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1,2,4,3,5-Benzotrithiadiazepine and its unexpected hydrolysis to unusual 7*H*,14*H*-dibenzo[*d*,*i*][1,2,6,7,3,8]tetrathiadiazecine

Alexander Yu. Makarov,[a] Makhmut M. Shakirov,[a] Konstantin V. Shuvaev,[b] Irina Yu. Bagryanskaya,[a] Yuri V. Gatilov[a] and Andrey V. Zibarev*[a]

[a] *Institute of Organic Chemistry, Russian Academy of Sciences, 630090 Novosibirsk, Russia. E-mail: zibarev@nioch.nsc.ru*
[b] *Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russia*

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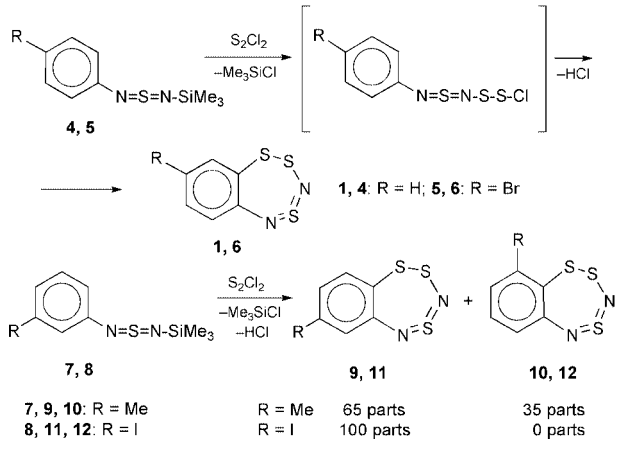
Previously unknown 1,2,4,3,5-benzotrithiadiazepine 1 was prepared by 1:1 condensation of Ph-N=S=N-SiMe$_3$ with S_2Cl_2 followed by intramolecular *ortho*-cyclization of [Ph-N=S=N-S-S-Cl] intermediate, and hydrolyzed in pyridine to unusual macrocyclic 7*H*,14*H*-dibenzo[*d*,*i*][1,2,6,7,3,8]tetrathiadiazecine 2.

Polysulfur–nitrogen π-excessive heterocycles, especially heterocyclic stable radicals (with the former frequently being precursors of the latter), are of keen interest for contemporary chemistry and materials science.[1–4] Among them, fused trithiadiazepines belong to a little studied system. While 1,3,5,2,4-benzotrithiadiazepine[5,6] **3** is described and subjected to preliminary investigation,[6–8] its non-symmetric isomer 1,2,4,3,5-benzotrithiadiazepine **1** was unknown. The present article deals with the preparation of **1** and its unexpected hydrolysis in pyridine to unusual macrocyclic 7*H*,14*H*-dibenzo-[*d*,*i*][1,2,6,7,3,8]tetrathiadiazecine **2**.

For the synthesis of **1**, the intramolecular electrophilic cyclization of Ar-N=S=N-SiMe$_3$ azathienes into 1,3,2,4-benzodithiadiazines under the action of SCl_2[6,9] was extended to S_2Cl_2. This allows the preparation† of the target heterocycle **1** from C_6H_5-N=S=N-SiMe$_3$ **4** (Scheme 1). The cyclization is also successful with 4-BrC_6H_4-N=S=N-SiMe$_3$ **5** (providing compound **6**, an 8-Br derivative of **1**) and 3-RC_6H_4-N=S=N-SiMe$_3$ (**7**, R = CH_3; **8**, R = I). In the latter case of *meta*-substituted precursors the cyclization is regioselective leading predominantly or even exclusively to 7-R substituted derivatives of **1** (Scheme 1). The ratio of the major 7-R isomer to the minor 9-R one is 65:35 for R = CH_3, as shown by ^{1}H NMR spectroscopy.† With R = I, only the 7-I isomer **11** was observed and its structure has unambiguously been confirmed by X-ray crystallography (Fig. 1).‡

Contrary to the successful synthesis of **1**, an attempt to prepare its symmetric isomer **3**[5,6] by the similar approach from C_6H_5-S-N=S=N-SiMe$_3$ and SCl_2 fails. This result agrees with previously reported[6] one.



Scheme 1

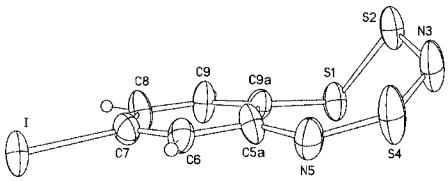


Fig. 1 The X-ray structure of molecule **11**. Selected bond lengths (Å), bond and torsion angles (°): S(1)–S(2) 2.051(6), S(2)–N(3) 1.69(2), N(3)–S(4) 1.52(2), S(4)–N(5) 1.55(1), N(5)–C(5a) 1.41(2), S(1)–C(9a) 1.76(1); C(9a)–S(1)–S(2) 104.6(5), S(1)–S(2)–N(3) 104.2(6), S(2)–N(3)–S(4) 124.6(9), N(3)–S(4)–N(5) 127.1(8), S(4)–N(5)–C(5a) 138(1), N(5)–C(5a)–C(9a) 125(1), C(5a)–C(9a)–S(1) 124(1), C(5a)–C(9a)–S(1)–S(2) −61(1), C(9a)–S(1)–S(2)–N(3) 80.2(8), S(1)–S(2)–N(3)–S(4) −48(2), S(2)–N(3)–S(4)–N(5) 8(2), N(3)–S(4)–N(5)–C(5a) −11(2), S(4)–N(5)–C(5a)–C(9a) 35(3).

According to the data of X-ray crystallography (Fig. 1)‡ and MP2/6-31G* calculations (Fig. 2),‡ the heterocycle of **1** is significantly bent (similar to that of benzopentathiepine)[10] in contrast to the perfectly planar heterocycle of **3**[5b] and its tetrafluoro derivative.[11] The heterocycle conformation (Fig. 1) features the planarity of the C(5a)-N(5)=S(4)=N(3)-S(2) fragment within ± 0.03(1) Å. The S(1) and C(9a) atoms deviate from this plane by 1.35(2) and 0.48(3) Å, respectively. It is seen (Figs. 1 and 2) that the conformation and bond lengths of the title heterocycle are practically the same for a free molecule compared to that packed in the crystal, which is in striking contrast to the situation with related 1,3,2,4-benzodithiadiazines where molecular conformation significantly changes on going from a gas phase to the solid state.[12]

The heteroatom reactivity of **1** differs from that of **3**. For example, it is reported that **3** is stable towards hydrolysis in weak bases and acids[7b] and undergoes fast transformation into 1,3,2-benzodithiazolium chloride under the action of Me$_3$SiCl (a side-product of its preparation).[7a,13] Compound **1** interacts with Me$_3$SiCl to give 1,2,3-benzodithiazolium chloride **13** (Scheme 2) extremely slowly.† However, the most interesting finding is that hydrolysis of **1** in pyridine results unexpectedly in the unusual macrocyclic compound **2** (Scheme 2).† In the absence of pyridine (for example, in THF) the hydrolysis proceeds very slowly if at all. Catalytic or even equimolar

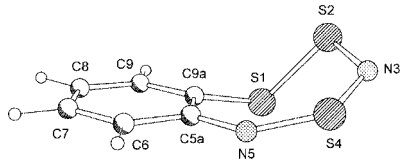


Fig. 2 The MP2/6-31G* structure of molecule **1**. Selected bond lengths (Å), bond and torsion angles (°): S(1)–S(2) 2.086, S(2)–N(3) 1.688, N(3)–S(4) 1.614, S(4)–N(5) 1.594, N(5)–C(5a) 1.381, S(1)–C(9a) 1.757; C(9a)–S(1)–S(2) 106.5, S(1)–S(2)–N(3) 105.0, S(2)–N(3)–S(4) 124.9, N(3)–S(4)–N(5) 126.9, S(4)–N(5)–C(5a) 137.8, N(5)–C(5a)–C(9a) 127.6, C(5a)–C(9a)–S(1) 122.3, C(5a)–C(9a)–S(1)–S(2)–67.1, C(9a)–S(1)–S(2)–N(3) 78.8, S(1)–S(2)–N(3)–S(4) −42.1, S(2)–N(3)–S(4)–N(5) 3.1, N(3)–S(4)–N(5)–C(5a) −2.5, S(4)–N(5)–C(5a)–C(9a) 21.9.

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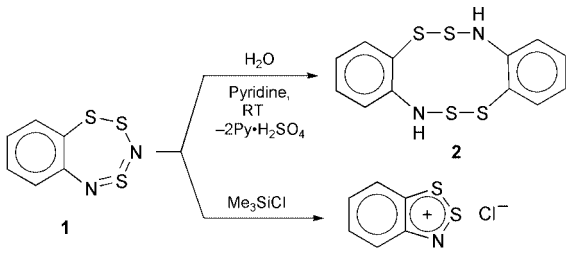

Scheme 2

amounts of pyridine facilitate the hydrolysis in THF insignificantly.

According to the X-ray diffraction data (Fig. 3) the molecule **2** possesses an inversion center. The macrocycle conformation can be described as a chair featuring two transannular N–H···S hydrogen bonds with a H···S distance of 2.60 Å.

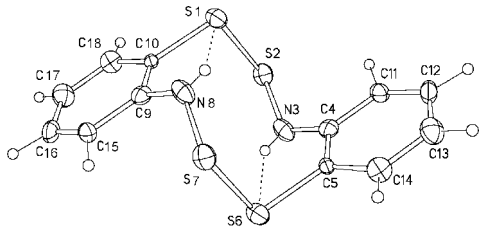

Fig. 3 The X-ray structure of molecule **2**. Selected bond lengths (Å), bond and torsion angles (°): S(1)-S(2) 2.082(5), S(2)-N(3) 1.66(1), N(3)-C(4) 1.42(2), C(4)-C(5) 1.37(2), C(5)-S(6) 1.80(1), S(6)-S(7) 2.082(5); S(1)-S(2)-N(3) 107.1(5), S(2)-N(3)-C(4) 124(1), N(3)-C(4)-C(5) 121(1), C(4)-C(5)-S(6) 121.2(9), C(5)-S(6)-S(7) 100.9(4), C(10)-S(1)-S(2)-N(3) −68.3(7), S(1)-S(2)-N(3)- C(4) −69(1), S(2)-N(3)-C(4)-C(5) 144(1), C(4)-C(5)-S(6)-S(7) −97(1). The dotted lines show N-H···S hydrogen bonds.

Thus, two novel polysulfur–nitrogen heterocyclic systems have been prepared by original approaches and structurally characterized.

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Notes and references

† *Syntheses. Compounds* **1–6**, **9–11**. In an argon atmosphere, solutions of 1.35 g (0.01 mol) of S_2Cl_2 and 0.01 mol of Ar-N=S=N-$SiMe_3$ (Ar = C_6H_5, 4-BrC_6H_4, 3-$CH_3C_6H_4$ and 3-IC_6H_4),[6,9] each in 30 cm³ of CH_2Cl_2, were slowly mixed by adding them dropwise to 300 cm³ of CH_2Cl_2 at 20 °C, over a period of 1 h, with stirring. After a further 1 h, the reaction solution was filtered, the solvent distilled off under reduced pressure, and the residue was chromatographed on silica (CCl_4).

Compound **1**, 10%, red oil. MS *m*/*z* 199.9534 (M^+; calculated for $C_6H_4N_2S_3$ 199.9537). NMR (Bruker DRX-500 throughout the work) δ ($CDCl_3$): ^{1}H: 7.59, 7.34, 6.98; ^{13}C: 151.1, 146.0, 132.7, 130.6, 130.4, 124.9; ^{15}N [NH_3 (liq.)]: 318.9 (s), 292.0 (d, *J* 3.3 Hz). UV (heptane) λ_{max}/nm (log ε): 457 (3.39), 322 (3.53), 272 (3.85), 267 (3.83), 258 (3.75).

Compound **6**, 4%, orange–red crystals, mp 80–81 °C (hexane). MS *m*/*z* 277.8642 (M^+; calculated for $C_6H_3BrN_2S_3$ 277.8642, ^{79}Br). NMR δ ($CDCl_3$): ^{1}H: 7.78, 7.46, 7.19; ^{13}C: 150.0, 147.6, 134.5, 133.0, 131.0, 117.1; ^{14}N [NH_3 (liq.)]: 319, 292. UV (heptane) λ_{max}/nm (log ε): 464 (3.51), 325 (3.60), 277 (3.98), 229 (4.32), 208 (4.32).

Compounds **9** and **10** (~2:1 mixture, ^{1}H NMR), 7%, red oil. MS *m*/*z* 213.9697 (M^+; calculated for $C_7H_6N_2S_3$ 213.9693). NMR δ ($CDCl_3$): ^{1}H: **9**, 7.48, 7.14, 6.80, 2.34; **10**, 7.22, 7.17, 6.91, 2.49; ^{13}C: **9**, 150.9, 142.8, 140.4, 131.9, 130.1, 125.2, 20.8; **10**, 152.1, 145.2, 140.4, 129.7, 128.0, 125.5, 21.3; ^{15}N [NH_3 (liq.)]: **9**, 319.2 (s), 292.1 (d, *J* 3.3 Hz); **10**, 319.8 (s), 292.3 (d, *J* 3.3 Hz).

Compound **11**, 3%, red crystals, mp 100–101 °C (hexane). MS *m*/*z* 325.8505 (M^+; calculated for $C_6H_3IN_2S_3$ 325.8505). NMR δ ($CDCl_3$): ^{1}H: 7.70, 7.30, 7.29; ^{13}C: 151.9, 145.5, 138.5, 133.2, 132.7, 95.5; ^{14}N [NH_3 (liq.)]: 325, 289. UV (EtOH) λ_{max}/nm (log ε): 458 (3.24), 324 (3.45), 273 (3.95), 214 (4.07).

Compound **2**. To a solution of 100 mg (5×10^{-4} mol) of **1** in 0.6 cm³ of pyridine was added 36 mg (2×10^{-3} mol) of H_2O. After 24 h the precipitate (which consisted of a mixture of **2** and pyridinium sulfate, according to the MS and IR data) was filtered off, washed with pyridine and recrystallized from toluene. Compound **2**, 5 %, colorless crystals, mp 215–217 °C. MS *m*/*z* 309.9729 (M^+; calculated for $C_{12}H_{10}N_2S_4$ 309.9727). IR ν/cm^{-1} (KBr): 3274s, 3050w, 1585m, 1470s, 1443m, 1269s, 901m, 757s, 612s, 575m, 448s. Evaporation of the filtrate under reduced pressure affords viscous oil assumed to be (GC-MS, ^{1}H and ^{13}C NMR) a mixture of 2,2′-diaminodiphenyl disulfide and related polysulfanes.

Compound **13**. To a solution of 105 mg (5.25×10^{-4} mol) of **1** in 4 cm³ of CH_2Cl_2 was added 228 mg (2.1×10^{-3} mol) of Me_3SiCl. After 21 d the precipitate was filtered off and recrystallized from $SOCl_2$–CCl_4 (3:1). Compound **13**, 10%, yellow crystals, mp 194–196 °C (decomp.) MS *m*/*z* 153.9775 ($M^+ - {}^{35}Cl$; calculated for $C_6H_4NS_2$ 153.9785). NMR δ (CF_3CO_2H): ^{1}H: 9.09, 9.00, 8.65, 8.46; ^{13}C: 164.0, 156.2, 139.1, 133.9, 128.1, 123.4; ^{14}N [NH_3 (liq.)]: 406. UV λ_{max}/nm (log ε) (CF_3CO_2H): 426 (3.25), 347 (4.38).

After evaporation of the filtrate under reduced pressure unreacted **1** was recovered in 80% yield.

‡ *X-ray crystallography and ab initio calculations. X-ray structure data for* **2** *and* **11**. *Compound* **2**: $C_{12}H_{10}N_2S_4$, *M* = 310.46, monoclinic, *a* = 8.101(2), *b* = 4.7156(9), *c* = 16.905(5) Å, β = 95.57(2)°, *U* = 642.7(3) Å³, space group $P2_1/c$, *Z* = 2, d_c = 1.604 g cm^{-3}, μ(MoKα) = 0.719 mm^{-1}, 875 reflections measured, 807 unique (R_{int} = 0.037) which were used in all calculations. The final *R* was 0.0873 (for 505 observed reflections).

Compound **11**: $C_6H_3IN_2S_3$, *M* = 326.18, monoclinic, *a* = 4.117(2), *b* = 11.048(7), *c* = 20.63(1) Å, β = 91.74(5)°, *U* = 938.2(9) Å³, space group $P2_1/c$, *Z* = 4, d_c = 2.309 g cm^{-3}, μ(MoKα) = 4.023 mm^{-1}, 1859 reflections measure, 1616 unique (R_{int} = 0.040) which were used in all calculations. The final *R* was 0.0831 (for 943 observed reflections).

CCDC 164031 (**2**) and 164032 (**11**). See http://www.rsc.org/suppdata/cc/b1/b105001j/ for electronic files in .cif or other electronic format.

The MP2/6-31G calculations* were performed using the GAMESS program.[14]

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