.0), 3.32 s (3H, CH_3), 4.00 m (4H, CH_2N), 4.18 m (4H, CH_2O). Found, %: C 41.12; H 5.06; N 10.32; S 15.61. $C_{14}H_{21}N_3O_7S_2$. Calculated, %: C 41.27; H 5.20; N 10.31; S 15.74.

1-Benzyl-3,5-bis(3-mercaptoacetoxypropyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (IX). Yield 46%, colorless transparent oily substance. R_f 0.44 (benzene–ethyl acetate, 5 : 1). IR spectrum (thin film), cm^{-1}: 3085–3030 w–m (several bands, C_6H_5), 2570 m (SH), 1745 v.s (ester C=O), 1680 v.s (isocyanurate C=O), 1295–1270 s, 1150 s (C–O), 760 s (isocyanurate ring), 685–702 s (C_6H_5). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 1.92 t (2H, SH, 8.0), 2.02 m (4H, CH_2), 3.14 d (4H, CH_2S, 8.0), 4.00 m (4H, CH_2N), 4.15 m (4H, CH_2O), 5.00 s (2H, CH_2Ph), 7.33 m (5H, C_6H_5). Found, %: C 49.21; H 5.15; N 8.45; S 13.11. $C_{20}H_{25}N_3O_7S_2$. Calculated, %: C 49.68; H 5.21; N 8.69; S 13.26.

3,5-Bis(2-mercaptoacetoxyethyl)-1-[2-(*o*-methoxyphenoxy)ethyl]-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (X). Yield 37%, colorless transparent oily substance). R_f 0.51 (benzene–ethyl acetate, 2 : 1). IR spectum (thin film), cm^{-1}: 3040–3015 w (several bands, C_6H_4), 2560 m (SH), 1730 s (ester C=O), 1690 v.s (isocyanurate C=O), 1585 m (C_6H_4), 1285, 1145 s (ester C–O), 1245, 1215 s (C_{arom}–O), 1120, 1020 s (C_{alif}–O), 758 s (isocyanurate ring), 745 m (shoulder, C_6H_4). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 1.92 t (2H, SH, 8.0), 3.17 d (4H, CH_2S, 8.0), 3.83 s (3H, OCH_3), 4.17–4.46 m (12H, $NCH_2 \cdot CH_2O$), 6.92 m (4H, C_6H_4). Found, %: C 46.51; H 4.78; N 8.06; S 12.31. $C_{20}H_{25}N_3O_9S_2$. Calculated, %: C 46.59; H 4.89; N 8.15; S 12.44.

3,5-Bis(4,9-dioxo-3,10-dioxa-6,7-dithiadodeca-1,12-diyl)-1-methyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (XI). Solutions of 1.8 g of thiol **VI** in 60 ml of absolute dichloromethane and of 1.27 g of iodine in 150 ml of absolute dichloromethane were added dropwise with vigorous stirring (18°C) to a solution of 1.1 g of triethylamine in 60 ml of absolute dichloromethane until the reaction mixture changed from colorless to yellowish (7 ml of the iodine remained unused). Stirring was continued for an additional 4 h, after which the reaction mixture was washed with 50 ml of water with some crystals of sodium thiosulfate added, 50 ml of 0.1 N HCl, and water (2 × 50 ml), and dried with $MgSO_4$. The solvent was distilled off, and the residue was subjected to column chromatography on silica gel, eluent benzene followed by benzene–ethyl acetate, 10 : 1. Yield 1.1 g (61%), crystallizes from the solvent as colorless needles. mp 151–152°C. R_f 0.38 (benzene–ethyl acetate, 2 : 1). IR spectum (Vaseline), cm^{-1}: 1740, 1730 s (ester C=O), 1670 v.s (isocyanurate C=O), 1258 s, 1147 s (C–O), 758 s (isocyanurate ring). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 3.38 s (3H, CH_3), 3.51 s (4H, CH_2S), 4.26 m (4H, CH_2N, 4.6), 4.48 m (4H, CH_2O, 4.6). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm ($^1J_{CH}$, Hz): 29.71 q (CH_3, 142.7), 41.11 t (CH_2S, 142.7), 41.75 t (CH_2N, 144.3), 61.81 t (CH_2O, 150.9), 149.17 s (iso-

cyanurate C=O, exocycl.), 149.26 s (isocyanurate C=O, endocycl.), 169.73 s (O–C=O). Found, %: C 38.13; H 4.00; N 11.13; S 16.96. $C_{12}H_{15}N_3O_7S_2$. Calculated, %: C 38.19; H 4.01; N 11.13; S 16.99.

Compounds **XII**–**XV** were obtained in a similar way.

3,5-Bis(5,10-oxo-4,11-dioxa-7,8-dithiadodeca-1,14-diyl)-1-methyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (XII). Yield 12%. Colorless crystals. mp 132°C. R_f 0.58 (benzene–ethyl acetate, 1 : 1). IR spectrum (Vaseline), cm^{-1}: 1740, 1715 s (ester C=O), 1685 v.s (isocyanurate C=O), 1280, 1270 s, 1150 s (C–O), 752 s (isocyanurate ring). ^1H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 2.07 m (4H, CH_2), 3.34 s (3H, CH_3), 3.60 s (4H, CH_2S), 4.07 m (4H, CH_2N, 5.8), 4.20 m (4H, CH_2O, 5.8). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm ($^1J_{CH}$, Hz): 27.50 t (CH_2, 128.2), 29.67 q (CH_3, 143.0), 40.59 t (CH_2N, 143.0), 41.92 t (CH_2S, 142.1), 63.38 t (CH_2O, 150.0), 149.50 s (isocyanurate C=O), 169.57 s (O–C≡O). Found, %: C 41.40; H 4.50; N 10.14; S 15.77. $C_{14}H_{19}N_3O_7S_2$. Calculated, %: C 41.47; H 4.72; N 10.36; S 15.82.

1-Benzyl-3,5-bis(4,9-dioxo-3,10-dioxa-6,7-dithiadodeca-1,12-diyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (XIII). Yield 47%. Colorless thick-like crystals. mp 176–178°C. R_f 0.37 (benzene–ethyl acetate, 5 : 1). IR spectum (Vaseline), cm^{-1}: 1745, 1730 s (ester C=O), 1690 v.s (isocyanurate C=O), 1268, 1252 s, 1145 s (C–O), 770 s (isocyanurate ring), 720 s, 690 m (C_6H_5). ^1H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 3.38s (4 H, CH_2S), 4.27 m (4H, CH_2N, 5.0), 4.46 m (4H, CH_2O, 5.0), 5.08 s (2H, CH_2Ph); (C_6H_5): 7.31 m (2H, *m*), 7.34 m (1H, *p*), 7.45 m (2H, *o*). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm ($^1J_{CH}$, Hz): 40.88 t (CH_2S, 143.1), 41.69 t (CH_2N, 144.1), 46.57 t ($PhCH_2$, 143.3), 61.67 t (CH_2O, 149.9); (C_6H_5): 128.52 d.t (*p*, 161.1, 6.8), 128.92 d.d (*o*, 161.1, 6.8), 129.19 d. t (*m*, 157.7, 5.0), 135.82 m (C^1), 149.14 s (isocyanurate C=O), 169.71 s (O–C=O). Found, %: C 47.77; H 4.20; N 9.29; S 14.07. $C_{18}H_{19}N_3O_7S_2$. Calculated, %: C 47.68; H 4.22; N 9.27; S 14.14.

1-Benzyl-3,5-bis(5,10-dioxo-4,11-dioxa-7,8-dithiatetradeca-1,14-diyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (XIV). After column chromatography, a thick oily substance was isolated, which was crystallized by trituration with ether. Yield 10%. mp 103–115°C. R_f 0.53 (benzene–ethyl acetate, 3 : 1). IR spectrum (Vaseline), cm^{-1}: 1730–1720 s (ester C=O), 1680–1670 v.s (isocyanurate C=O), 1270 s, 1145–1112 s (C–O), 750 s (isocyanurate ring), 692 s (C_6H_5). ^1H NMR spectrum ($CDCl_3$), δ, ppm ($^3J_{HH}$, Hz): 2.06 m (4H, CH_2), 3.34 s (4H, CH_2S), 4.06 m (4H, CH_2N, 5.7), 4.18 m (4H, CH_2O, 5.7), 5.02 s (2H, CH_2Ph); (C_6H_5): 7.31 m (3H, *m* and *p*), 7.47 m (2H, *o*). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm ($^1J_{CH}$, Hz): 27.54 t (CH_2, 128.8), 40.94 t (CH_2N, 142.4), 41.53 t (CH_2S, 142.4), 46.44 t ($PhCH_2$, 142.4), 63.71 t (CH_2O, 149.2); (C_6H_5): 128.60 d.t (*p*, 159.4, 7.6); 129.03 d.d (*o*, 161.1, 6.8), 129.65 d.t (*m*, 161.1, 3.0), 136.06 s (C^1), 149.49 s (isocyanurate C=O), 169.49 s (O–C=O). Found, %: C 50.05; H 5.12; N 8.55; S 13.34. $C_{20}H_{23} \cdot N_3O_7S_2$. Calculated, %: C 49.89; H 4.81; N 8.73; S 13.32.

3,5-Bis(4,9-dioxo-3,10-dioxa-6,7-dithiadodeca-1,12-diyl)-1-[2-(*o*-methoxyphenoxy)ethyl]-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (XV). Yield 55%. Colorless crystals. mp 129–131°C. R_f 0.47 (benzene–ethyl acetate, 1 : 1). IR spectrum (Vaseline), cm^{-1}: 1730 s (ester C=O), 1690 v.s (isocyanurate C=O), 1582, 1500 m (C_6H_4), 1262, 1290 m, 1245 s, 1210, 1175 m, 1140 s, 1120, 1022 m (C–O–C), 758 m (isocyanurate ring), 742 s (C_6H_4). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.45 s (4H, CH_2S), 3.83 s (3H, CH_3), 4.27 m (6H, CH_2N), 4.38 m (2H, CH_2OPh), 4.47 m (4H, CH_2O), 6.86–6.97 m (4H, C_6H_4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm ($^1J_{CH}$, Hz): 41.04 t (CH_2S, 143.3), 41.80 t (endocycl. CH_2N, 143.3), 42.09 t (exocycl. CH_2N, 144.1), 56.23 q (CH_3O, 144.1), 61.81 t (endocycl. CH_2O, 150.9), 65.47 t (CH_2OPh, 146.7); (C_6H_4): 112.43 and 114.18 d. d (*o*, *o*', 157.7, 6.8), 121.15 and 122.15 d.d (*m*, *m*', 161.9, 7.6), 148.04 and 149.22 s (C^1, $C^{1'}$), 149.84 and 148.93 s (isocyanurate C=O), 169.75 s (O–C=O). Found, %: C 46.39; H 4.54; N 7.95; S 12.86. $C_{20}H_{23}N_3O_9S_2$. Calculated, %: C 46.78; H 4.50; N 8.18; S 12.49.

1-[2-(*o*-Methoxyphenoxy)ethyl] isocyanurate (XVI) was obtained by the procedure in [14] from disodium salt of 2-(*o*-methoxyphenoxy)ethylbiuret (**XVII**) and diethyl carbonate (refluxing in methanol, 10 h) and recrystallized from 2-propanol. Yield 85%. mp 190–192°C. IR spectrum (Vaseline), cm^{-1}: 3505, 3432, 3200, 3160, 3100 w–m (NH), 1775, 1740 s, 1690 v.s (isocyanurate C=O), 1635 m (NH), 1590 m (C_6H_4), 1242 s, 1210 m (C_{arom}–O), 1125, 1020 s (C_{alif}–O), 760 s (isocyanurate ring), 740 s (C_6H_4). Found, %: C 51.54; H 4.89; N 14.89. $C_{12}H_{13}N_3O_5$. Calculated, %: C 51.61; H 4.69; N 15.05.

2-(*o*-Methoxyphenoxy)ethylbiuret (XVII). Nitrobiuret, 18 g, was added to a solution of 20.4 g of 2-(*o*-methoxyphenoxy)ethylamine in a mixture of 200 ml of water and 100 ml of 2-propanol. The mixture was stirred for 2 h at 18–20°C and then heated under reflux for 30 min. The precipitate was filtered off and recrystallized from 2-propanol. Yield 15 g (50%). mp 188–189°C. IR spectum (Vaseline), cm^{-1}: 3430, 3365, 3305, 3200 m (NH), 1775, 1680 v.s (“amide-I”), 1590,

1500 m (C_6H_4), 1530 m ("amide-II"), 1248, 1220 s (C_{arom}–O), 1120, 1020 m (C_{alif}–O), 740 m (C_6H_4). Found, %: C 52.50; H 5.98; N 16.31. $C_{11}H_{15}N_3O_4$. Calculated, %: C 52.17; H 5.97; N 16.59.

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