Novel S–N Ring Contractions using Dithiadiazoles; the Synthesis and *X*-Ray Crystal Structures of $[\mathrm{Ph\overline{CNSSN}}][\mathrm{S_3N_2}]\mathrm{Cl}$ and $[(\mathrm{Ph\overline{CNSSN}})_2\mathrm{Cl}][\mathrm{S_3N_3}]$†

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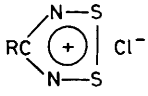
When 4-phenyl-1,2,3,5-dithiadiazole dimer $(\mathrm{Ph\overline{CNSSN}})_2$ dehalogenates cyclotetrathiatriazenium chloride, $[\mathrm{S_4N_3}]\mathrm{Cl}$, and cyclopentathiazenium chloride, $[\mathrm{S_5N_5}]\mathrm{Cl}$, in acetonitrile, novel ring contractions occur to give the title compounds (**1**) and (**2**).

1,2,3,5-Dithiadiazolium chlorides, (**3**), can be dechlorinated chemically[1] (*e.g.* by $\mathrm{NCS^-}$, Zn/Cu couple) or electrochemically[2] to give dithiadiazoles, (**4**); sulphuryl chloride reacts with dithiadiazoles, (**4**), to regenerate (**3**) in high yield.[1] We have therefore investigated the potential of a simply prepared[3] dithiadiazole, (**4a**; R = Ph), as a dechlorinating agent. We have found that the ionic compounds $[\mathrm{S_4N_3}]\mathrm{Cl}$[4] and $[\mathrm{S_5N_5}]\mathrm{Cl}$[5] are indeed dechlorinated by (**4a**) in acetonitrile with simultaneous ring contraction to $\mathrm{S_3N_2}^{+\cdot}$ and $\mathrm{S_3N_3}^-$, respectively, giving the title compounds (**1**) and (**2**).

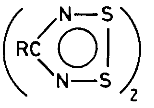
Green platelets of (**1**), suitable for *X*-ray analysis, were formed as a minor product when an acetonitrile solution of (**4a**) was allowed to diffuse through a glass sinter into a saturated acetonitrile solution of $[\mathrm{S_4N_3}]\mathrm{Cl}$ above excess solid $[\mathrm{S_4N_3}]\mathrm{Cl}$.‡ The *X*-ray structure indicated the possibility of synthesis from $\mathrm{S_3N_2Cl^+}$ salts; reaction of $[\mathrm{S_3N_2Cl}][\mathrm{FeCl_4}]$[6] with (**4a**) in acetonitrile produced $[\mathrm{Ph\overline{CNSSN}}][\mathrm{FeCl_4}]$ and the required compound (**1**) in 70% yield. This is the preferred synthesis.

The asymmetric unit of (**1**) combines the monomeric component of (**4a**), $(\mathrm{Ph\overline{CNSSN}})_2$, and isoelectronic (**5**), $(\mathrm{S_3N_2Cl})_2$,[7] as shown in Figure 1.§

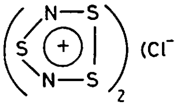
Elongated bright golden prisms of (**2**), suitable for X-ray analysis, were formed as the major product when an acetonitrile solution of (**4a**) was allowed to diffuse through a glass sinter into a saturated solution of $[\mathrm{S_5N_5}]\mathrm{Cl}$ above excess $[\mathrm{S_5N_5}]\mathrm{Cl}$.‡ Compound (**2**) crystallises as a layer lattice



(**3**)



(**4**) a; R = Ph



(**5**)

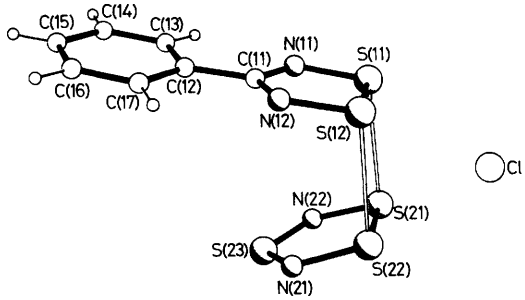


Figure 1. The structure of (**1**), with the atom labelling scheme. Selected distances: S(11)–S(12) 2.055(2), S(11)–N(11) 1.618(5), S(12)–N(12) 1.613(5), N(11)–C(11) 1.339(6), N(12)–C(11) 1.340(6), S(21)–S(22) 2.152(2), S(21)–N(22) 1.632(5), S(22)–N(21) 1.632(5), S(23)–N(21) 1.570(5), S(23)–N(22) 1.556(5), S(11) · · · S(21) 2.864(2), S(12) · · · S(22) 2.812(2), Cl · · · S(11) 3.134(3), Cl · · · S(12) 3.100(3), Cl · · · S(21) 2.907(3), Cl · · · S(22) 2.954(3) Å.

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† 4-Phenyl-1,2,3,5-dithiadiazole-1,2,4,3,5-trithiadiazenium chloride and bis(4-phenyl-1,2,3,5-dithiadiazolium)chloride 1,3,5,2,4,6-trithiatriazinide, respectively.

‡ *Crystal growth* of $[\mathrm{Ph\overline{CNSSN}}][\mathrm{S_3N_2}]\mathrm{Cl}$: $\mathrm{S_4N_3Cl}$ (0.100 g) was placed in one bulb of a two-bulbed vessel with $(\mathrm{Ph\overline{CNSSN}})_2$ (0.088 g) in the other bulb. Acetonitrile (8 ml) was added to each side. Inversion of the reaction vessel allowed the solutions to mix by slow diffusion, over a period of one week, through a medium porosity glass sinter. Removal of the brown solution (by syringe and pumping) revealed many orange ($\mathrm{S_4N_4}$ and $[\mathrm{Ph\overline{CNSSN}}]\mathrm{Cl}$) and black crystals ($[\mathrm{Ph\overline{CNSSN}}]_2\mathrm{Cl}$) interspersed by a small number of shiny green platelets. The green platelets were identified by *X*-ray analysis as $[\mathrm{Ph\overline{CNSSN}}][\mathrm{S_3N_2}]\mathrm{Cl}$.

Large scale preparation of $[\mathrm{Ph\overline{CNSSN}}][\mathrm{S_3N_2}]\mathrm{Cl}$: $[\mathrm{S_3N_2Cl}][\mathrm{FeCl_4}]$ (0.300 g) and $(\mathrm{Ph\overline{CNSSN}})_2$ (0.300 g were placed together, with a Teflon coated stirrer bar, in one bulb of a two-bulbed vessel. Acetonitrile (10 ml) was added and immediately a dark green precipitate was formed. The mixture was stirred for one day, the brown solution filtered, and the green precipitate washed with back distilled MeCN (3 × 10 ml). The solvent was removed by pumping to give a brown sticky tar and a crude green solid which was extracted in a Soxhlet extractor with acetonitrile for one day. Yield of $[\mathrm{Ph\overline{CNSSN}}][\mathrm{S_3N_2}]\mathrm{Cl}$ 56%.

Crystal growth of $[(\mathrm{Ph\overline{CNSSN}})_2\mathrm{Cl}][\mathrm{S_3N_3}]$: $[\mathrm{S_5N_5}]\mathrm{Cl}$ (0.200 g) was placed in one bulb of a two-bulbed vessel with $(\mathrm{Ph\overline{CNSSN}})_2$ (0.150 g) in the other bulb. Acetonitrile (8 ml) was added to each side. Inversion of the reaction vessel allowed the solutions to mix by slow diffusion through a medium porosity glass sinter. Removal of the brown solution (by syringe and pumping) yielded many large golden crystals, a few orange crystals ($[\mathrm{Ph\overline{CNSSN}}]\mathrm{Cl}$ and $\mathrm{S_4N_4}$), and some black needles ($[\mathrm{Ph\overline{CNSSN}}]_2\mathrm{Cl}$). The golden crystals were identified by *X*-ray analysis as $[(\mathrm{Ph\overline{CNSSN}})_2\mathrm{Cl}][\mathrm{S_3N_3}]$.

§ *Crystal data* for (**1**): $[\mathrm{PhCN_2S_2}][\mathrm{S_3N_2}]\mathrm{Cl}$, $\mathrm{C_7H_5N_4S_5Cl}$, $M = 340.9$, monoclinic, space group $P2_1/c$, $a = 9.452(2)$, $b = 14.995(3)$, $c = 9.716(2)$ Å, $\beta = 114.07(1)°$, $U = 1257.3$ Å^3, $Z = 4$, $D_c = 1.774$ g cm^{-3}, $F(000) = 688$, $\mu(\text{Mo-}K_\alpha) = 1.08$ mm^{-1}, $\lambda = 0.71073$ Å. Crystal size 0.37 × 0.48 × 0.04 mm, in Lindemann capillary, $T = 295$ K, Siemens AED2 diffractometer, 32 reflections (2θ 20—25°) for cell refinement. Data collection by ω–θ scan, range 0.51° below α_1 to 0.51° above α_2; scan time 17.5—70 s, $2\theta_{\text{max.}} = 50°$; h −11 to 11, k 0 to 17, l 0 to 11, plus a few equivalents with $k, l < 0$. 3 Standard reflections, no significant variation. No absorption or extinction correction. 2450 Reflections measured, 2223 unique, 1327 with $F > 4\sigma_c(F)$ (σ_c from counting statistics), $R_{\text{int.}} = 0.031$. Structure solution by direct methods and difference syntheses (SHELXTL programs), blocked-cascade least-squares refinement on F. $R = 0.049$, $R_w = 0.0045$.

For (**2**): $[\mathrm{PhCN_2S_2}]_2[\mathrm{S_3N_3}]\mathrm{Cl}$, $\mathrm{C_{14}H_{10}N_7S_7Cl}$, $M = 536.2$, triclinic, space group $P\bar{1}$, $a = 9.509(2)$, $b = 10.641(2)$, $c = 12.187(3)$, $\alpha = 98.29(1)$, $\beta = 107.61(1)$, $\gamma = 112.08(1)°$, $U = 1041.7$ Å^3, $Z = 2$, $D_c = 1.709$ g cm^{-3}, $F(000) = 544$, $\mu(\text{Mo-}K_\alpha) = 0.88$ mm^{-1}. Crystal size 0.2 × 0.4 × 0.7 mm, in Lindemann capillary, $T = 295$ K. Data collection and structure determination as above, except as noted: scan range 0.85° below α_1 to 0.85° above α_2, scan time 17.5—52.5 s; $2\theta_{\text{max.}} = 50°$; h −11 to 11, k −12 to 12, l 0 to 14 plus a partial equivalent set with h 3 to 11, k −12 to 12, l −14 to 0. 5318 Reflections measured, 3698 unique, 2836 with $F > 4\sigma_c(F)$, $R_{\text{int.}} = 0.012$, $R = 0.083$, $R_w = 0.039$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

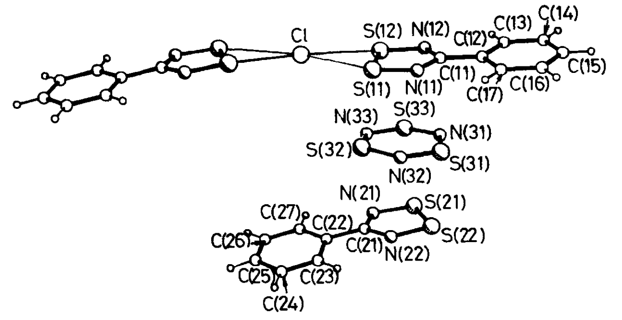

Figure 2. The structure of (**2**), showing the labelling of the asymmetric unit, the ring stacking, and the Cl-centred cation. Selected distances: S(11)–S(12) 2.034(1), S(11)–N(11) 1.597(3), S(12)–N(12) 1.611(3), N(11)–C(11) 1.359(5), N(12)–C(11) 1.329(3), S(21)–S(22) 2.047(1), S(21)–N(21) 1.607(3), S(22)–N(22) 1.606(3), N(21)–C(21) 1.340(5), N(22)–C(21) 1.344(3), S(31)–N(31) 1.587(4), S(31)–N(32) 1.597(4), S(32)–N(32) 1.615(3), S(32)–N(33) 1.590(4), S(33)–N(31) 1.603(3), S(33)–N(33) 1.593(4), Cl · · · S(11) 2.964(2), Cl · · · S(12) 2.903(2), Cl · · · S(21) 3.082(2), Cl · · · S(22) 2.897(2) Å.

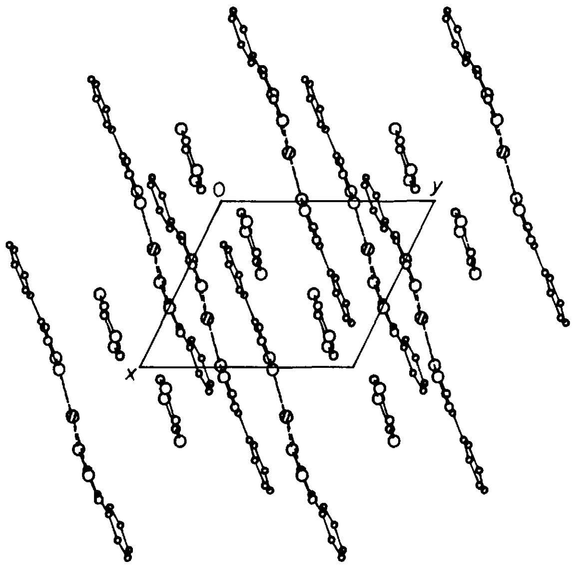

Figure 3. Parallel stacking of rings in (**2**), seen in projection along the *c* axis.

(Figures 2 and 3) composed of the new essentially planar cation $[\mathrm{Ph}\overline{\mathrm{CNSSN}}]\mathrm{Cl}[\mathrm{Ph}\overline{\mathrm{CNSSN}}]^+$ and approximately planar $S_3N_3^-$. This is a new route to a trithiatriazinide—normally prepared from a quaternary ammonium azide and S_4N_4 in ethanol.[8] The bond parameters in the new cation $[(\mathrm{Ph}\overline{\mathrm{CNSSN}})_2\mathrm{Cl}]^+$ (*e.g.* d_{SN} = 1.6 Å and d_{SS} = 2.04 Å) are intermediate between those in $[\mathrm{Ph}\overline{\mathrm{CNSSN}}]\mathrm{Cl}$ (1.59 and 1.99 Å) and in $(\mathrm{Ph}\overline{\mathrm{CNSSN}})_2$ (1.62 and 2.09 Å). The bond parameters for the $S_3N_3^-$ anion do not differ significantly from those in $[\mathrm{Bu^n}_4\mathrm{N}][S_3N_3]$.[9]

This work shows the value of $(\mathrm{Ph}\overline{\mathrm{CNSSN}})_2$ for dechlorination of Cl/S/N compounds under mild conditions; the cited reactions ultimately produce the known $S_3N_3^-$ and $S_3N_2^{+\cdot}$ rings *via* novel ring contractions, with the formation of S_4N_4 as a by-product.

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