

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

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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^{1,2} that reaction of heterylamines with dibromoisocyanurate (DBI) gave symmetric heterylidiazenes.

We have shown that, unlike the previously described conversions, reaction of 3,5-dichloro-4-aminoisothiazole³ 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-dichlorobis(isothiazolo[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 CH₂Cl₂ with Cu-powder in the presence of collidine.[†]

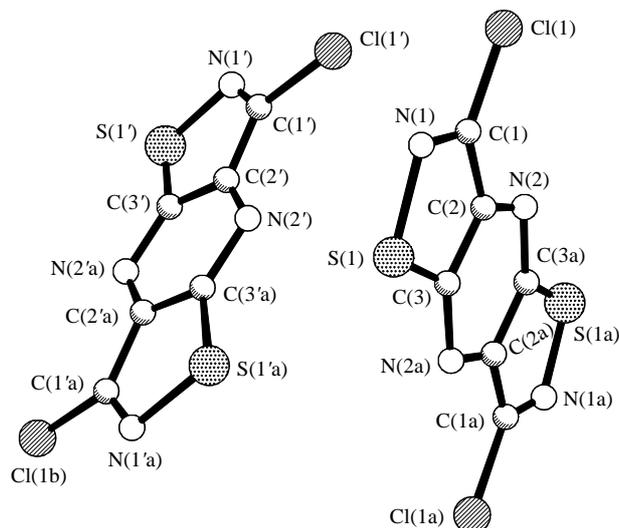
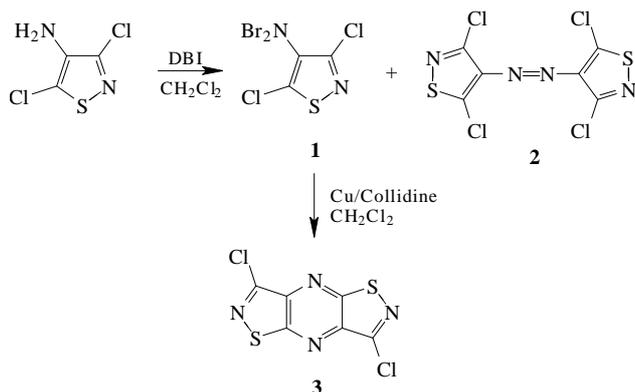


Figure 1 Crystal structure of **3**.

References

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

[†] To a solution of 3,5-dichloro-4-aminoisothiazole (0.22 g, 1.3 mmol) in CH₂Cl₂ (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*_f = 0.70 (benzene–hexane 1 : 1); IR (*ν*/cm⁻¹): 1583, 1532, 1197, 985, 785, 750, 736; ¹³C NMR, CDCl₃, *δ*/ppm: 128.3 (C–NBr₂); 141.3 (N=C–Cl); 167.4 (C–S); MS, *m/z* (%): M⁺ 330 (5), 328 (14), 326 (15), 324 (6), 251 (M⁺–Br, 100%); 0.04 g (18%) of **2**, red crystals, *R*_f = 0.37 (benzene–hexane 1 : 1), mp 219–220 °C; IR (*ν*/cm⁻¹): 1472, 1362, 1137, 986, 855, 840; MS, *m/z* (%): M⁺ 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 CH₂Cl₂ (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; ¹³C NMR, [²H₆]DMSO, *δ*/ppm: 162.1 (C–S); 145.6 (N=C–Cl); 138.6 (C–C–Cl); MS, *m/z* (%): M⁺ 266 (25), 264 (100), 262 (100).

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[‡] Crystal data for **3**: C₆Cl₂N₄S₂, *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, *α* = 104.57(1), *β* = 106.74(1), *γ* = 104.38(1)°, *V* = 451.9(1) Å³, *Z* = 2 (two crystallographically independent molecules, occupying special positions in the inversion centre), *d*_c = 1.934 g cm⁻³. Unit cell parameters and 2478 reflection intensities were measured using an automated four-circle Siemens P3/PC diffractometer (293 K, λMoKα, graphite monochromator, *θ*/2*θ*-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*₁ = 0.031 for 2069 unique reflections with *I* > 2σ(*I*) and *wR*₂ = 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.