CHEMCOMM
Communication
www.rsc.org/chemcomm

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*

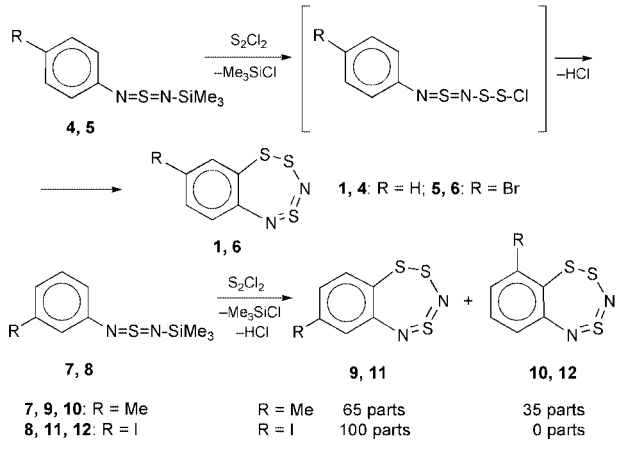
Received (in Cambridge, UK) 6th June 2001, Accepted 2nd August 2001
First published as an Advance Article on the web 3rd September 2001

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

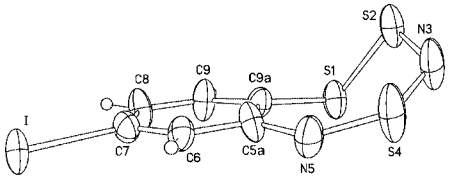


Fig. 1 The X-ray structure of molecule **11**. Selected bond lengths (Å), bond and torsion angles (°): S(1)–S(2) 2.051(6), S(2)–N(3) 1.69(2), N(3)–S(4) 1.52(2), S(4)–N(5) 1.55(1), N(5)–C(5a) 1.41(2), S(1)–C(9a) 1.76(1); C(9a)–S(1)–S(2) 104.6(5), S(1)–S(2)–N(3) 104.2(6), S(2)–N(3)–S(4) 124.6(9), N(3)–S(4)–N(5)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

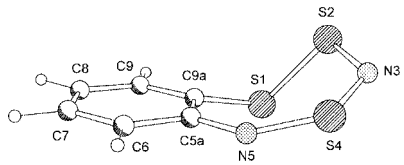
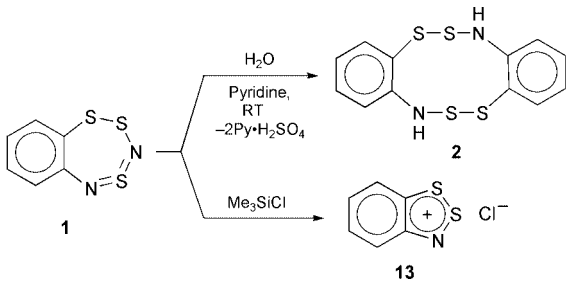


Fig. 2 The MP2/6-31G* structure of molecule **1**. Selected bond lengths (Å), bond and torsion angles (°): S(1)–S(2) 2.086, S(2)–N(3) 1.688, N(3)–S(4) 1.614, S(4)–N(5) 1.594, N(5)–C(5a) 1.381, S(1)–C(9a) 1.757; C(9a)–S(1)–S(2) 106.5, S(1)–S(2)–N(3) 105.0, S(2)–N(3)–S(4) 124.9, N(3)–S(4)–N(5) 126.9, S(4)–N(5)–C(5a)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

 DOI: 10.1039/b105001j



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.

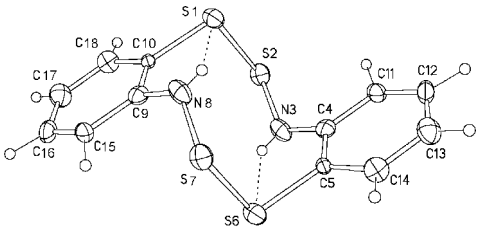


Fig. 3 The X-ray structure of molecule **2**. Selected bond lengths (Å), bond and torsion angles (°): S(1)-S(2) 2.082(5), S(2)-N(3) 1.66(1), N(3)-C(4) 1.42(2), C(4)-C(5) 1.37(2), C(5)-S(6) 1.80(1), S(6)-S(7) 2.082(5); S(1)-S(2)-N(3) 107.1(5), S(2)-N(3)-C(4) 124(1), N(3)-C(4)-C(5) 121(1), C(4)-C(5)-S(6) 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.

The authors are grateful to the Russian Foundation for Basic Research for financial support of their work (project 99-03-33115 and grant 01-03-06190) and access to the Cambridge Structural Database (grant 99-07-90133) and to the STN International databases *via* STN Center at their Institute (grant 00-03-32721).

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]

1 C. W. Rees, *J. Heterocycl. Chem.*, 1992, **29**, 639; X.-G. Duan, X.-L. Duan, C. W. Rees and T.-Y. Yue, *J. Heterocycl. Chem.*, 1996, **33**, 1419.
2 J. M. Rawson, A. J. Banister and I. Lavender, *Adv. Heterocycl. Chem.*, 1995, **62**, 137; J. M. Rawson and G. D. McManus, *Coord. Chem. Rev.*, 1999, **189**, 135; T. M. Barclay, A. W. Cordes, R. C. Haddon, M. E. Itkis, R. T. Oakley, R. W. Reed and H. Zhang, *J. Am. Chem. Soc.*, 1999, **121**, 969.
3 T. Torroba, *J. Prakt. Chem.*, 1999, **341**, 99.
4 I. V. Vlasyuk, V. A. Bagryansky, N. P. Gritsan, Yu. N. Molin, A. Yu. Makarov, Yu. V. Gatilov, V. V. Shcherbukhin and A. V. Zibarev, *Phys. Chem. Chem. Phys.*, 2001, **3**, 409.
5 (*a*) J. L. Morris, C. W. Rees and J. D. Rigg, *J. Chem. Soc., Chem. Commun.*, 1985, 55; (*b*) S. T. A. K. Daley, C. W. Rees and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, 57.
6 A. W. Cordes, M. Hojo, H. Koenig, M. C. Noble, R. T. Oakley and W. T. Pennington, *Inorg. Chem.*, 1986, **25**, 1137.
7 J. L. Morris and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 211; J. L. Morris and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 217.
8 M. J. Plater and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1991, 317.
9 I. Yu. Bagryanskaya, Yu. V. Gatilov, A. Yu. Makarov, A. M. Maksimov, A. O. Miller, M. M. Shakirov and A. V. Zibarev, *Heteroat. Chem.*, 1999, **10**, 113; A. Yu. Makarov, I. Yu. Bagryanskaya, Yu. V. Gatilov, T. V. Mikhalina, M. M. Shakirov, L. N. Shchegoleva and A. V. Zibarev, *Heteroat. Chem.*, 2001, **12**, in the press.
10 F. Feher and B. Engelen, *Z. Anorg. Allg. Chem.*, 1979, **452**, 37.
11 I. Yu. Bagryanskaya, H. Bock, Yu. V. Gatilov, A. Haas, M. M. Shakirov, B. Solouki and A. V. Zibarev, *Chem. Ber./Recueil*, 1997, **130**, 247.
12 F. Blockhuys, S. L. Hinchley, A. Yu. Makarov, Yu. V. Gatilov, A. V. Zibarev, J. D. Woollins and D. W. H. Rankin, *Chem. Eur. J.*, 2001, **7**, 3592.
13 A. V. Zibarev, A. V. Rogoza, S. N. Konchenko, M. A. Fedotov and G. G. Furin, *Zh. Obshch. Khim.*, 1991, **61**, 441 (*Chem. Abstr.*, **115**, 92167).
14 M. V. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.