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Macrocyclic Ammonio-*N*-nitroimines

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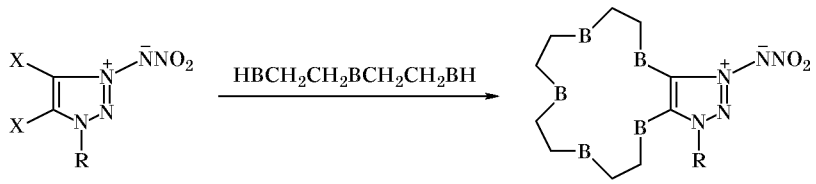
Abstract—Condensation of 4,5-bis(chloromethyl)-1-methyl-1,2,3-triazole with polyethylene glycols and polyethylenepolyamines gave crown-ethers and azacrown compounds which were converted into the corresponding *N*-nitroimines.

A great number of publications on the synthesis and properties of macrocyclic compounds deals with those containing oxygen and nitrogen as heteroatoms. *N*-Nitroimides derived from crown compounds were not reported, though their synthesis undoubtedly attracts attention from the viewpoint of structural modification. Two approaches to the synthesis of such macrocycles are possible: (1) cyclization of functionally substituted ammonio-*N*-nitroimides with salts derived from polyethylene glycols or linear polyethylenepolyaza compounds (Scheme 1) and (2) introduction of an *N*-nitroimide fragment to nitrogen atom of a heterocycle fused with crown ether (Scheme 2).

Aza macrorings are synthesized mainly by cyclization of *N*-tosyl derivatives of linear polyamines with diol bis(*p*-toluenesulfonates) in the presence of bases [1, 2, 3]. In the synthesis of polyaza macrocycles aliphatic dihalogen derivatives can be used instead of *p*-toluenesulfonates [3, 4] (Scheme 3).

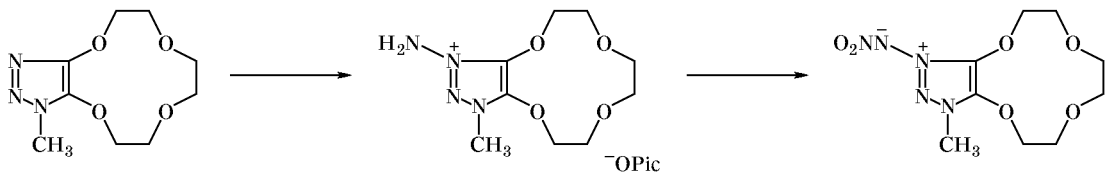
The condensation of 4,5-bis(chloromethyl)-1-methyl-1,2,3-triazol-3-io-*N*-nitroimide (**I**) with 1,4,7-tritosyl-1,4,7-triazaheptane in the presence of potassium carbonate and benzyltriethylammonium chloride as catalyst gave the corresponding *N*-nitroimide **II** in only 4% yield. The major product was compound **III** (Scheme 4); its formation indicates easy elimination of the nitroimide fragment by the action of bases. Therefore, we examined another approach, according to which aza crown ether **III** was initially obtained from 4,5-bis(chloromethyl)-1-methyl-1,2,3-triazole (**IV**) (Scheme 5). The optimal reaction temperature was 70–80°C. At lower temperature, linear products

Scheme 1.



B = O, NTs.

Scheme 2.



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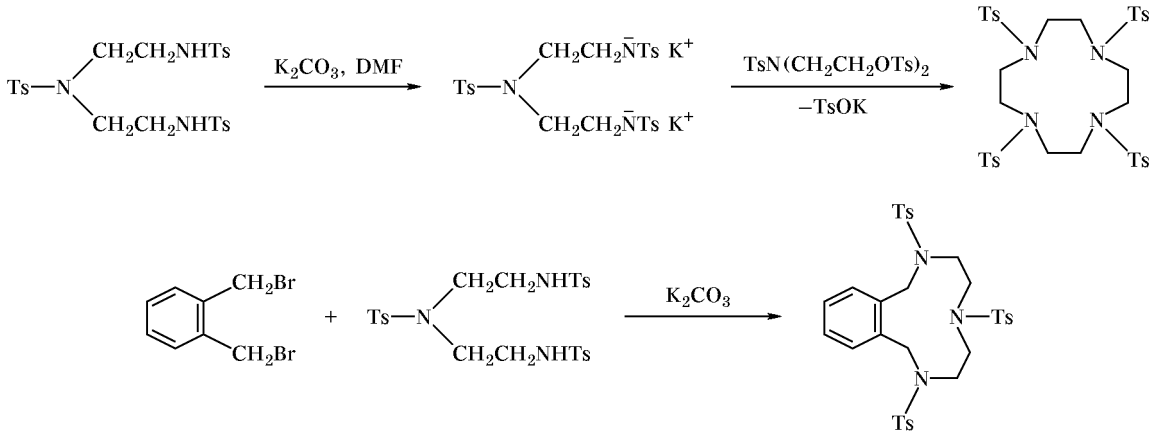
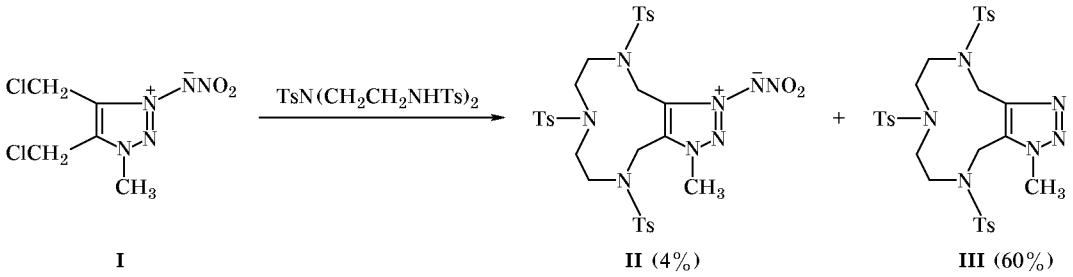
Scheme 3.

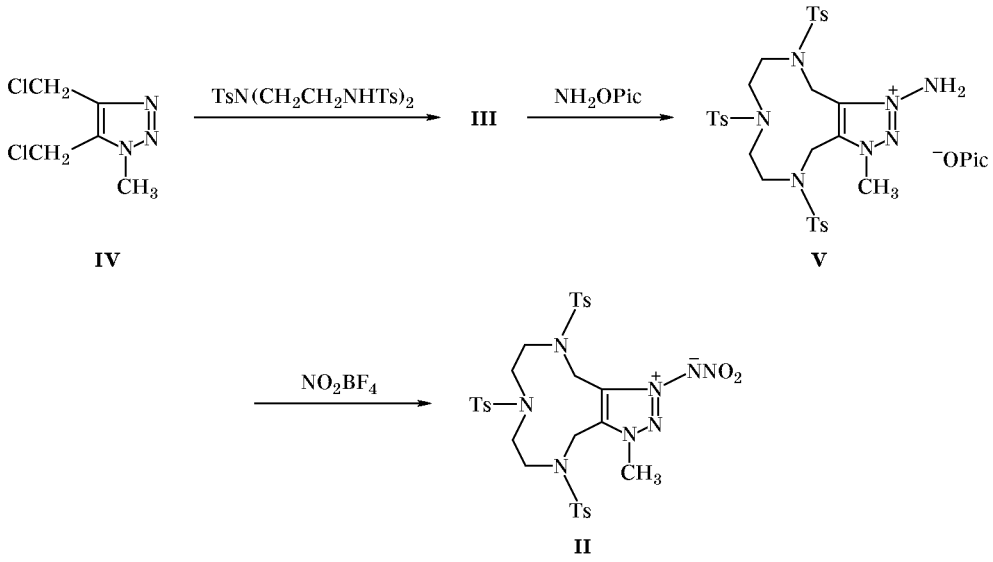


are formed, while heating above that temperature leads to decomposition of the initial compound. By amination of **III** with hydroxylamine *O*-picryl ether (NH_2OPic) in methylene chloride we obtained the corresponding 3-aminotriazolium picrate **V**, and the latter was treated with nitronium tetrafluoroborate in dry acetonitrile. As a result, we isolated *N*-nitroimide **II** with mp 200°C. Our studies have shown that in the presence of excess NO_2BF_4 both deamination of **V** and removal of tosyl groups from **II** occur. Therefore, the nitration should be carried out with a stoichiometric amount of nitronium tetrafluoroborate, and

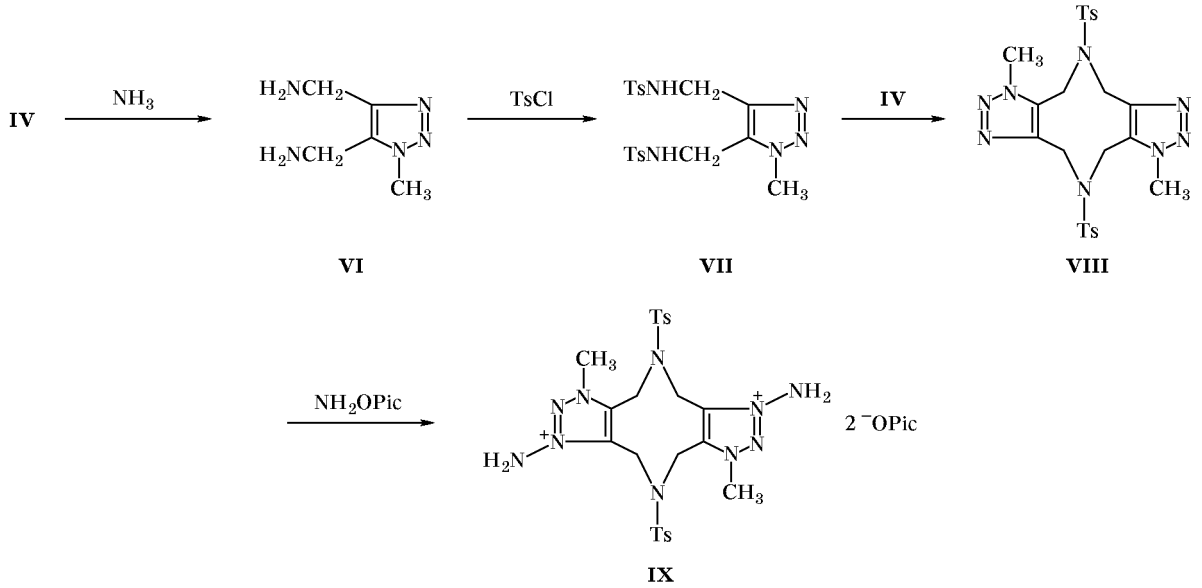
Scheme 4.



Scheme 5.



Scheme 6.



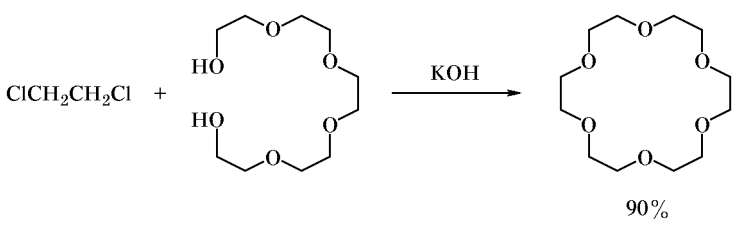
the temperature should not exceed –15°C. Compound **II** is the first representative of *N*-nitroimides in the aza crown ether series.

Next we planned to synthesize a macrocyclic compound having two *N*-nitroimide fragments. For this purpose, bis(chloromethyl)triazole **IV** was brought into reaction with diamine **VI** which was synthesized from **IV** according to Scheme 6. The reaction was carried out at 70°C, and in 2 h we obtained cyclic product **VIII** as a mixture of two isomers. Amination of **VIII** with excess hydroxylamine *O*-picryl ether in methylene chloride gave isomeric picrates **IX** which were treated with nitronium tetrafluoroborate in acetonitrile. As a result, we isolated a mixture of initial amino derivatives **IX** as tetrafluoroborates (Scheme 6). We failed to obtain the desired *N*-nitroimino derivatives by repeated nitration of these salts.

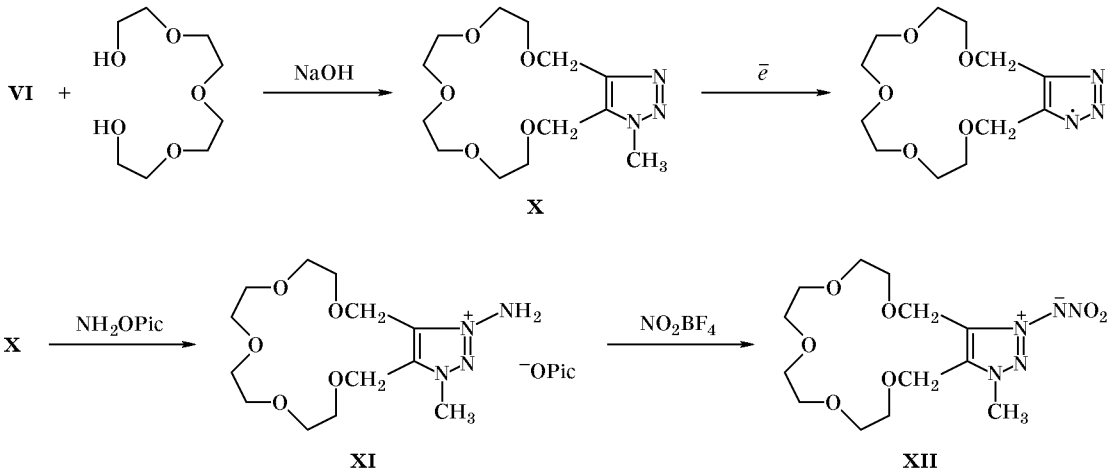
It is known [1, 4, 5] that crown ethers are usually synthesized in dioxane or diethylene glycol dimethyl ether as solvent, making use of matrix effects of alkali metal cations which fit the cavity of the crown ether being formed. The best results are usually obtained with Na^+ and K^+ ions [1]. According to the data of [5], high-temperature syntheses of crown ethers (heating above 80°C) often result in reduced yields of the target products. The optimal temperature was proposed to be 60°C. Under these conditions, the reaction takes 4 h, and a number of halogen derivatives can be involved (Scheme 7).

We have studied the condensation of bis(chloromethyl)triazole **IV** with tetraethylene glycol in dioxane at 60°C and found that the reaction takes 3 h in the presence of Li, Na^+, or K^+ ions. In all cases product **X** was isolated as a thick brown oil (Scheme 8). In the presence of lithium and potassium cations the yield of **X** was lower (30–40%) than in the presence of sodium cation (60%). Our attempts to improve the procedure for preparation of compound **X** by using 4,5-bis(hydroxymethyl)-1-methyl-1,2,3-triazole instead of **IV** were unsuccessful: the yield of product **X** did not exceed 50%. Crown ether **X** gives no molecular ion peak in the mass spectrum, and only fragment ion peaks with *m*/*z* 286 and 287 (formed by elimination of CH_3) and those resulting from

Scheme 7.



Scheme 8.

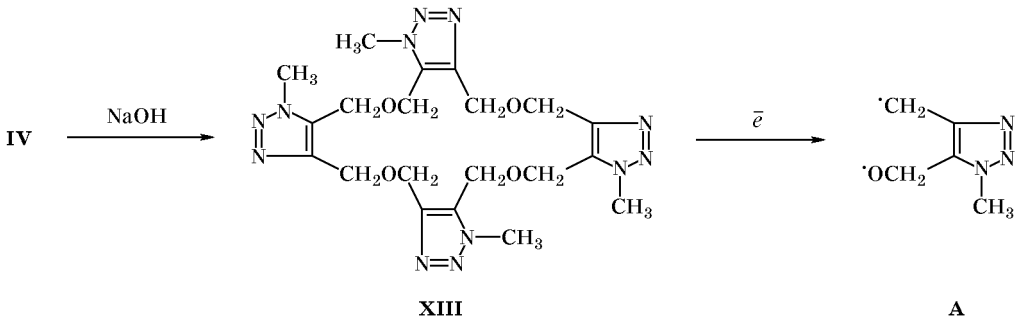


elimination of CH_2CH_2O are observed. The amination of **X** with hydroxylamine *O*-picryl ether in anhydrous methylene chloride afforded picrate **XI**. Its ^1H NMR spectrum contained a multiplet at δ 3.67 ppm from the polyether ring protons and singlets at δ 4.41 and 5.05 ppm from the methylene group protons. These data indicate that only one isomer is formed. Also, signals from the picrate ion (δ 8.67 ppm) and methyl group (δ 4.58 ppm) were present. The nitration of **XI** with NO_2BF_4 gave *N*-nitroimide **XII** with mp 140°C (Scheme 8); compound **XII** is the first stable *N*-nitroimide in the crown ether series. The product is capable of forming various complexes with alkali metal cations, which made its purification and identification difficult.

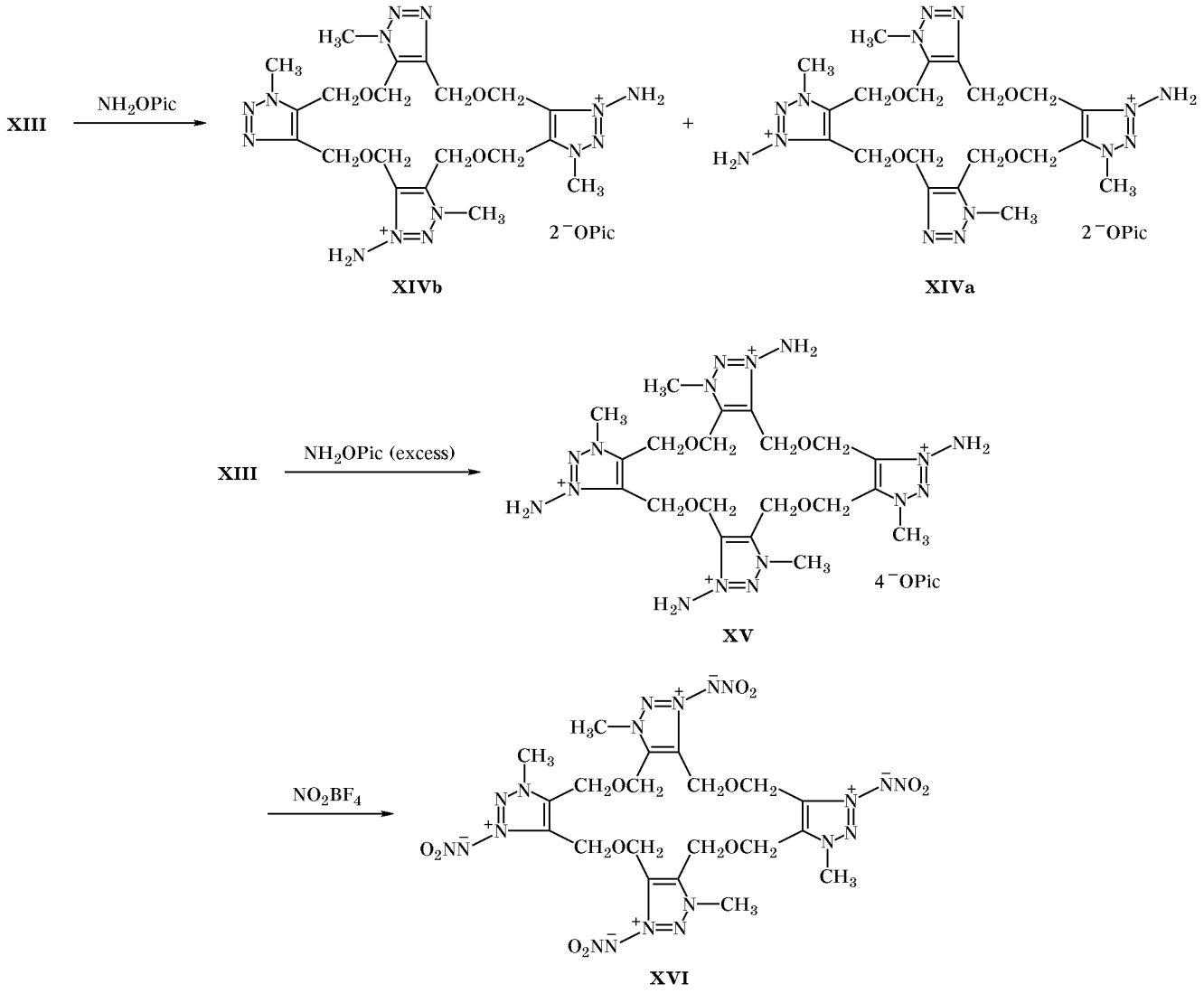
By cyclization of dichloride **IV** with 4,5-bis(hydroxymethyl)-1-methyl-1,2,3-triazole in the presence of NaOH we tried to synthesize a crown ether having several *N*-nitroimide fragments. As a result, we obtained product **XIII** in 30% yield (Scheme 9). The yield of the product was increased when 4,5-bis(chloromethyl)-1-methyl-1,2,3-triazole (**IV**) alone was used. The maximal yield of **XIII** was 60%. Its molecular weight determined experimentally was consistent with the calculated value. No molecular ion peak was found in the mass spectrum of **XIII**, but a strong peak with *m*/*z* (*I* = 28 rel. units) was observed, which suggests easy decomposition of crown ether **XIII** with formation of diradical **A**. The ^1H NMR spectrum of **XIII** contained singlets at δ 3.94, 4.59, and 4.62 ppm from the methyl and methylene groups, respectively; these data indicate a symmetrical structure of the product. Taking into account that the CH_2Cl groups in the initial compound are nonequivalent and hence the energies of the C–Cl bonds are not similar, the 1,3 : 1,3 isomer seems to be preferred. This assumption is also confirmed by the fact that the resulting crown ether reacts with a stoichiometric amount of hydroxylamine *O*-picryl ether to form diamino derivative **XIV** as a mixture of two isomers (Scheme 10); product **XIV** was isolated by treatment of the reaction mixture with pentane.

In the presence of a 20% excess of NH_2OPic we obtained 50% of tetrapicrate **XV**, and the amination took no less than 10 h, presumably because of steric effect of the amino groups being introduced. The

Scheme 9.



Scheme 10.



subsequent nitration of **XV** with a stoichiometric amount of nitronium tetrafluoroborate gave tetra-*N*-nitroimide **XVI**. We failed to raise the yield of **XVI** by increasing the amount of the nitrating agent. *N*-Nitroimide **XVI** is a low-melting substance, mp 110°C.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75-IR spectrometer. The ^{13}C NMR spectra were measured on a Bruker-250 instrument, and the ^{1}H NMR spectra, on a Jeol-90 spectrometer (90 MHz). The mass spectra were run on a Varian-XC spectrometer.

14-Methyl-3,6,9-tritosyl-3,6,9,12,13,14-hexaazabicyclo[9.3.0]tetradeca-1(11),12-dien-12-io-12-nitroimide (II). To a suspension of 0.3 g of compound **IV** in 20 ml of anhydrous acetonitrile we added with stirring at –10°C 0.04 g of NO_2BF_4 in portions. The mixture was stirred for 30 min at –10°C, 50 mg of anhydrous K_2CO_3 was added, and the mixture was stirred for 1 h at 0°C and filtered. The precipitate was washed with 5 ml of chloroform, the filtrate was combined with the washings and was evaporated to dryness under reduced pressure (10 mm, bath temperature <40°C), and the residue was recrystallized from acetonitrile. Yield 0.1 g (40%), mp 219–220°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1150, 1320, 1600, 1250, 1440, 1460, 1640, 2920, 3100. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.53 s (CH_3), 2.6 s ($2CH_3$), 3.17 s ($2CH_2$), 3.36 s ($2CH_2$), 4.65 s (CH_3), 4.87 s (CH_2), 5.17 s (CH_2), 7.6 m (8CH), 7.8 m

(4CH). Found, %: C 50.07; H 5.13; N 15.74; S 12.82. $C_{30}H_{36}N_8O_8S_3$. Calculated, %: C 49.18; H 4.90; N 15.26; S 13.08.

14-Methyl-3,6,9-tritosyl-3,6,9,12,13,14-hexaazabicyclo[9.3.0]tetradeca-1(11),12-diene (III). *a*. To a solution of 1.2 g of benzyltriethylammonium chloride in 60 ml of DMF we added with stirring 1.2 g of anhydrous K_2CO_3 and 3.6 g 1,4,7-tritosyl-1,3,7-triazaheptane. The mixture was stirred for 20 min at 20°C and heated to 40°C, a solution of 1.2 g of 4,5-bis(chloromethyl)-1-methyl-1,2,3-triazole (**IV**) in 10 ml of DMF was added over a period of 15 min, and the mixture was stirred for 2 h at 50°C and for 2 h at 80°C, cooled, and filtered. The filtrate was evaporated under reduced temperature (10 mm, bath temperature 70°C) to 1/3 of the initial volume, 100 ml of distilled water was added to the residue, and the precipitate was filtered off, washed with water, recrystallized from acetone, and dried in air. Yield 2.5 g (56%), mp 210–211°C. IR spectrum (KBr), ν, cm^{-1}: 1090, 1170, 1340, 1450, 1500, 1610, 1670, 2850, 2970. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.4 s (CH_3), 2.5 s ($2CH_3$), 3.1 m ($2CH_2$), 3.53 m ($2CH_2$), 4.29 s (CH_2), 4.36 s (CH_3), 4.58 s (CH_2), 7.6 m (4CH), 7.8 m (8CH). Found, %: C 53.18; H 5.68; N 12.65; S 13.46. $C_{30}H_{36}N_6O_6S_3$. Calculated, %: C 53.57; H 5.36; N 12.50; S 14.28.

b. To a solution of 0.15 g of benzyltriethylammonium chloride in 10 ml of DMF we added with stirring 0.1 g of anhydrous K_2CO_3 and 0.4 g of 1,4,7-tritosyl-1,3,7-triazaheptane. The mixture was heated to 50°C, and a solution of 0.2 g of dichloride **I** in 10 ml of DMF was added dropwise with vigorous stirring. The mixture was stirred for 1 h at 50°C and for 2 h at 80°C, cooled, and filtered, the filtrate was evaporated under reduced pressure (10 mm, bath temperature 70°C) to 1/3 of the initial volume, 50 ml of distilled water was added, and the precipitate was filtered off, washed with 50 ml of water, reprecipitated twice from acetone with water, and dried in air. Yield 0.32 g (57%), mp 200–203°C (no depression of the melting point was observed on mixing with a sample obtained as described in *a*). The IR spectra of the products obtained by methods *a* and *b* were identical.

12-Amino-14-methyl-3,6,9-tritosyl-3,6,9,12,13,14-hexaazabicyclo[9.3.0]tetradeca-1(11),12-dien-12-ium picrate (V). To a solution of 0.2 g of hydroxylamine *O*-picryl ether in 40 ml of chloroform we added with stirring at 20°C a solution of 0.5 g of compound **III** in 10 ml of chloroform. The mixture was stirred for 1 h at 20°C and for 1 h at 40°C. It was then cooled, the precipitate was filtered off, 15 ml of pentane was added to the filtrate, and the precipitate was filtered off, washed with pentane, and dried in air. Yield 0.6 g (90%), mp 244–245°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1070, 1160, 1280, 1340, 1440, 1490, 1510, 1560, 1610, 1630, 3100, 3550, 3620. ^1H NMR spectrum (acetone-d_6), δ, ppm: 2.5 s ($3CH_3$), 3.15 s ($2CH_2$), 3.6 s ($2CH_2$), 4.6 s (CH_3), 4.75 s (CH_2), 5.03 s (CH_2), 6.3 br.s (NH_2), 7.6 m (8CH), 7.8 m (4CH), 8.6 s (2CH). Found, %: C 46.80; H 4.36; S 9.99. $C_{36}H_{40}N_{10}O_{13}S_3$. Calculated, %: C 47.10; H 4.37; S 10.46.

4,5-Bis(aminomethyl)-1-methyl-1,2,3-triazole (VI). A solution of 0.6 g of dichloride **IV** in 5 ml of chloroform was added dropwise with stirring at 20°C to a solution of 2 ml of 30% NH_4OH in 10 ml of alcohol. The mixture was heated under reflux for 1 h, cooled, kept for 14 h at 20°C, and filtered, and the filtrate was evaporated to dryness under reduced pressure (10 mm, bath temperature 50°C). The residue was dissolved in 5 ml of dioxane, the solution was filtered, 20 ml of methylene chloride was added to the filtrate, the precipitate was filtered off, the filtrate was evaporated to dryness under reduced pressure (10 mm), and the residue was dried in a vacuum (1 mm) for 1 h. Product **VI** was isolated as an oily substance. Yield 0.4 g (85%). IR spectrum (KBr), ν, cm^{-1}: 1090, 1160, 1450, 1640, 2900, 3300. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.0 s (CH_3), 4.60 s ($2CH_2$), 6.5 br.s (NH_2).

1-Methyl-4,5-bis(tosylaminomethyl)-1,2,3-triazole (VII). A solution of 0.7 g of compound **VI** and 0.5 g of NaOH in 7 ml of distilled water was added dropwise over a period of 30 min to a solution of 2.5 g of *p*-toluenesulfonyl chloride in 20 ml of diethyl ether, vigorously stirred at 20°C. The mixture was stirred for 2 h at 20°C and was left to stand for 10 h at 20°C, the solution was separated from the precipitate by decanting, and the precipitate was washed with water until neutral washings and with ether until complete crystallization. The precipitate was dissolved in chloroform and reprecipitated with ether. Yield 0.8 g (65%), mp 134–136°C. IR spectrum (KBr), ν, cm^{-1}: 1090, 1170, 1340, 1450, 1500, 1600, 1640, 3000, 3400. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.3 s ($2CH_3$), 4.1 s (CH_3), 4.65 s ($2CH_2$), 7.5 m (8CH). Found, %: C 51.51; H 5.61. $C_{19}H_{23}N_5O_4S_2$. Calculated, %: C 50.79; H 5.12.

6,14-Dimethyl-3,11-ditosyl-3,6,7,8,11,14,15,16-octaazatricyclo[11.3.0.0^{5,9}]hexadeca-1(13),5(9),7,15-tetraene (VIII). Finely powdered anhydrous K_2CO_3, 0.19 g, was added with stirring at 20°C to a solution of 0.35 g of compound **VII** and 0.19 g of benzyltriethylammonium chloride in 10 ml of DMF. The mixture was stirred for 15 min at 20°C and heated to

40°C, and a solution of 0.18 g of compound **I** in 5 ml of DMF was added over a period of 10 min. The mixture was kept for 4 h at 70°C, cooled, and poured into 30 ml of distilled water, and the precipitate was filtered off, washed with 3–5 portions of water, and dried in air. The product was purified by reprecipitation from acetonitrile with chloroform. Yield 0.26 g (58%), mp 176–178°C. IR spectrum (KBr), ν, cm^{-1}: 1080, 1330, 1430, 1460, 1590, 1620, 2930, 3060. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.3 s ($2CH_3$), 3.85 s ($2CH_3$), 4.45 s ($2CH_2$), 4.6 s ($2CH_2$), 7.5 m (8CH). Found, %: C 51.94; H 5.79. $C_{24}H_{28}N_8O_4S_2$. Calculated, %: C 51.79; H 5.36.

6,14-Diamino-8,16-dimethyl-3,11-ditosyl-3,6,7,-8,11,14,15,16-octaazatricyclo[11.3.0.0^{5,9}]hexadeca-1(13),5(9),7,15-tetraene-6,14-diium dipicrate (IX). A solution of 0.25 g of compound **VIII** in 30 ml of dry methylene chloride was added with stirring at 20°C to a solution of 0.25 g of hydroxylamine *O*-picryl ether in 30 ml of dry methylene chloride. The mixture was stirred for 4 h at 20°C and was left to stand for 10 h at 20°C, 10 ml of pentane was added, and the precipitate was filtered off and recrystallized from aqueous alcohol. Yield 0.35 g (70%), mp 198–200°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1080, 1150, 1330, 1420, 1450, 1350, 1560, 1600, 1640, 2950, 3100, 3150, 3350. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.3 s ($2CH_3$), 4.05 s ($2CH_3$), 4.55 s ($2CH_2$), 4.7 s ($2CH_2$), 7.55 m (8CH), 8.6 s (4CH). Found, %: C 41.99; H 4.60; S 6.07. $C_{36}H_{36}N_{16}O_{18}S_2$. Calculated, %: C 41.38; H 3.44; S 6.13.

18-Methyl-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.3.0]eicosa-1(17),19-diene (X). *a*. Potassium hydroxide, 0.32 g, was added at 20°C to a solution of 0.4 g of 4,5-bis(hydroxymethyl)-1-methyl-1,2,3-triazole in 30 ml of DMF. The mixture was stirred for 10 min at 20°C, 1.5 g of tetraethylene glycol bis(*p*-toluenesulfonate) was added, and the mixture was heated under stirring to 60°C, stirred for 2 h at that temperatire, cooled, and evaporated under reduced pressure (10 mm, bath temperature 70°C) to 1/4 of the initial volume. Diethyl ether, 20 ml, was added to the residue, and the precipitate was filtered off, the filtrate was evaporated to dryness under reduced pressure (10 mm, water bath), 10 ml of distilled water was added to the residue, and the product was extracted into chloroform (3 × 5 ml). The combined extracts were dried over magnesium sulfate and evaporated to dryness, and the residue was dried under reduced pressure (10 mm, bath temperature 50°C) for 1 h. Compound **X** was isolated as a yellow oily substance, yield 0.5 g (50%).

b. To a solution of 0.3 g of tetraethylene glycol in 15 ml of dioxane at 20°C we added 0.27 g of sodium hydroxide, the mixture was stirred for 30 min at 20°C, a solution of 0.3 g of compound **IV** in 5 ml of dioxane was added over a period of 15 min, and the mixture was stirred for 4 h at 50°C and cooled. The precipitate was filtered off and washed with 5 ml of dioxane, the filtrate was evaporated to dryness under reduced pressure (10 mm, bath temperature 50°C), 5 ml of distilled water was added to the residue, and the product was extracted into methylene chloride (3 × 5 ml). The combined extracts were dried over magnesium sulfate and evaporated to dryness. Compound **X** was isolated as a yellow oily substance. Yield 0.3 g (60%). IR spectrum (KBr), ν, cm^{-1}: 1100, 1250, 1280, 1350, 1450, 1620, 2880. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.6 m ($8CH_2$), 3.97 s (CH_3), 4.73 s (CH_2), 4.83 s (CH_2). Mass spectrum (70 eV), *m*/*z* (*I*, rel. units): 300 (2); 296 (16); 251, 252 (18); 207, 208 (17); 163, 164 (22); 44 (28); 15 (27). Found, %: C 52.42; H 6.78. $C_{13}H_{23}N_3O_5$. Calculated, %: C 52.00; H 7.66.

18-Amino-20-methyl-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.3.0]eicosa-1(17),18-dien-18-ium picrate (XI). *a*. A solution of 0.25 g of compound **X** in 5 ml of chloroform was added at 20°C to a solution of 0.25 g of hydroxylamine *O*-picryl ether in 20 ml of chloroform. The mixture was stirred for 2 h at 20°C and was left to stand for 10 h, 10 ml of pentane was added, and the tarry precipitate was filtered off and recrystallized from alcohol. Yield 0.3 g (60%), mp 109°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1070, 1150, 1265, 1310–1360, 1430, 1500, 1540, 1620, 2900, 3100, 3400. ^1H NMR spectrum (acetone-d_6), δ, ppm: 8.62 s (2CH), 6.5 br.s (NH_2), 5.05 s (CH_2), 4.41 s (CH_2), 3.58 s (CH_3), 3.67 m ($8CH_2$). Found, %: C 41.43; H 3.87. $C_{19}H_{25}N_7O_{12}$. Calculated, %: C 41.83; H 4.95.

20-Methyl-3,6,9,12,15-pentaoxa-18,19,20-triazabicyclo[15.3.0]eicosa-1(17),18-dien-18-io-18-nitroimide (XII). Nitronium tetrafluoroborate, 0.23 g, was added in portions with stirring at –10°C to a solution of 0.5 g of compound **XI** in 20 ml of anhydrous acetonitrile. The mixture was stirred for 30 min at –10°C, 0.15 g of anhydrous K_2CO_3 was added, the mixture was stirred for 30 min at 0°C, the precipitate was filtered off, and the filtrate was evaporated to dryness under reduced pressure (10 mm, bath temperature <40°C). The residue was washed with 20 ml of hot water, reprecipitated from acetonitrile with ether, and dried in air. Yield 0.07 g (25%), mp 142–143°C. IR spectrum (KBr), ν, cm^{-1}: 1270, 1440 ($NNNO_2$). ^1H NMR spectrum (CD_3CN), δ, ppm: 4.1 s

(CH_3), 4.8 s (CH_2), 4.88 s (CH_2), 3.68 m ($8CH_2$). Found, %: C 43.39; H 6.87; N 18.74. $C_{13}H_{23}N_5O_7$. Calculated, %: C 43.21; H 6.37; N 19.39.

6,16,22,32-Tetramethyl-3,11,19,27-tetraoxa-6,7,-8,14,15,16,22,23,24,30,31,32-dodecaazapentacyclo-[27.3.0.0^{5,9}.0^{13,17}.0^{21,25}]dotriaconta-1(29),5(9),7,-13(17),14,21(25),23,30-octaene (XIII). A solution of 3 g of compound **IV** in 10 ml of dioxane was added over a period of 20 min to a suspension of 2 g of sodium hydroxide in 40 ml of dioxane, vigorously stirred at 40°C. The mixture was stirred for 4 h at 60°C and cooled, the precipitate was filtered off, the filtrate was evaporated to dryness under reduced pressure (10 mm, bath temperature ≤50°C), 10 ml of distilled water was added to the residue, and the product was extracted into methylene chloride (2 × 10 ml). The extract was dried over magnesium sulfate and evaporated to dryness, and the residue was evacuated for 1 h (1 mm). Compound **XIII** was isolated as a yellow oily substance. Yield 1.25 g (70%). IR spectrum (KBr), ν, cm^{-1}: 1070, 1100, 1240, 1380, 1440, 1470, 1650, 2850, 2950. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.94 s ($4CH_3$), 4.59 s ($4CH_2$), 4.62 s ($4CH_2$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.721 (CH_3), 34.76 and 34.90 (CH_2), 131.158 and 142.069 (C). Mass spectrum, *m*/*z* (*I*, rel. units): 125 (37), 110 (42), 15 (39). *M* 470.

8,30(or 8,24)-Diamino-6,16,22,32-tetramethyl-3,11,19,27-tetraoxa-6,7,8,14,15,16,22,23,24,30,31,32-dodecaazapentacyclo[27.3.0.0^{5,9}.0^{13,17}.0^{21,25}]dotriaconta-1(29),5(9),7,13(17),14,21(25),23,30-octaene-8,30(or 8,24)-diium dipicrate (XIV). A solution of 1 g of compound **XIII** in 50 ml of methylene chloride was added at 20°C to a solution of 2 g of hydroxylamine *O*-picryl ether in 150 ml of methylene chloride. The mixture was stirred for 2 h, 100 ml of pentane was added, and the precipitate was filtered off, recrystallized from methylene chloride, and dried under reduced pressure (10 mm, bath temperature 40°C) for 1 h. Yield 1.5 g (75%), mp 117–119°C. IR spectrum (KBr), ν, cm^{-1}: 3100, 3300, 1640, 1610, 1550, 1340, 1320, 1250, 1140, 1080. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 4.0 d ($4CH_3$), 4.3 d ($4CH_3$), 4.6 d ($2CH_2$), 4.7 d ($2CH_2$), 5.2 d ($2CH_2$), 5.3 d ($2CH_2$), 8.6 s (8CH), 5.7 br.s ($2NH_2$). Found, %: C 39.27; H 3.61; N 20.85. $C_{32}H_{36}N_{20}O_{18}$. Calculated, %: C 38.86; H 3.64; N 21.45.

8,14,24,30-Tetraamino-6,16,22,32-tetramethyl-3,11,19,27-tetraoxa-6,7,8,14,15,16,22,23,24,30,31,32-dodecaazapentacyclo[27.3.0.0^{5,9}.0^{13,17}.0^{21,25}]dotriaconta-1(29),5(9),7,13(17),14,21(25),23,30-octaene-8,14,24,30-tetraium tetrapicrate (XV). A solution of 1 g of compound **XIII** in 50 ml of methylene chloride was added at 20°C to a solution of 2 g of hydroxylamine *O*-picryl ether in 200 ml of methylene chloride. The mixture was stirred for 2 h at 20°C and was left overnight, and the precipitate was filtered off, recrystallized from alcohol, and dried under reduced pressure (10 mm) for 1 h. Yield 1.5 g (50%), mp 169–170°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 3100, 3300, 1640, 1610, 1550, 1340, 1320, 1260, 1150, 1080. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 4.3 s ($4CH_3$), 5.3 s ($4CH_2$), 6.5 br.s (NH_2), 5.35 s ($4CH_2$), 8.54 s (8CH). Found, %: C 35.27; H 2.99. $C_{44}H_{44}N_{28}O_{28}$. Calculated, %: C 35.50; H 2.97.

6,16,22,32-Tetramethyl-3,11,19,27-tetraoxa-6,7,-8,14,15,16,22,23,24,30,31,32-dodecaazapentacyclo-[27.3.0.0^{5,9}.0^{13,17}.0^{21,25}]dotriaconta-1(29),5(9),7,-13(17),14,21(25),23,30-octaene-8,14,24,30-tetraio-8,14,24,30-tetrakis(nitroimide) (XVI). Nitronium tetrafluoroborate, 0.16 g, was added in portions to a suspension of 0.5 g of compound **XV** in 10 ml of anhydrous acetonitrile, stirred at –10°C. The mixture was stirred for 1 h at –10°C, 0.2 g of potassium carbonate was added, and the mixture was stirred for 1 h at –5°C and filtered. The filtrate was evaporated to dryness, and the residue was reprecipitated from acetonitrile with ether and dried in air. Yield 0.1 g (50%), mp 110°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1270–1280, 1420, 1110, 3100. ^{1}H NMR spectrum (CD_3CN), δ, ppm): 4.4 s ($4CH_3$), 5.32 s ($4CH_2$), 5.47 s ($4CH_2$). Found, %: C 32.60; H 3.7. $C_{20}H_{28}N_{20}O_{12}$. Calculated, %: C 32.43; H 3.78.

Determination of the molecular weight of crown ether XIII. *a. Rast procedure.* Camphor was used as reference, mp 177°C (0.8 g); sample weight 0.051 g. ΔT 5.5°C. M_{calc} 463.

b. From refractive index. Acetonitrile was used as reference, d = 0.78 g/ml, n_D^{22} = 1.3412. Crown ether, d = 1.2 g/ml, n_D^{22} = 1.5488. A solution of crown ether in acetonitrile (1 : 10), d = 0.87 g/ml, n_D^{22} = 1.3540. Calculation by the Lorentz–Lorentz formula assuming refraction additivity gave M = 482.

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