

# Synthesis of 3,7-dichlorobisisothiazolo[4,5-*b*:4',5'-*e*]pyrazine: the first representative of a new heterocyclic system

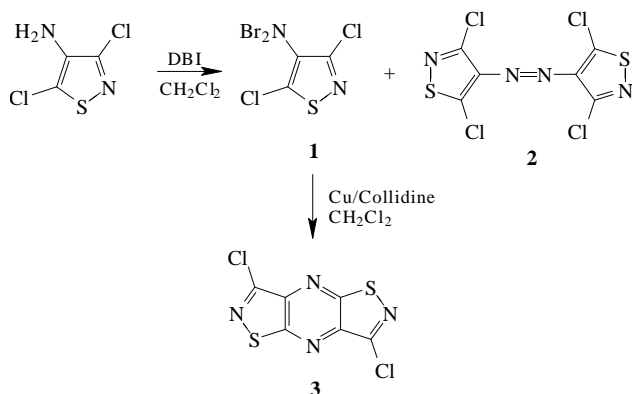
Sergey G. Zlotin,\* Konstantin S. Chunikhin and Marina O. Dekaprilevich

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.  
Fax: +7 095 135 5328; e-mail: L121@cacr.ioc.ac.ru

The title compound has been synthesized for the first time by reaction of 3,5-dichloro-4-(dibromamino)isothiazole with Cu-powder in the presence of collidine.

It has been reported<sup>1,2</sup> that reaction of heterylamines with dibromoisocyanurate (DBI) gave symmetric heteryldiazenes.

We have shown that, unlike the previously described conversions, reaction of 3,5-dichloro-4-aminoisothiazole<sup>3</sup> with DBI gave a relatively stable 3,5-dichloro-4-(dibromamino)-isothiazole **1** (yield 75%) along with a small quantity of the expected *N,N'*-bis(3,5-dichloroisothiazol-4-yl)diazene **2** (yield 18%). The compound **1** gradually transformed at room temperature to a mixture of compounds, from which we have been able to isolate the diazene **2** and 3,7-dichlorobisisothiazolo[4,5-*b*:4',5'-*e*]pyrazine **3**. We have managed to obtain the heterocycle **3** in 67% yield by treating a solution of **1** (either isolated by TLC or prepared *in situ* from 3,5-dichloro-4-aminoisothiazole) in CH<sub>2</sub>Cl<sub>2</sub> with Cu-powder in the presence of collidine.<sup>†</sup>



As far as we know, the compound **3** is the first representative of a condensed heterocyclic system of bisisothiazolo[4,5-*b*:4',5'-*e*]pyrazine. The structure of **3** has been established by <sup>13</sup>C NMR, MS spectra and X-ray analysis.<sup>‡</sup>

<sup>†</sup> To a solution of 3,5-dichloro-4-aminoisothiazole (0.22 g, 1.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added DBI (0.74 g, 2.6 mmol). The mixture was stirred for 2 h at room temperature. The resulting precipitate was filtered off, the solvent evaporated under reduced pressure and the residue was chromatographed on silica gel to give: 0.32 g (75%) of **1**, yellow-brown liquid, *R*<sub>f</sub> = 0.70 (benzene–hexane 1 : 1); IR (ν/cm<sup>-1</sup>): 1583, 1532, 1197, 985, 785, 750, 736; <sup>13</sup>C NMR, CDCl<sub>3</sub>, δ/ppm: 128.3 (C–NBr<sub>2</sub>); 141.3 (N=C–Cl); 167.4 (C–S); MS, *m/z* (%): M<sup>+</sup> 330 (5), 328 (14), 326 (15), 324 (6), 251 (M<sup>+</sup>–Br, 100%); 0.04 g (18%) of **2**, red crystals, *R*<sub>f</sub> = 0.37 (benzene–hexane 1 : 1), mp 219–220 °C; IR (ν/cm<sup>-1</sup>): 1472, 1362, 1137, 986, 855, 840; MS, *m/z* (%): M<sup>+</sup> 338 (7), 336 (23), 334 (41), 332 (34).

A mixture of 3,5-dichloro-4-aminoisothiazole (0.95 g, 5.6 mmol), DBI (2.09 g, 7.3 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 ml), was stirred for 30 min at room temperature and the resulting precipitate was filtered off. To the solution were added Cu-powder (0.54 g) and collidine (1.36 g, 11 mmol) and the mixture was kept for 48 h at room temperature. The precipitate was filtered off, the solvent evaporated *in vacuo* and the residue was recrystallised from DMF, washed with water and air dried to give 0.5 g (67%) of **3**, yellow crystals, mp 207–208 °C; <sup>13</sup>C NMR, [DMSO-*d*<sub>6</sub>]DMSO, δ/ppm: 162.1 (C–S); 145.6 (N=C–Cl); 138.6 (C–C–Cl); MS, *m/z* (%): M<sup>+</sup> 266 (25), 264 (100), 262 (100).

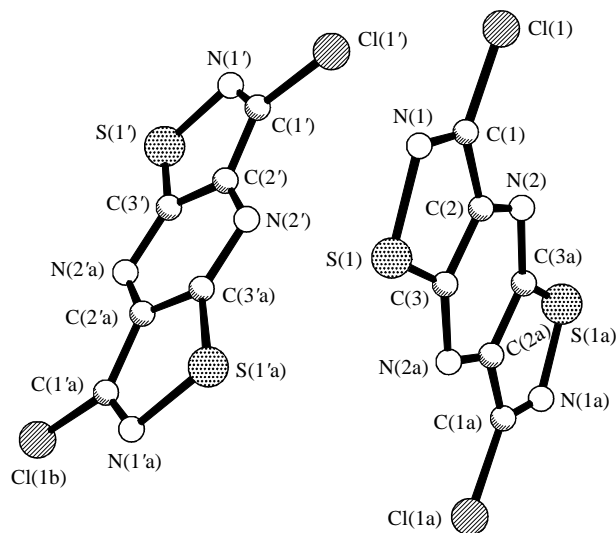


Figure 1 Crystal structure of **3**.

## References

- 1 S. E. Semenov, A. M. Churakov, S. L. Ioffe, E. A. Vinogradova, S. G. Zlotin and O. A. Luk'yanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1940 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1727).
- 2 A. B. Sheremetev and O. V. Kharitonova, *Mendeleev Commun.*, 1992, 157.
- 3 K. R. H. Wooldridge, *Adv. Heterocycl. Chem.*, 1972, **14**, 1.

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<sup>‡</sup> Crystal data for **3**: C<sub>6</sub>Cl<sub>2</sub>N<sub>4</sub>S<sub>2</sub>, *M* = 263.12, triclinic, space group *P* $\bar{1}$ , at 20 °C: *a* = 6.7695(9), *b* = 7.887(1), *c* = 9.735(1) Å,  $\alpha$  = 104.57(1),  $\beta$  = 106.74(1),  $\gamma$  = 104.38(1)°, *V* = 451.9(1) Å<sup>3</sup>, *Z* = 2 (two crystallographically independent molecules, occupying special positions in the inversion centre), *d*<sub>c</sub> = 1.934 g cm<sup>-3</sup>. Unit cell parameters and 2478 reflection intensities were measured using an automated four-circle Siemens P3/PC diffractometer (293 K, λMoKα, graphite monochromator, θ/2θ-scan, θ < 30°). The structure was solved by direct methods and refined by a full-matrix least-squares technique in anisotropic approximation. The final discrepancy factors are *R*<sub>1</sub> = 0.031 for 2069 unique reflections with *I* > 2σ(*I*) and *wR*<sub>2</sub> = 0.086 for 2232 unique reflections. All calculations were carried out using SHELXTL PLUS and SHELXL-93 programs. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 1997, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/16.