1,1′,2,2′,3,3′-Tetrathiadiazafulvalenes; preparation and characterisation of *trans*-[ClCNS$_2$C=CS$_2$NCCl]

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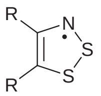
Reduction of 4,5-dichloro-1,2,3-dithiazolylium chloride with two equivalents of triphenylantimony in liquid SO$_2$ affords the 1,1′,2,2′,3,3′-tetrathiadiazafulvalene *trans*-[ClCNS$_2$C=CS$_2$NCCl]; the structural features and redox chemistry of this novel ring system are described.

A wide range of 1,2,3-dithiazolyl radicals **1** have been characterized in solution by EPR spectroscopy.[1,2] Little, however, is known of the structural fate of such species. Do they associate weakly into S-bonded dimers, as do many 1,2,3,5-dithiadiazolyls **2**[3] and 1,3,2-dithiazolyls **3**,[4–6] or might they bond through carbon, thereby giving access to fulvalene derivatives? In order to investigate this possibility, we have examined the redox chemistry of 4,5-dichloro-1,2,3-dithiazolylium chloride **4** (Appel's salt[7]), and have discovered that double reduction of this material affords **5** [eqn. (1)], the first example of a 1,1′,2,2′,3,3′-tetrathiadiazafulvalene.



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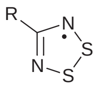

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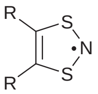

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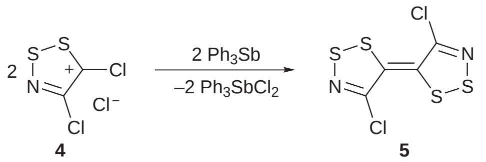

(1)

The yield of **5** from **4** is very sensitive to the reaction conditions. We have explored the use of a variety of reducing agents and solvents, and to date the most effective combination utilizes triphenylantimony in liquid sulfur dioxide. Accordingly, when 50 ml of SO$_2$ was condensed at 77 K onto solid **4** (2.08 g, 10.0 mmol) and triphenylantimony (3.88 g, 11.0 mmol) in an H-cell, and the mixture allowed to warm slowly (2 h) to room temperature, a dark brown precipitate was produced. This solid was filtered off and back-washed twice with liquid SO$_2$. The solvent was removed from the reactor, and the residual solid washed sequentially with 50 ml MeCN, 50 ml aq. EtOH and 50 ml CH$_2$Cl$_2$. The solid was then extracted with 4 × 80 ml hot carbon disulfide, the deep purple extracts combined and the solvent removed to leave crude **5**, which was recrystallized from toluene as dark black–purple needles (0.42 g, 1.5 mmol, 30%), mp 120–121 °C, $\lambda_{\max}$ (CH$_2$Cl$_2$) 565 nm (ε = 1.3 × 10^4 l mol^{-1} cm^{-1}).‡

The crystal stucture§ of **5** consists of discrete molecular units. The molecules, which lie on a crystallographic inversion centre, are planar to within 0.011 Å, and adopt a slipped π-stack structure running along the x direction. Fig. 1 illustrates the packing of a coplanar array of molecules, and provides a summary of both inter- and intra-molecular contacts. The pattern of intramolecular distances is consistent with the valence bond representation shown. Taken collectively, the S–S, S–N and S–C distances are all slightly longer than those observed in 1,2,3-dithiazolylium salts,[8] as expected from the lower oxidation state.

Previous investigations of the chemistry of Appel's salt have focussed on its reactions with nucleophiles.[9] Its reduction, as described here, parallels the behavior of 3-chloro-1,2-dithiolylium salts, which can be reduced to 1,1′,2,2′-tetrathiafulvalenes.[10] In the present case we have no evidence for a *cis*-isomer, presumably because of prohibitive steric interactions between the two chlorines. We have been unable to detect (by EPR spectroscopy) any signal attributable to **1** (R = Cl), a presumed intermediate in the reaction; its association (and subsequent reduction) are extremely rapid. Cyclic voltammetry on solutions of **5** in CH$_2$Cl$_2$ (NBu$^n_4$PF$_6$ supporting electrolyte, ref. SCE) reveals a reversible oxidation wave to the radical cation [**5**]$^+$ at $E_{\frac{1}{2}}$ = 0.80 V, with a second reversible oxidation wave at $E_{\frac{1}{2}}$ = 1.25 V, corresponding to formation of the closed shell dication [**5**]$^{2+}$. There is also an irreversible reduction process near −1.10 V. Similar behaviour has been observed for benzo-bis-1,2,3-dithiazoles.[11] Chemical oxidation to the radical cation can be effected by bromine. When dissolved in liquid SO$_2$ in the presence of AlCl$_3$, the radical cation salt [**5**]Br exhibits a strong and persistent EPR signal (g = 2.015) consisting of a 1 : 2 : 3 : 2 : 1 quintet arising from hyperfine coupling (a_N = 0.096 mT) to two equivalent nitrogen nuclei. Given the many advances in molecular conductor design that have arisen from the classical tetrathiafulvalene framework,[12] we believe this new system also holds rich potential as a molecular building block. To this end we are currently investigating the charge transfer chemistry of **5** and related compounds.

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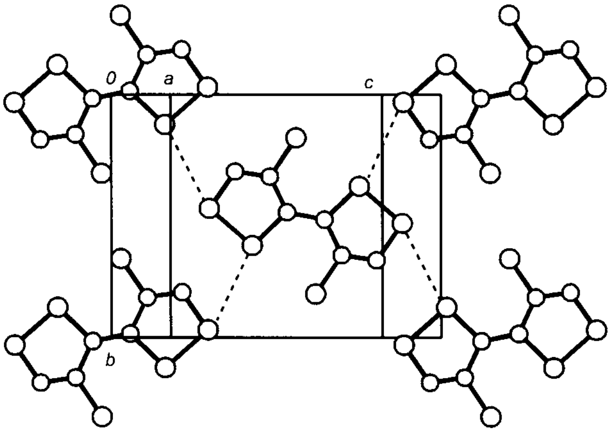

Fig. 1 Crystal packing in **5**. Selected bond lengths (Å): S–S 2.0759(15), S–N 1.657(4), S–C 1.768(4), N–C 1.276(6), N(C–C) 1.458(5), C–C 1.383(7), C–Cl 1.719(4). The intermolecular S···S distance (dashed line) is 3.4929(16) Å.

Notes and References

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‡ Satisfactory elemental (C and N) analyses have been obtained for **5**.

§ *Crystal data* for **5**: data were collected (at 293 K) on an Enraf-Nonius CAD-4 automated diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using θ–2θ scans to $2\theta_{\max}$ = 52°. The structure was solved by direct methods and refined by full-matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. $C_4Cl_2N_2S_4$, M = 275.20, monoclinic, space group $P2_1/c$, a = 3.9795(10), b = 8.9447(14), c = 11.973(2) Å, β = 92.537(17)°, U = 425.76(14) Å^3, Z = 2, D_c = 2.15 g cm^{-3}, μ = 1.64 mm^{-1}. 55 Parameters were refined using 827 unique observed reflections [$I > 1.0\sigma(I)$] to give R = 0.046 and R_w = 0.048. CCDC 182/838.

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