Sterically protected 1,2,3-dithiazolyl radicals: preparation and structural characterization of 4-chloro-5-pentafluorophenyl-1,2,3-dithiazolyl

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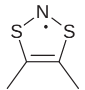
Steric protection afforded by a pentafluorophenyl group at the 5-position facilitates the first isolation and structural characterization of a monocyclic 1,2,3-dithiazolyl as its S–S bonded dimer.

The solid state structures of many 1,3,2-dithiazolyl radicals **1** have been established by X-ray crystallography. Dimerization through long S–S bonds is normally observed,[1,2] but unassociated radicals are also known.[3,4] By contrast, the solid state properties of 1,2,3-dithiazolyls **2** have remained elusive, as have the structural and chemical implications of the two possible resonance formulations **2a** and **2b**. Recently, however, we demonstrated that the reduction of the 4,5-dichloro-1,2,3-dithiazolylium chloride (Appel's salt[5]) leads to C–C coupling at the 5-position, with the eventual formation of the tetrathiadiazafulvalene **3**.[6] This tendency to associate through carbon (resonance structure **2b**), and hence rearrange, illustrates one of the fundamental difficulties associated with the use of 1,2,3-dithiazolyls as building blocks for molecular conductors.[7] In our efforts to overcome this problem we have shown that delocalization of spin density away from the 5-position, as in the fused ring derivative **4**, suppresses C–C association.[8] We are now investigating the effect of sterically bulky substituents on radical association, and have found that the attachment of a pentafluorophenyl group at the 5-position provides an effective block to C–C bond formation. This has allowed us to isolate and characterize structurally, for the first time, a simple monocyclic 1,2,3-dithiazolyl radical as its S··S bonded dimer.



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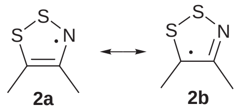
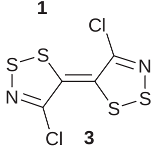


2a **2b**



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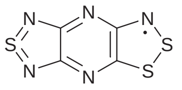

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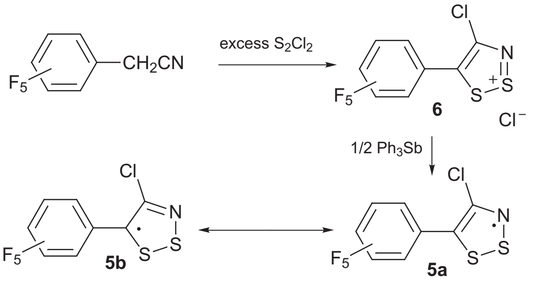
The synthesis of the title compound **5** involved the preparation of the corresponding dithiazolylium cation (Scheme 1) by the reaction of pentafluorophenylacetonitrile (2.6 g, 0.125 mmol) with excess (5 ml) S_2Cl_2 in 10 ml CH_2Cl_2 containing Bu^n_4NCl (0.20 g). After 10 days a canary yellow solid (2.7 g, 0.079 mmol, 63%) was filtered off and recrystallized from hot MeCN to afford orange needles of **6**, mp 211–213 °C. The reduction of **6** (0.68 g, 2.0 mmol) to **5** was very sensitive to the reaction temperature and the nature of the reducing agent. The best results were obtained using Ph_3Sb (0.38 g, 1.06 mmol) as reductant, and the reaction was performed in liquid SO_2 (5 ml) at −70 °C. After 5 min the solvent was evaporated from the still cold mixture to leave a black matrix, from which **5** (0.17 g, 0.54 mmol, 27 %) could be sublimed, at 45 °C/10^{-2} Torr, as lustrous green–black blocks, mp > 52 °C (decomp.).†



Scheme 1

Compound **5** dissolves in CH_2Cl_2 at room temperature to afford bright yellow solutions which exhibit a strong and persistent EPR signal (g = 2.0089) characteristic of a simple 1,2,3-dithiazolyl radical.[9,10] In addition to the expected triplet structure arising from hyperfine coupling to nitrogen, the spectrum (Fig. 1) also displays rich secondary structure arising from coupling to the 4-chlorine and to all five fluorines on the 5-C_6F_5 group. The a_N value (0.61 mT) is consistent with that expected for a simple 1,2,3-dithiazolyl. Cyclic voltammetry on solutions of **5** in MeCN (Pt electrodes, $Bu^n_4NPF_6$ supporting electrolyte) reveals a reversible oxidation wave with $E_{\frac{1}{2}}$(ox) = 0.38 V (*vs.* SCE) and an irreversible reduction wave with a E_{pc} (red) of −1.1 V (*vs.* SCE). The $E_{\frac{1}{2}}$(ox) potential is more anodic than that for benzodithiazolyls,[8] as expected from the more localized electron distribution in the monocyclic derivative. Indeed the potential is similar to those observed in 1,2,3,5-dithiadiazolyl radicals,[11] where spin density is formally restricted to the five-atom CN_2S_2 ring.

The crystal and molecular structures‡ of both **5** and **6** have been established by X-ray crystallography. The structure of the salt **6** (Fig. 2) consists of ion pairs in which the S–S bond of the cation is bridged by a chloride anion, with S··Cl contacts of 2.8947(16) and 2.9617(18) Å. This arrangement is reminiscent of that observed in the halide salts of 1,2,3,5-dithiadiazolylium cations.[12] The mean plane of the heterocyclic ring makes a dihedral angle of 68.6° with the plane of the C_6F_5 group. The internal structural parameters are typical of a 1,2,3-dithiazoly-

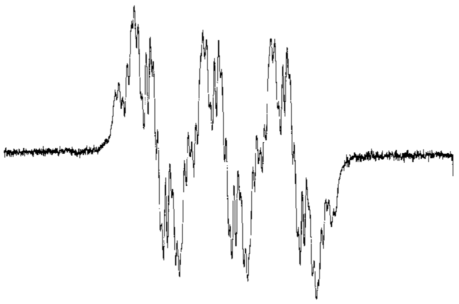


Fig. 1 EPR spectrum (293 K, CH_2Cl_2, SW = 4 mT, g = 2.0089) of radical **5**. Hyperfine coupling constants (derived by simulation with Bruker Simfonia) are a_N = 0.610, a_F = 0.175 (2 F), 0.038 (1 F), 0.031 (2 F), a_{Cl} = 0.1050 (^{37}Cl), 0.0875 (^{35}Cl) mT.

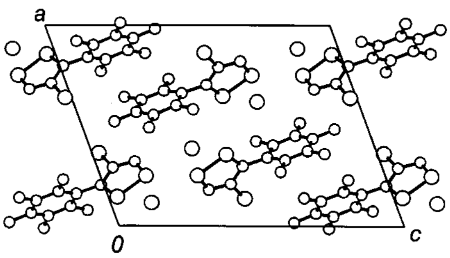


Fig. 2 PLUTO drawing of the cation/anion packing in the chloride salt of **6**. Bond distances within the heterocyclic ring are: *d*(S–S) 2.0284(4), *d*(S–N) 1.605(4), *d*(S–C) 1.673(4), *d*(N–C) 1.309(5), *d*(C–C) 1.393(2) Å.

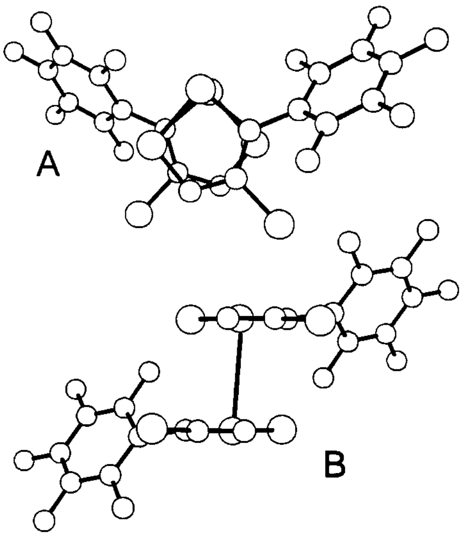
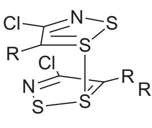


Fig. 3 PLUTO drawings of the radical dimer of **5**, showing the orientation of the overlap of the heterocyclic rings (A) and the interannular S··S contact (B). Bond distances within the heterocyclic ring are: *d*(S–S) 2.0717(8), *d*(S–N) 1.639(2), *d*(S–C) 1.724(2), *d*(N–C) 1.317(3), *d*(C–C) 1.390(3) Å.

lium salt.[13,14] In the structure of **5** the plane of the C_6F_5 group is again twisted (by 58.3°) away from the plane of the C_2S_2N ring, thereby providing the desired sterically protected 'pocket' for the 5-carbon. The radicals are nonetheless dimerized (Fig. 3). The two halves of the dimer are related by a two-fold axis, and are linked by a single interannular S··S contact of 3.2987(13) Å. This interaction is longer than the corresponding S··S interactions found in *any* known dimer of **1**, and stretches even further the conventional limit of a covalent S–S bond.[15] Taken collectively, the changes observed in the internal bond lengths (Fig. 2 and 3) upon reduction of the 6π-cation to the 7π-radical dimer are consistent with the bonding properties of the singly occupied molecular orbital of the radical.[15]

The mode of association of **5** provides an interesting lesson regarding the interplay of steric and electronic requirements. Dimerization cannot occur at the 5-carbons, for steric reasons, and so occurs through the 1-sulfurs, *i.e.* **7a**, as a result of which these atoms become hypervalent (with a S=C double bond). This arrangement is electronically *less* favored than dimerization at the 2-position, *i.e.* **7b**, which generates a hypervalent sulfur with a S=N double bond, or the more delocalized four-centre modes **7c** and **7d**, which are reminiscent of the cofacial dimers commonly observed for 1,2,3,5-dithiadiazolyls.[16] Structure **7a** is, however, the *only* cofacial dimerization mode that precludes Cl/R or Cl/Cl and R/R steric interactions. The steric protection afforded by the C_6F_5 groups also affects the packing of dimers. Thus, instead of forming π-stacks, the dimers are clustered about a $\bar{4}$ site, with the dimers linked by S··S′ contacts of 3.7286(9) Å.



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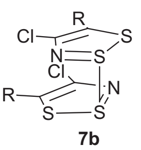

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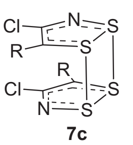

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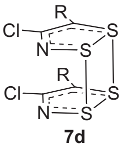

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Notes and references

† Satisfactory chemical analysis were obtained for compounds **5** and **6**.

‡ *Crystal data* for **5** and **6**: Data were collected at 293 K on Siemens P4 (**5**) and Enraf-Nonius (**6**) automated diffractometers with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using omega (**5**) and θ–2θ (**6**) scans. The structures were solved by direct methods and refined by full-matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. Compound **5**: $ClS_2F_5NC_8$, M = 304.66, tetragonal, space group $I\bar{4}2d$, with a = 13.8634(8), c = 21.0268(4) Å, V = 4041.2(4) Å^3, Z = 16, D_c = 2.00 g cm^{-3}, μ = 0.82 mm^{-1}. 155 Parameters were refined using 1622 unique observed reflections [$I > 0.0\ \sigma(I)$] to give R = 0.029 and R_w = 0.033. Compound **6**: $Cl_2S_2F_5NC_8$, M = 340.11, monoclinic, space group $P2_1/n$, with a = 12.334(2), b = 6.0917(17), c = 15.947(3) Å, β = 110.382(16)°, V = 1123.4(4) Å^3, Z = 4, D_c = 2.01 g cm^{-3}, μ = 0.98 mm^{-1}. 163 Parameters were refined using 1502 unique observed reflections [$I > 2.0\ \sigma(I)$] to give R = 0.044 and R_w = 0.050. CCDC 182/1168.

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