# Crystal structures and magnetic properties of a sterically encumbered dithiadiazolyl radical, 2,4,6-$(F_3C)_3C_6H_2CNSSN^{\cdot}$

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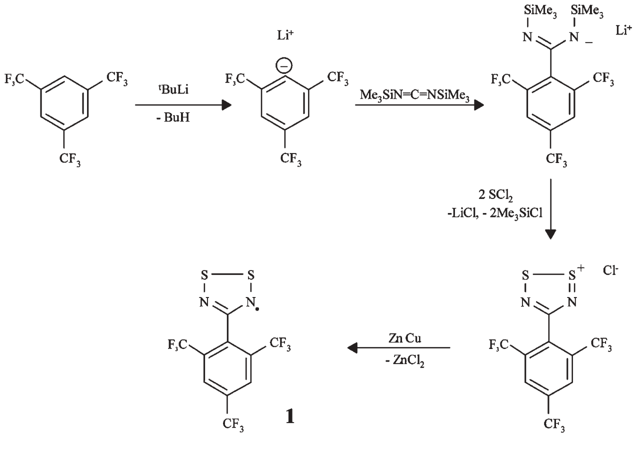
**The sterically protected dithiadiazolyl radical $(F_3C)_3C_6H_2$-CNSSN$^{\cdot}$ (1) crystallises in two polymorphs: 1α, comprised of monomeric units and 1β, containing a mixture of both π*–π* dimers and $S = ½$ monomers; whilst both polymorphs exhibit similar structure-directing motifs, the variation in packing leads to different magnetic behaviour.**

Dithiadiazolyl radicals have aroused particular interest in recent years as building blocks in the design of novel conducting[1] and/or magnetic materials.[2] The most versatile synthetic route to these ring systems is based upon a protocol developed[3,4] by Oakley in which a precursor amidinate is formed from the nucleophilic addition of $N(SiMe_3)_2^-$ to a nitrile.[3] Subsequent condensation with $ECl_2$ (E = S, Se) yields the dithiadiazolylium or diselenadiazolylium salts in high yield.[4] This methodology has been applied to a large range of phenyl derivatives. However there are some limitations to this methodology; these include nitriles bearing α-protons (or indeed other acidic protons), which are susceptible to deprotonation[3] by $N(SiMe_3)_2^-$, and sterically hindered nitriles, in which the bulky substituents hinder nucleophilic attack at the nitrilic carbon. We have been particularly attracted to the latter category since sterically demanding groups may suppress the π*–π* dimerisation process[5] which renders many dithiadiazolyl radicals diamagnetic in the solid state. Here we utilise an alternative route to the key benzamidinate intermediate (Scheme 1) which should provide access to a number of previously inaccessible dithiadiazolyl derivatives, exemplified by radical **1**.



**Scheme 1** Synthesis of **1** from *sym*-$C_6H_3(CF_3)_3$.

The two *ortho*-$CF_3$ groups in target radical **1** are likely to inhibit the majority of common π*–π* dimerisation motifs observed in dithiadiazolyl radicals (Fig. 1), with the possible exception of the *trans*-antarafacial dimer connected by just a pair of S···S contacts (Fig. 1d).

Previous studies of silylated benzamidinate derivatives with bulky substituents have shown that a number of derivatives can be synthesised *via* lithiation of an appropriate aromatic, followed by treatment with $Me_3SiNCNSiMe_3$ (Scheme 1).[6] Our initial attempts to prepare radical **1** from 1,3,5-$C_6H_3(CF_3)_3$ revealed that this step appears very sensitive to the choice of solvent.[7] However if the *N*-lithio silylated amidine is washed with hexane before condensation with $SCl_2$ in toluene, reasonable yields of [**1**]Cl are achieved.† Reduction of [**1**]Cl with Zn/Cu couple in liquid $SO_2$ yielded crude **1**. Sublimation of **1** at $10^{-1}$ Torr at 65–20 °C yielded **1α** as red needles and blocks whereas sublimation at 45–20 °C yielded **1β** as black/red blocks that were different in shape and overall appearance to the α-phase.

Single crystal X-ray studies‡ on **1α** revealed two molecules in the asymmetric unit. The heterocyclic bond lengths and angles are unexceptional, although the bulk of the tris(trifluoromethyl)phenyl group leads to a large torsion angle between the heterocyclic and phenyl ring planes (80.2 and 89.3° for the two independent molecules). Molecules of **1α** are linked together *via* pairs of S···N contacts in the range 3.128–3.170 Å (*cf.* sum of the van der Waals radii at 3.20 Å) forming molecular chains along the crystallographic *a*-axis (Fig. 2). The twist angles between the heterocyclic rings alternate between 14.4° and 74.1°. One such chain is shown in Fig. 2.

In contrast, structural studies on **1β** show that it contains four crystallographically independent molecules. Their molecular geometries are similar to those of **1α** with torsion angles between heterocyclic and aromatic rings in the range 69.4–72.9°. However one of the four molecules (A) forms a *trans*-antarafacial π*–π* dimer with S···S contacts of 3.445 Å. Whilst this is longer than the S···S distances in the only other *trans*-antarafacial dithiadiazolyl radical previously reported (3.141 Å),[8] it is still likely to give rise to

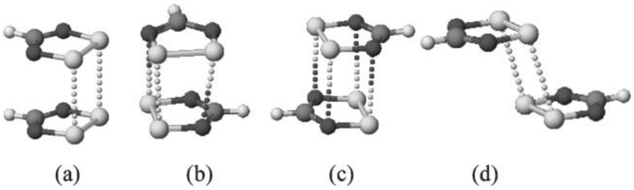


**Fig. 1** Common modes of π*–π* dimerisation in dithiadiazolyl radicals; (a) *cis*-oid; (b) twisted; (c) *trans*-cofacial; (d) *trans*-antarafacial.

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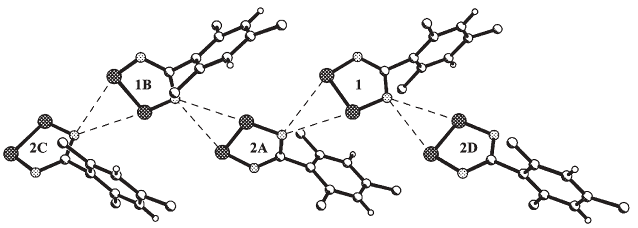

**Fig. 2** Molecular packing of **1α**. Fluorine atoms have been removed for clarity. Labels **1** and **2** distinguish the two crystallographically independent molecules. Symmetry operators: **2C** $x - ½, y + ½, z + ½$; **1B** $x - ½, 2.5 - y, z$; **2A** $-x, 2 - y, ½ + z$; **1** $x, y, z$; **2D** $½ - x, y + ½, z + ½$.

a thermally well-isolated singlet ground state.[9] All four radicals are linked to other molecules *via* heterocyclic S···N contacts analogous to **1α** (Fig. 3) with the S···N contacts falling in the range 2.935–3.352 Å. These S···N contacts have previously been identified as being a structure-directing interaction in ClCNSSN and related radicals.[10] The twist angles between the heterocyclic rings fall in the region 83.5–87.7°.

The fundamental role of polymorphism in molecular magnetic materials has been reviewed elsewhere[11] and provides an elegant example of the way in which the overall magnetic response is dictated by the solid state structure. Whilst many of the local structural features of the intermolecular contacts in **1α** and **1β** are similar, the overall packing patterns are substantially different. Polymorph **1α** comprises one-dimensional chains of $S = ½$ spins, whereas **1β** comprises discrete trimers of $S = ½$ spins. Magnetic studies on polycrystalline samples of both **1α** and **1β** were made on a Quantum Design SQUID magnetometer between 2 K and 350 K for **1α** and 2 K and 400 K for **1β** in an applied field of 1000 G. Measurements were corrected for sample diamagnetism (Pascal's constants) as well as the diamagnetism of the sample holder.

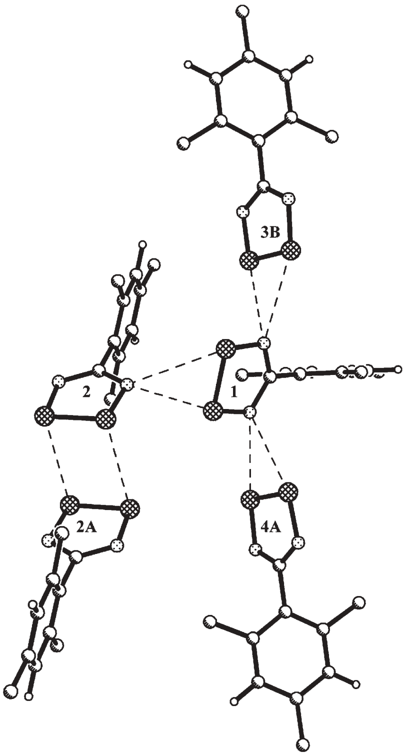

**Fig. 3** Close contacts between the four crystallographically independent molecules (**1–4**) in **1β** and the π*–π* interaction between **2** and its symmetry equivalent **2A**. Symmetry operators **A**: $2 - x, -y, 1 - z$; **B**: $2 - x, 1 - y, 1 - z$. Fluorine atoms have been removed for clarity.

Compound **1α** exhibits Curie–Weiss behaviour down to 50 K with $C = 0.36$ and $\theta = -21$ K, indicative of an $S = ½$ spin ($C = 0.375$) with antiferromagnetic interactions. The mean field approximation[12] allows a first estimate of the exchange coupling *via* eqn (1) where $z$ is the number of nearest neighbours:

$$\theta = z2\boldsymbol{J}S(S + 1)/3k \qquad (1)$$

Assuming that the magnetic exchange is propagated *via* the close S···N contacts,[13] then each molecule has two nearest neighbours and $\boldsymbol{J}$ is *ca.* −21 K. A single-parameter curve fit ($g$-value fixed to 2.01 typical for dithiadiazolyl radicals[5]) to a Heisenberg linear chain model [eqn (2)],

$$\boldsymbol{H} = -2\boldsymbol{J}\,[\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \ldots] \qquad (2)$$

produced a good fit to the data down to 35 K with $\boldsymbol{J} = -23$ K (Fig. 4) but did not exhibit the broad maximum in $\chi$ expected for an antiferromagnetically-coupled chain (around 28 K in this instance).[12] Instead the susceptibility continues to increase on further cooling. This may be due to a Curie-type component to the susceptibility arising from sample defects caused by poor crystallinity and/or paramagnetic contributions arising from the finite nature of the linear chains (a two parameter fit to take into account Curie paramagnetism yielded $\boldsymbol{J} = -29$ K and the fraction of Curie spins $\rho = 0.17$ and provided a satisfactory fit over the entire temperature range). Magnetisation *vs.* field plots at 2 K showed no anomalous behaviour.

The susceptibility per asymmetric unit of **1β** (*i.e.* per four radicals) follows Curie–Weiss behaviour between 50 K and 275 K with $\theta = -29$ K and $C = 1.12$ suggesting that just three of the four radicals are contributing to the sample paramagnetism. This is consistent with one of the four molecules in the asymmetric unit (molecule **2** in Fig. 3) being involved in a π*–π* bonded dimer with

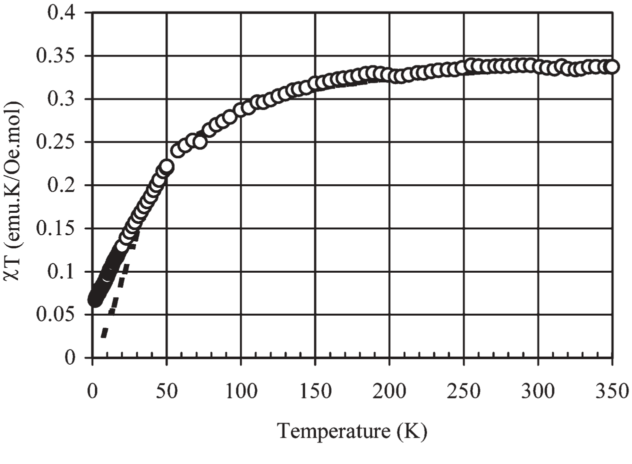

**Fig. 4** Temperature dependence of $\chi T$ for **1α**. The dashed line (---) represents the curve fit to the data using a single-parameter linear chain model ($\boldsymbol{J} = -23$ K).

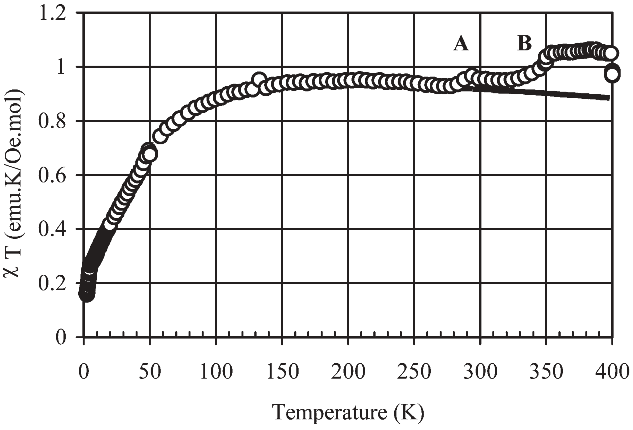

**Fig. 5** Temperature dependence of $\chi T$ for **1β**. The dotted line represents the curve fit to the data using a simple trimer model and a mean field term to model inter-trimer interactions.

a singlet ground state. The negative Weiss constant reflects antiferromagnetic interactions between them. The nature of the close heterocyclic contacts in **1β** would indicate that its magnetic behaviour should best be modelled in terms of a trimer through the Hamiltonian:

$$\boldsymbol{H} = -2\boldsymbol{J}[\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3] \qquad (3)$$

Application of Kambe's vector coupling method[14] to this system generates three possible spin states; one quartet state ($E = -\boldsymbol{J}$) and two doublet states ($E = +2\boldsymbol{J}$ and $E = 0$). A single-parameter fit of the data with a $g$-value fixed at 2.01 yields $\boldsymbol{J} = -26$ K, indicative of an $S = ½$ spin ground state, but is unable to account for the further decrease in $\chi T$ below 15 K. The inclusion of a small mean-field correction to account for inter-trimer antiferromagnetic exchange provided an improved fit ($\theta = -2$ K with $\boldsymbol{J} = -24$ K) down to 5 K (Fig. 5).

The exchange interactions in **1α** and **1β** (−23 K and −26 K) are comparable with theoretically calculated $\boldsymbol{J}$ values as well as those values extracted from curve fits to experimental data for other dithiadiazolyl radicals. These fall in the range $|\boldsymbol{J}| < 40$ K.[13]

Above 280 K there is a discontinuous increase in $\chi T$ for **1β**, followed by a further increase in $\chi T$ at 330 K (labelled A and B in Fig. 5) towards the value expected for four $S = ½$ spins. The origin of this behaviour is under further investigation. However it is worth noting that similar increases in sample paramagnetism have been observed for a range of dithiazolyl and dithiadiazolyl radicals,[15] and has been associated with pre-melting effects.

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## Notes and references

† **Preparation of 1**. A solution of 1,3,5-tris(trifluoromethyl)benzene (1 g, 3.54 mmol) in ether (15 ml) was cooled to −78 °C then *n*-butyllithium (3.54 mmol, 2.2 ml of 1.6 M solution in hexane) added dropwise. The pale yellow solution was stirred overnight at room temperature then *N*,*N*′-bis(trimethylsilyl)carbodiimide (0.66 g, 3.54 mmol) was added and the mixture stirred (18 h). The orange mixture was dried *in vacuo*, stirred with hexane (15 ml, 1 h), dried again *in vacuo*, then toluene (20 ml) added and the mixture cooled to 10 °C before the dropwise addition of sulfur dichloride (0.62 ml, 9.7 mmol). The mixture was stirred overnight and the bright yellow precipitate isolated by filtration and then washed with hexane (4 × 20 ml). Crude yield of [**1**]Cl 0.67 g. The salt [**1**]Cl (0.5 g) was reduced with zinc/copper couple (0.2 g, 3.1 mmol) in liquid $SO_2$ (∼8 ml), then filtered and washed with $SO_2$ to yield a dark purple/black solid. Crystals were isolated by vacuum sublimation as described in the text. Typical purified yield: 100–150 mg, ∼25%. Samples provided satisfactory microanalytical data, *m*/*z* and EPR spectra.

‡ Intensity data for **1α** and **1β** were collected on a Nonius Kappa diffractometer equipped with CCD detector using Cu-Kα radiation ($\lambda = 0.71073$ Å).

Crystal data for compound **1α**: $C_{10}F_9H_2N_2S_2$, $M = 3085.26$, orthorhombic, $Pna2_1$, $a = 17.6507(6)$, $b = 7.9712(3)$, $c = 19.0992(6)$ Å, $V = 2687.21(16)$ Å$^3$, $\mu$(Mo-Kα) = 0.501 mm$^{-1}$, $T = 180(2)$ K, $Z = 8$, $D_c = 1.905$ Mg m$^{-3}$, $F(000) = 1512$, independent reflections 6056 ($R_{int} = 0.0531$). The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELXTL program package.[16] Non-hydrogen atoms were anisotropically refined. Final $R$ for reflections with $I > 2\sigma(I)$ $R_1 = 0.0466$ and w$R_2 = 0.0967$; for all data $R_1 = 0.0813$ and w$R_2 = 0.1104$.

Crystal data for compound **1β**: $C_{10}H_2F_9N_2S_2$, $M = 1541.12$, triclinic, $P\bar{1}$, $a = 8.2750(17)$, $b = 16.5911(33)$, $c = 20.2044(40)$ Å, $\alpha = 101.1251(8)$, $\beta = 94.1342(8)$, $\gamma = 101.1281(15)$°, $V = 2653.31(12)$ Å$^3$, $\mu$(Mo-Kα) = 0.507 mm$^{-1}$, $T = 180(2)$ K, $Z = 8$, $D_c = 1.929$ Mg m$^{-3}$, $F(000) = 1512$. Of 25701 reflections measured, 11625 were independent ($R_{int} = 0.05$). The structure was solved by direct methods using the program SIR92.[17] The refinement and graphical calculations were performed using the CRYSTALS program suite.[18] Final $R = 0.0527$ [5223 reflections with $I > 3\sigma(I)$] and w$R = 0.1248$. Final $R$ for reflections with $I > 3\sigma(I)$ $R = 0.0527$ and w$R = 0.0573$. CCDC 274779 and 274725. See http://dx.doi.org/10.1039/b508371k for crystallographic data in CIF or other electronic format.

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