**Electronic supplementary materials** *Mendeleev Commun*., 2010, **20**, 4–6

# Synthesis and structure of the pyrimidinophanes with a sulfur atom in the spacer

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## General

The mass spectra (EI) were obtained on a Finnigan MAT-212 mass spectrometer (resolution was 1000; data were processed using the MSS MASPEC II data system 32; direct inlet of the sample into the ion source, programming of the temperature from 20 to 300°C, energy of ionizing electrons was 70 eV, electron emission current was 1.0 mA). High resolution mass measurements were performed on the same instrument by mass matching procedure, reference substance is perfluorokerosene. MALDI-TOF spectra were obtained on a DYNAMO-3 spectrometer).

NMR experiments were performed on a Bruker AVANCE-600 spectrometer (14.1 T). Chemical shifts (ppm) are referenced to the internal TMS signal (0 ppm) in all cases. The IR spectra were recorded on a Vector 22 FTIR Spectrometer (Bruker) in the 4000-400 $cm^{-1}$ range at a resolution of 1 $cm^{-1}$. Elemental analyses were performed by the Analytical Laboratory at the A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Center of Russian Academy of Sciences. Microanalyses of C, H, N were performed with a CHN-3 analyzer. The melting points were measured on a Boetius hot-stage apparatus and were not corrected. Chromatography was performed in a thin layer on Silufol-254 plates; visualization was carried out with UV light. For column chromatography silica gel (60 mesh) from Fluka was used.

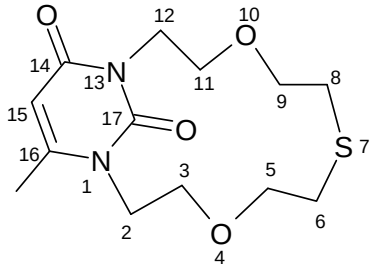
All solvents were purified according to standard protocols.

## Pyrimidinophanes containing one uracil unit and sulfur atom

Catalytic amounts of $[NBu_4]HSO_4$ and a suspension of 8.5 mmol of $Na_2S$ in DMF were added to the solution of 6.5 mmol of 1,3-bis(ω-bromoalkyl)uracil or quinazoline-2,4-dione in DMF at 60ºC. Stirring was continued at 100-110ºC until the consumption of the starting materials (monitored by TLC). The solvent was removed under reduced pressure, and the residue

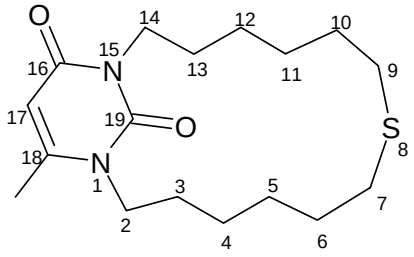
was purified using column chromatography ($SiO_2$, EtOAc/light petroleum 1:1) to afford the product.

**16-Methyl-1,13-diaza-4,10-dioxa-7-thiabicyclo[11.3.1]heptadec-15-ene-14,17-dione 2a**



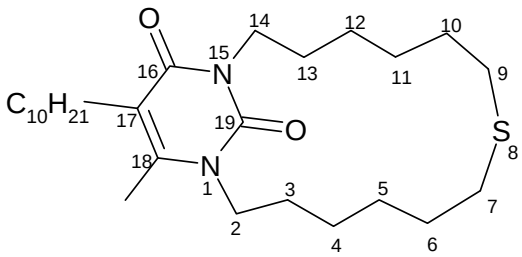
0.55 g (28%) of pyrimidinophane **2a**, mp 98-102ºC, was obtained from 2.20 g (6.49 mmol) of compound **1a** and 0.66 g (8.46 mmol) of $Na_2S$ in 120 ml of DMF. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 5.60 (s, 1H, $C^{15}H$), 4.32 (m, 1H, $C^{12}H$), 4.22 (m, 1H, $C^{12}H$), 4.20 (m, 1H, $C^2H$), 3.88 (m, 1H, $C^{11}H$), 3.81 (m, 1H, $C^3H$), 3.78 (m, 1H, $C^9H$), 3.76 (m, 1H, $C^{11}H$), 3.75 (m, 1H, $C^2H$), 3.70 (m, 1H, $C^5H$), 3.69 (m, 1H, $C^3H$), 3.57 (m, 1H, $C^9H$), 3.41 (m, 1H, $C^5H$), 2.67 (m, 1H, $C^8H$), 2.62 (m, 2H, $C^6H_2$), 2.55 (m, 1H, $C^8H$), 2.20 (s, 3H, $C^{16}CH_3$). $^{13}$C NMR spectrum, δ, ppm: 162.5 ($C^{17}$), 152.7 ($C^{16}$), 152.5 ($C^{14}$), 101.6 ($C^{15}$), 72.5 ($C^9$), 70.2 ($C^5$), 67.0 ($C^3$), 66.5 ($C^{11}$), 45.3 ($C^2$), 40.5 ($C^{12}$), 31.8 ($C^8$), 30.8 ($C^6$), 20.8 ($C^6\underline{C}H_3$). Mass-spectrum, m/z ($I_{rel}$, %): 301 (3) $[M+1]^+$, 300 (18) $[M]^+$, 197 (25), 171 (74), 166 (15), 153 (35), 127 (21), 110 (15). Found (%): C, 51.87; H, 6.64; N, 9.31; S, 10.81. $M^+$ 300.1141. Calc. for $C_{13}H_{20}N_2O_4S$ (%): C, 51.98; H, 6.71; N, 9.33; S, 10.68. M 300.11438.

**18-Methyl-1,15-diaza-8-thiabicyclo[13.3.1]nonadec-17-ene-16,19-dione 2b**



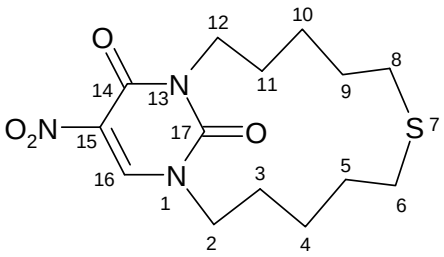
0.51 g (24%) of pyrimidinophane **2b**, mp 85.5-86.5ºC, was obtained from 2.94 g (6.50 mmol) of compound **1b** and 0.66 g (8.46 mmol) of $Na_2S$ in 100 ml of DMF. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 5.57 (s, 1H, $C^{17}H$), 4.02 (t, 2H, $C^{14}H_2$, J=6.6), 3.93 (t, 2H, $C^2H_2$, J=6.6), 2.47-2.43 (m, 4H, $C^7H_2$, $C^9H_2$), 2.24 (s, 3H, $C^{18}CH_3$), 1.70-1.55 (m, 8H, $C^3H_2$, $C^6H_2$, $C^{10}H_2$, $C^{13}H_2$), 1.48-1.25 (m, 8H, $C^4H_2C^5H_2$, $C^{11}H_2C^{12}H_2$). Mass-spectrum, m/z ($I_{rel}$, %): 325 (27) $[M+1]^+$, 324 (99) $[M]^+$, 309 (39) $[M-15]^+$, 307 (21), 291 (27), 243 (39), 241 (26), 224 (14), 211 (51), 209 (50), 195 (32), 167 (20), 154 (20), 153 (13), 141 (29), 140 (43), 127 (100), 126 (17), 115 (41), 114 (34), 110 (33). Found (%): C, 62.80; H, 8.61; N, 8.77; S, 9.79. $M^+$ 324.1869. Calc. for $C_{17}H_{28}N_2O_2S$ (%): C, 62.93; H, 8.70; N, 8.63; S, 9.88. M 324.1872.

**17-Decyl-18-methyl-1,15-diaza-8-thiabicyclo[13.3.1]nonadec-17-ene-16,19-dione 2c**



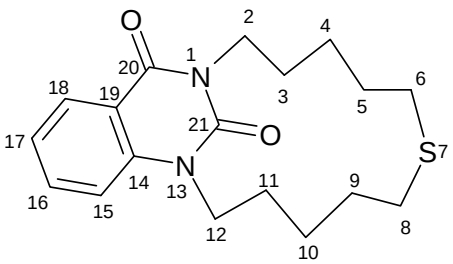
0.58 g (19%) of pyrimidinophane **2c**, mp 60-61ºC, was obtained from 3.85 g (6.50 mmol) of compound **1c** and 0.66 g (8.46 mmol) of $Na_2S$ in 130 ml of DMF. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 4.06-4.03 (m, 2H, $C^{14}H_2$), 4.00-3.96 (m, 2H, $C^2H_2$), 2.46-2.41 (m, 6H, $C^{17}CH_2$, $C^7H_2$, $C^9H_2$), 2.25 (s, 3H, $C^{18}CH_3$), 1.68-1.25 (m, 24H, $C^3H_2C^4H_2C^5H_2C^6H_2$, $C^{10}H_2C^{11}H_2C^{12}H_2C^{13}H_2$, $C^{17}C(C\underline{H}_2)_8$), 0.87 (t, 3H, $C^{17}(C)_9C\underline{H}_3$, J=6.8). Mass-spectrum, m/z ($I_{rel}$, %): 465 (31) $[M+1]^+$, 464 (100) $[M]^+$, 449 (23) $[M-15]^+$, 351 (19), 338 (23), 337 (53), 267 (21), 141 (12), 115 (17). Found (%): C, 69.90; H, 10.52; N, 5.92; S, 6.76. $M^+$ 464.3432. Calc. for $C_{27}H_{48}N_2O_2S$ (%): C, 69.78; H, 10.41; N, 6.03; S, 6.90. M 464.34366.

**15-Nitro-1,13-diaza-7-thiabicyclo[11.3.1]heptadec-15-ene-14,17-dione 2d**



0.28 g (13%) of pyrimidinophane **2d**, mp 118-121ºC, was obtained from 2.96 g (6.51 mmol) of compound **1d** and 0.66 g (8.46 mmol) of $Na_2S$ in 100 ml of DMF. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 8.65 (s, 1H, $C^{16}H$), 4.16-3.93 (m, 4H, $C^2CH_2$, $C^{12}CH_2$), 2.70-2.30 (m, 4H, $C^6CH_2$, $C^8CH_2$), 1.82-1.40 (m, 12H, $C^3H_2C^4H_2C^5H_2$, $C^9H_2C^{10}H_2C^{11}H_2$). Found (%): C, 51.50; H, 6.55; N, 12.70; S, 9.87. Calc. for $C_{14}H_{21}N_3O_4S$ (%): C, 51.36; H, 6.47; N, 12.83; S, 9.79. MALDI-TOF spectrum: 327 $[M]^+$.

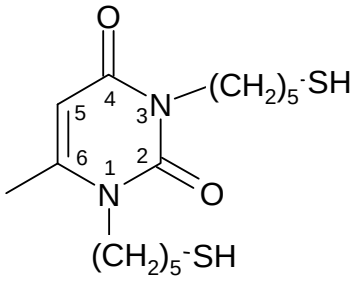
**1,13-Diaza-7-thiatricyclo[11.7.1.0$^{14,19}$]henicosa-14(19),15,17-triene-20,21-dione 4**



0.82 g (38%) of pyrimidinophane **4**, mp 106-107ºC, was obtained from 3.00 g (6.52 mmol) of compound **3** and 0.66 g (8.46 mmol) of $Na_2S$ in 130 ml of DMF. $^1$H NMR spectrum

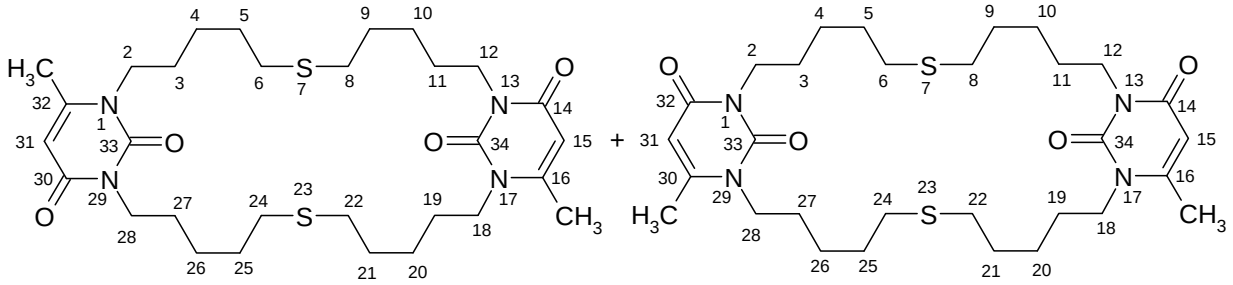
($CDCl_3$, δ, ppm, J/Hz): 8.25 (d.d, 1H, $C^{15}H$, J=7.8, 1.3), 7.66-7.63 (d.d.d, 1H, $C^{17}H$, J=8.6, 7.7, 1.3), 7.26-7.21 (m, 2H, $C^{16}H$, $C^{18}H$), 4.90-4.60 (br.s, 1H, $C^{12}H$), 4.40-4.15 (br.s, 2H, $C^{2}H_2$), 3.90-3.70 (br.s, 1H, $C^{12}H$), 2.70-2.30 (br.s, 4H, $C^{6}H_2$, $C^{8}H_2$), 1.95-1.80 (m, 4H, $C^{3}H_2$, $C^{11}H_2$), 1.60-1.40 (m, 8H, $C^{4}H_2C^{5}H_2$, $C^{9}H_2C^{10}H_2$). IR spectrum (KBr), ν/$cm^{-1}$: 3440, 3393, 3336, 3063, 3032, 3003, 2928, 2851, 1696, 1654, 1610, 1483, 1456, 1436, 1400, 1383, 1364, 1340, 1295, 1263, 1213, 1178, 1139, 1120, 1103, 1067, 1044, 1023, 1001, 979, 946, 932, 902, 857, 845, 827, 808, 795, 760, 734, 699, 686, 677, 622, 555, 524, 455. Mass-spectrum, m/z ($I_{rel}$, %): 333 (19) $[M+1]^+$, 332 (100) $[M]^+$, 299 (27), 277 (16), 265 (66), 264 (33), 233 (50), 231 (46), 176 (39), 163 (76), 146 (44), 132 (84), 101 (33). Found (%): C, 65.17; H, 7.20; N, 8.31; S, 9.77. $M^+$ 332.1560. Calc. for $C_{18}H_{24}N_2O_2S$ (%): C, 65.03; H, 7.28; N, 8.43; S, 9.65. M 332.1558.

**1,3-Bis(5-mercaptopentyl)-6-methyl-1*H*-pyrimidine-2,4-dione 6**



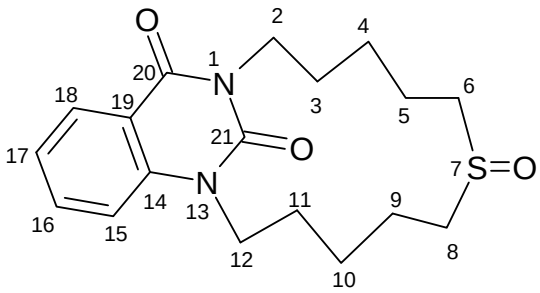

To the solution of 2.00 g of compound **1e** (4.72 mmol) in 60 ml of methanol 0.72 g of thiourea (9.44 mmol) was added. Reaction mixture was refluxed for 25 h, the solvent was removed and the diethyl ether was added. The precipitate of thiuronium salt **5** was separated and the solution of 0.57 g NaOH (14.16 mmol) in 50 ml of water was added. Reaction mixture was stirred for 2 hours at 50ºC, acidified with HCl until pH<7 and extracted with dichloromethane. The solvent was removed under reduced pressure, and the residue was purified using column chromatography ($SiO_2$, EtOAc/light petroleum 2:1) to afford 0.37 g of the product **6** as an oil. $^1H$ NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 5.56 (s, 1H, $C^{5}H$), 3.91 (t, 2H, $N^{3}CH_2$, J=7.4), 3.80 (t, 2H, $N^{1}CH_2$, J=7.9), 2.57-2.50 (m, 4H, $2CH_2S$), 2.23 (s, 3H, $C^{6}CH_3$), 1.69-1.59 (m, 8H, $2NCC\underline{H_2}CC\underline{H_2}$), 1.51-1.40 (m, 4H, $2NCCC\underline{H_2}CC$), 1.34 (t, 1H, SH, J=7.7), 1.32 (t, 1H, SH, J=7.9). IR spectrum (KBr), ν/$cm^{-1}$: 3434, 3091, 2930, 2856, 2556, 2352, 2280, 1700, 1658, 1621, 1538, 1467, 1430, 1401, 1360, 1323, 1269, 1210, 1050, 816, 769, 730, 655, 626, 580, 548, 440, 424, 414. Found (%): C 54.33; H 7.88; N 8.61; S 19.54. Calc. for $C_{15}H_{26}N_2O_2S_2$ (%): C 54.51; H 7.93; N 8.48; S 19.40.

**Mixture of 16,32-dimethyl-1,13,17,29-tetraaza-7,23-dithiatricyclo[27.3.1.1$^{13,17}$]-tetratriaconta-15,31-diene-14,30,33,34-tetraone 7a and 16,30-dimethyl-1,13,17,29-tetraaza-7,23-dithiatricyclo[23.3.1.1$^{13,17}$]tetratriaconta-15,30-diene-14,32,33,34-tetraone 7b**



Solutions of 0.48 g of compound **1e** (1.13 mmole in 60 ml of $CH_3CN$ and 0.37 g of dithiol **6** (1.12 mmol) in 60 ml of $CH_3CN$ were added dropwise to the solution of 1.11 g of $Cs_2CO_3$ (3.39 mmol) and a catalytic amount of $[NBu_4]HSO_4$ in 80 ml of acetonitrile at 70-75ºC. Reaction mixture was stirred at 70-75ºC for 14 h. After cooling to room temperature the solvent was removed under reduced pressure, and the residue was purified using column chromatography ($SiO_2$, EtOAc/methanol 20:1) to afford 0.19 g (29%) of the mixture of pyrimidinophanes **7a,b**, mp 60-90ºC. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 5.57 (s, 2H, 2C$^5$H), 3.94-3.90 (m, 4H, N$^{13}$CH$_2$, N$^{29}$CH$_2$), 3.83-3.79 (m, 4H, N$^1$CH$_2$, N$^{17}$CH$_2$), 2.52-2.45 (m, 8H, 4CH$_2$S), 2.23 (s, 6H, C$^{16}$CH$_3$, C$^{32}$CH$_3$), 1.69-1.55 (m, 16H, 4NCC<u>H$_2$</u>CC<u>H$_2$</u>), 1.51-1.39 (m, 8H, 4NCCC<u>H$_2$</u>CC). Mass-spectrum, m/z ($I_{rel}$, %): 593 (6) $[M+1]^+$, 592 (10) $[M]^+$, 297 (25), 295 (18), 265 (14), 229 (36), 197 (31), 195 (41), 141 (22), 140 (34), 127 (100). Found (%): C, 60.57; H, 8.04; N, 9.57; S, 10.98. $M^+$ 592.3100. Calc. for $C_{30}H_{48}N_4S_2O_4$ (%): C, 60.78; H, 8.16; N, 9.45; S, 10.82. M 592.3117.

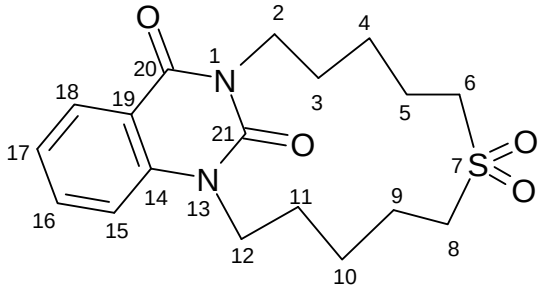
**7-Oxo-1,13-diaza-7-thiatricyclo[11.7.1.0$^{14,19}$]henicosa-14(19),15,17-triene-20,21-dione 8a**



To the solution of 0.15 g (0.45 mmol) of pyrimidinophane **4** in 20 ml of acetonitrile catalytic amounts of $MnSO_4$ (1 mg) were added, the solution was cooled to 0ºC and 0.2 ml of 34% $H_2O_2$ solution was added. The temperature was gradually risen to 20ºC and the mixture was stirred for 10 h. The solvent was removed under reduced pressure, the residue was recrystallized from isopropanol to give 0.12 g (77%) of pyrimidinophane **8a**, mp 215ºC. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 8.25 (d, 1H, C$^{15}$H, J=7.9), 7.67 (d.d, 1H, C$^{17}$H, J=7.9, 7.9), 7.27-7.26 (m,

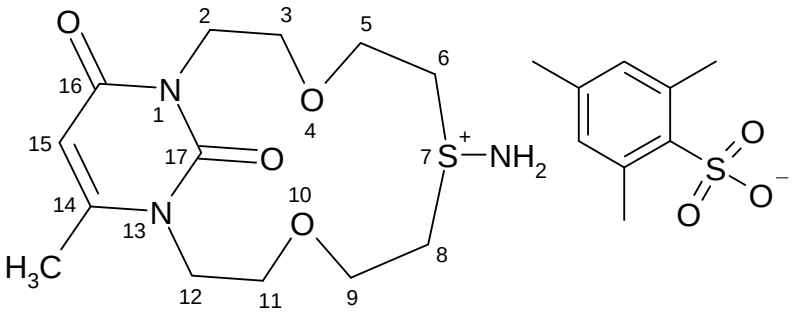
1H, C$^{16}$H), 7.21 (d, 1H, C$^{18}$H, J=8.3), 4.62-4.48 (m, 1H, NCH), 4.42-4.38 (m, 1H, NCH), 4.10-3.91 (m, 2H, 2NCH), 2.95-2.80 (m, 2H, $CH_2S$), 2.74-2.65 (m, 2H, $CH_2S$), 1.97-1.25 (m, 12H, 2NCC$\underline{H_2}$C$\underline{H_2}$C$\underline{H_2}$). IR spectrum (KBr), ν/cm$^{-1}$: 3444, 3072, 2929, 2857, 1694, 1651, 1609, 1484, 1461, 1443, 1403, 1385, 1366, 1334, 1296, 1266, 1213, 1186, 1127, 1105, 1038, 1016, 959, 943, 913, 867, 836, 796, 754, 695, 676, 634, 457, 439. Mass-spectrum, m/z ($I_{отн}$, %): 349 (9) $[M+1]^+$, 348 (40) $[M]^+$, 332 (17), 331 (89), 233 (13), 229 (20), 189 (13), 176 (27), 163 (40), 162 (17), 146 (40), 132 (100), 101 (16), 100 (12). Found (%): C, 62.15; H, 6.99; N, 7.92; S, 9.32. $M^+$ 348.1500. Calc. for $C_{18}H_{24}N_2O_3S$ (%): C, 62.04; H, 6.94; N, 8.04; S, 9.20. M 348.1508.

**7,7-Dioxo-1,13-diaza-7-thiatricyclo[11.7.1.0$^{14,19}$]henicosa-14(19),15,17-triene-20,21-dione 8b**




To the solution of 0.12 g (0.36 mmol) of pyrimidinophane **4** in 10 ml of acetonitrile catalytic amounts of $MnSO_4$ (1 mg) were added, the solution was cooled to 0ºC and 0.2 ml of 34% $H_2O_2$ solution and 7 ml of 0.2 M solution of $NaHCO_3$ were added. The temperature was gradually risen to 50ºC and the mixture was stirred for 10 h. After cooling the solvent was removed under reduced pressure, the residue was purified using column chromatography ($SiO_2$, EtOAc/methanol 35:1) to afford 0.06 g (46%) of pyrimidinophane **8b**, mp 188-189ºC. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 8.25 (d, 1H, C$^{15}$H, J=7.9), 7.68 (d.d, 1H, C$^{17}$H, J=8.3, 7.3), 7.29 (d.d, 1H, C$^{16}$H, J=7.9, 7.3), 7.19 (d, 1H, C$^{18}$H, J=8.3), 4.40-4.30 (m, 2H, $NCH_2$), 4.25-4.20 (m, 2H, $NCH_2$), 2.95-2.88 (m, 4H, 2$CH_2S$), 1.93-1.88 (m, 4H, 2NCC$\underline{H_2}$), 1.80-1.76 (m, 4H, 2C$\underline{H_2}$CS), 1.61-1.52 (m, 4H, 2NCCC$\underline{H_2}$). IR spectrum (KBr), ν/cm$^{-1}$: 3444, 3331, 3199, 3097, 2984, 2963, 2928, 2875, 2850, 2363, 1699, 1652, 1608, 1483, 1456, 1402, 1381, 1355, 1336, 1310, 1289, 1265, 1222, 1196, 1166, 1140, 1121, 1082, 1041, 1024, 969, 948, 933, 893, 876, 846, 803, 763, 743, 706, 690, 675, 569, 548, 508, 459, 425. Mass-spectrum, m/z ($I_{rel}$, %): 365 (23) $[M+1]^+$, 364 (100) $[M]^+$, 245 (16), 233 (28), 232 (20), 231(29), 203 (15), 190 (36), 189 (24), 188 (12), 177 (22), 176 (99), 175 (15), 163 (28), 162 (67), 146 (33), 133 (13), 132 (100), 119 (12). Found (%): C, 59.21; H, 6.72; N, 7.79; S, 8.92. $M^+$ 364.1441. Calc. for $C_{18}H_{24}N_2O_4S$ (%): C, 59.32; H, 6.64; N, 7.69; S, 8.80. M 364.1452.

**7-Amino-14-methyl-16,17-dioxo-1,13-diaza-4,10-dioxa-7-thioniabicyclo[11.3.1]heptadec-14-ene 2,4,6-trimethylbenzenesulfonate 9**

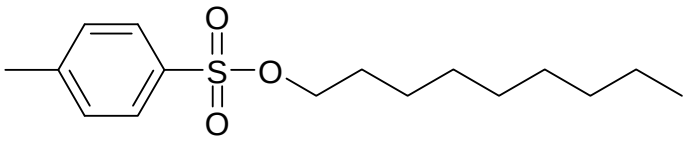


To the solution of 0.08 g (0.27 mmol) of pyrimidinophane **2a** in 15 ml of dichloromethane the solution of 0.24 g (1.14 mmol) of *O*-mesitylenesulfonylhydroxylamine in 10 ml of dichloromethane was added dropwise at 0ºC. The reaction mixture was stirred for 3 h, 0.11 g (79%) of highly hygroscopic compound **9** were obtained after the removal of the solvent. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 6.84 (s, 2H, 2ArH), 6.02 (s, 2H, $NH_2$), 5.57 (s, 1H, C$^{15}$H), 4.30-4.20 (m, 1H, NCH), 4.19-4.08 (m, 1H, NCH), 4.05-3.98 (m, 1H, NCH), 3.96-3.65 (m, 13H, NCH, 2NCC$\underline{H_2}$OC$\underline{H_2}$C$\underline{H_2}$), 2.63 (s, 6H, 2*o*-$CH_3$), 2.24 (s, 3H, *p*-$CH_3$), 2.17 (s, 3H, C$^{14}$$CH_3$). Found (%): C, 51.06; H, 6.59; N, 7.93; S, 12.18. Calc. for $C_{22}H_{33}N_3O_7S_2$ (%): C, 51.24; H, 6.45; N, 8.15; S, 12.44.

**Reactions of pyrimidinophanes with the esters of *p*-toluenesulfonic acid**

A pyrimidinophane was added to the 4 g of methyl or nonyl ester of *p*-toluenesulfonic acid and the reaction mixture was stirred for 6 hours at 80ºC. After cooling diethyl ether was added, the formed precipitate was separated, washed thrice with diethyl ether and dried *in vacuo.*

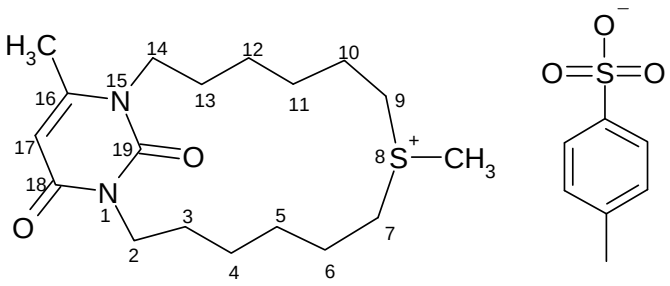
**Nonyl ester of *p*-toluenesulfonic acid 12**



50 ml of 30% NaOH solution was added to the solution of 14.40 g (100.00 mmol) of nonyl alcohol and 1.36 g (4.01 mmol) of $[NBu_4]HSO_4$ in 100 ml of benzene, and the solution of 21.00 g (110.24 mmol) of *p*-toluenesulfochloride in 50 ml of benzene was added dropwise to the resulting mixture. Reaction mixture was stirred for 13 h, the organic layer was separated, washed 4 times with water and dried over $MgSO_4$. After the removal of solvent the residue was dried *in vacuo* to give 26.15 g (88%) of nonyl ester of *p*-toluenesulfonic acid. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 7.79 (d, 2H, 2ArH, J=8.1), 7.34 (d, 2H, 2ArH, J=7.7), 4.02 (t, 2H, $OCH_2$, J=6.5),

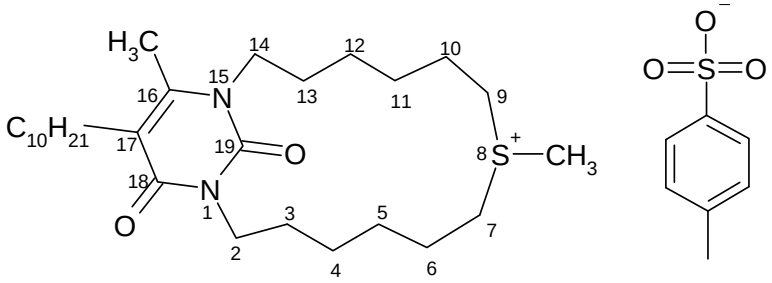
2.45 (s, 3H, $ArCH_3$), 1.30-1.15 (m, 14H, $7CH_2$), 0.87 (t, 3H, $CH_3$, J=6.9). Found (%): C, 64.21; H, 8.81; S, 10.88. Calc. for $C_{16}H_{26}O_3S$ (%): C, 64.39; H, 8.78; S, 10.74.

**8,16-Dimethyl-18,19-dioxo-1,15-diaza-8-thioniabicyclo[13.3.1]nonadec-16-ene toluene-4-sulfonate 10a**



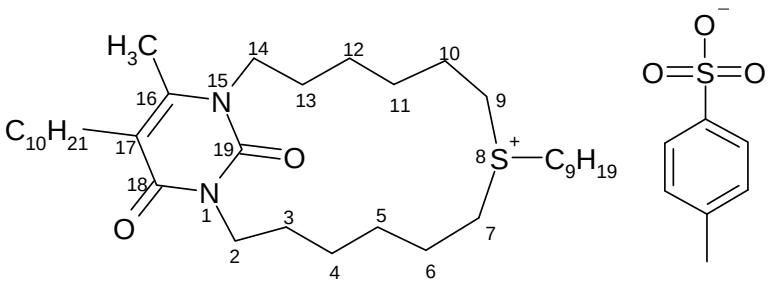
0.90 g (85%) of macrocycle **10a** was obtained from 0.60 g (1.85 mmol) of pyrimidinophane **2b** as an oil. $^1H$ NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 7.71 (d, 2H, 2ArH, J=7.7), 7.14 (d, 2H, 2ArH, J=7.7), 5.58 (s, 1H, $C^{17}H$), 4.00-3.71 (m, 4H, $2NCH_2$), 3.48 (s, 3H, $S^+CH_3$), 3.15-2.80 (m, 4H, $2CH_2S^+$), 2.34 (s, 3H, $ArCH_3$), 2.23 (s, 3H, $C^{16}CH_3$), 1.90-1.25 (m, 16H, $2NCC\underline{H_2}C\underline{H_2}C\underline{H_2}C\underline{H_2}CS^+$). Found (%): C, 58.58; H, 7.34; N, 5.55; S, 12.77. Calc. for $C_{25}H_{38}N_2O_5S_2$ (%): C, 58.79; H, 7.50; N, 5.49; S, 12.56.

**17-Decyl-8,16-dimethyl-18,19-dioxo-1,15-diaza-8-thioniabicyclo[13.3.1]nonadec-16-ene toluene-4-sulfonate 10b**



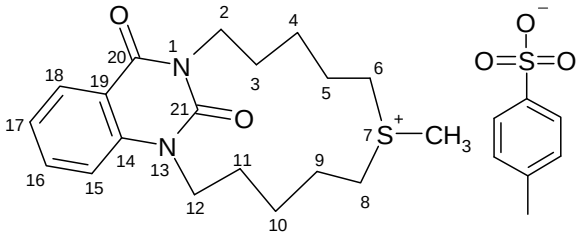
0.20 g (89%) of macrocycle **10b** was obtained from 0.08 g (0.18 mmol) of pyrimidinophane **2c** as an oil. $^1H$ NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 7.73 (d, 2H, 2ArH, J=7.3), 7.14 (d, 2H, 2ArH, J=7.3), 4.00-3.35 (m, 8H, $2NCH_2$, $2CH_2S^+$), 3.09 (s, 3H, $S^+CH_3$), 2.41 (t, 2H, $C^{17}CH_2$, J=7.6), 2.34 (s, 3H, $ArCH_3$), 2.24 (s, 3H, $C^{16}CH_3$), 1.90-1.50 (m, 8H, $2NCC\underline{H_2}CCC\underline{H_2}CS^+$), 1.45-1.20 (m, 24H, $12CH_2$), 0.88 (t, 3H, $C^{17}(C)_9C\underline{H_3}$, J=7.0). Found (%): C, 64.44, H, 9.06; N, 4.19; S, 10.01. Calc. for $C_{35}H_{58}N_2O_5S_2$ (%): C, 64.58; H, 8.98; N, 4.30; S, 9.85.

**17-Decyl-16-methyl-8-nonyl-18,19-dioxo-1,15-diaza-8-thioniabicyclo[13.3.1]nonadec-16-ene toluene-4-sulfonate 10c**



0.08 g (46%) of macrocycle **10c** was obtained from 0.10 g (0.23 mmol) of pyrimidinophane **2c** as an oil. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 7.76 (d, 2H, 2ArH, J=7.5), 7.13 (d, 2H, 2ArH, J=7.4), 4.00-3.42 (m, 10H, $2NCH_2$, $3CH_2S^+$), 2.45-2.40 (m, 2H, $C^{17}CH_2$), 2.33 (s, 3H, $ArCH_3$), 2.25 (s, 3H, $C^{16}CH_3$), 1.90-1.20 (m, 46H, $23CH_2$), 0.89-0.87 (m, 6H, $2CH_3$). Found (%): C, 67.89; H, 9.54; N, 3.43; S, 8.69. Calc. for $C_{43}H_{74}N_2O_5S_2$ (%): C, 67.67; H, 9.77; N, 3.67; S, 8.40.

**7-Methyl-20,21-dioxo-1,13-diaza-7-thioniatricyclo[11.7.1.0$^{14,19}$]henicosa-14(19),15,17-triene toluene-4-sulfonate 11**



0.10 g (64%) of macrocycle **11** was obtained from 0.10 g (0.30 mmol) of pyrimidinophane **4**, mp 210ºC. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 8.24 (d, 1H, $C^{15}H$, J=6.8), 7.72-7.66 (m, 3H, 2ArH, $C^{17}H$), 7.29 (d.d, 1H, $C^{16}H$, J=7.9, 7.3), 7.19 (d, 1H, $C^{18}H$, J=8.9), 7.11 (d, 2H, 2ArH, J=7.8), 4.71-4.64 (m, 1H, NCH), 4.29-4.25 (m, 1H, NCH), 4.19-4.15 (m, 1H, NCH), 4.00-3.93 (m, 1H, NCH), 3.75-3.65 (m, 2H, $CH_2S^+$), 3.63-3.52 (m, 2H, $CH_2S^+$), 3.16 (s, 3H, $S^+CH_3$), 2.32 (s, 3H, $ArCH_3$), 2.13-1.95 (m, 4H, $2NCC\underline{H_2}$), 1.85-1.75 (m, 4H, $2C\underline{H_2}CS^+$), 1.65-1.30 (m, 4H, $2NCCC\underline{H_2}CCS^+$). Found (%): C, 60.08; H, 6.53; N, 5.29; S, 12.48. Calc. for $C_{26}H_{34}N_2O_5S_2$ (%): C, 60.21; H, 6.61; N, 5.40; S, 12.36.