The First Solid State Paramagnetic 1,2,3,5-Dithiadiazolyl Radical; X-Ray Crystal Structure of $[p\text{-NCC}_6\text{F}_4\overline{\text{CNSSN}}]^\cdot$

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The solid state structure of the fluorinated 1,2,3,5-dithiadiazolyl radical $[p\text{-NCC}_6\text{F}_4\overline{\text{CNSSN}}]^\cdot$ is reported; it is the first dithiadiazolyl radical to retain its paramagnetic character in the solid state.

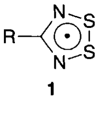
There is much current interest in heterocyclic thiazyl radicals, especially in view of their potential use as building blocks in the synthesis of organic conductors and magnets.[1] Of particular interest are the two isomeric forms of dithiadiazolyl radicals, **1** and **2**. Numerous mono- and bi-functional 1,2,3,5-dithiadiazolyl radicals, **1**, have been prepared,[2] some of which crystallise as segregated stacks. However, without exception, all these radicals dimerise in the solid state through sulfur–sulfur interactions. Consequently, the majority of these materials are diamagnetic insulators. Metallic properties have been improved by replacing the sulfur by selenium, which enhances orbital overlap with a consequent narrowing of the band gap.[3] Iodine doping, with the formation of charge transfer salts, has also enhanced conductivity.[4] We have examined several fluorinated dithiadiazolyl radicals. ESR studies indicate that electronegative substituents lead to a drift in unpaired electron density towards the chalcogen atoms with enhancement of SOMO–SOMO overlap.[5] Herein we report our preliminary results including structural data on the novel 1,2,3,5-dithiadiazolyl radical $[p\text{-NCC}_6\text{F}_4\overline{\text{CNSSN}}]^\cdot$ **3**.

Our first fluorinated 1,2,3,5-dithiadiazolyl radical, $[\text{C}_6\text{F}_5\overline{\text{CNSSN}}]_2$ **4**, was found to be, like all other 1,2,3,5-dithiadiazolyls, dimeric in the solid state.[6] However, as anticipated, the fluorinated aryl substituents caused a shortening of the intermonomer S···S distance compared with its protonated analogue ($d_{\text{S}\cdots\text{S}}$, $[\text{C}_6\text{F}_5\overline{\text{CNSSN}}]_2$, 3.067 Å; $[\text{C}_6\text{H}_5\overline{\text{CNSSN}}]_2$, 3.109 Å). The nature of the secondary bonding in **4** appeared to prejudice the formation of polymeric arrays. However, it has previously been shown that cyano-substituted phenyldithiadiazolyls undergo secondary interactions between the cyano N atom and the disulfur bridge, promoting cofacial packing of the radicals.[7] This led us to investigate the analogous fluorinated compound.

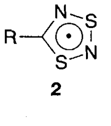
Fluorinated 1,2,3,5-dithiadiazolyl radicals are readily prepared in an analogous manner to their protonated analogues;[8] the chloride salt $[p\text{-NCC}_6\text{F}_4\overline{\text{CNSSN}}]\text{Cl}$ is obtained from $p\text{-NCC}_6\text{F}_4\text{CN}$, $\text{Li[N(SiMe}_3)]_2$ and SCl_2 using standard synthetic procedures.[8] Reduction of $[p\text{-NCC}_6\text{F}_4\overline{\text{CNSSN}}]\text{Cl}$ with Zn/Cu in THF followed by sublimation, (120 °C, 10^{-1} Torr) yields **3** as either small blocks (α-phase) or long needles (β-phase).

The structure of the α-phase of **3** (Fig. 1)† proved to be unprecedented in dithiadiazolyl chemistry. Contrary to expectations, the compound is built up of discrete $[p\text{-NCC}_6\text{F}_4\overline{\text{CNSSN}}]^\cdot$ radicals with no close intermolecular sulfur–sulfur contacts which are normally characteristic of such radicals in the solid state, the closest being 3.601 [S(1)···S(1B)] and 3.668 Å [S(2)···S(2C)]. Instead, the closest contacts to the disulfur bridge are with a cyano group, {$d_{\text{N}\cdots\text{S}}$ in **3** = 3.068 [S(1)···N(3A)] and 3.105 Å [S(2)···N(3A)], *cf.* $p\text{-NCC}_6\text{H}_4\overline{\text{CNSSN}}]_2$ = 3.04 Å[8]}. The thiazyl and C_6 rings are twisted by 32.2° relative to each other. This large twist angle is the probable cause of the asymmetry in the S···N bond lengths. The S···N and S···S interactions link the radicals into sheets. There are also some weak S···F interactions between the sheets of radicals, the shortest being 3.252 Å. Within the monomeric unit the S–S bond length of 2.090 Å remains essentially unchanged compared with other 1,2,3,5-dithiadiazolyl radicals, despite the absence of the usual multi-centre sulfur–sulfur interactions. Although the utilisation of the cyano substituents favours the formation of layered structures,[8] in this case the molecular packing of **3** (Fig. 2) precludes the formation of a conduction band.

The intensity of the solid state ESR signal of the α-phase of **3**, together with its room temperature magnetic moment of 1.6 μ_B confirm its paramagnetic nature. The variable temperature magnetic behaviour of **3** (Oxford Instruments Faraday Balance)



1



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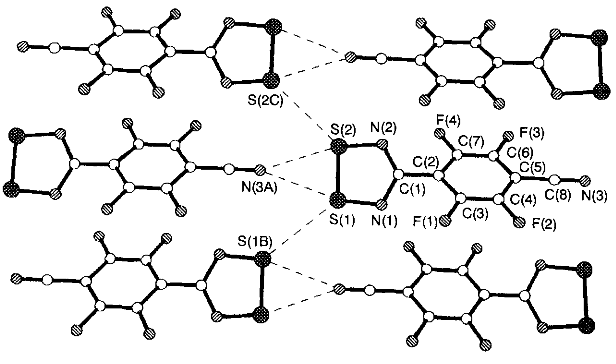

Fig. 1 Structure of **3**. Selected bond lengths (Å) and angles (°): S(1)–S(2) 2.0897(14), S(1)–N(1) 1.637(2), S(2)–N(2) 1.638(2), N(1)–C(1) 1.331(2), N(2)–C(1) 1.324(2), C(1)–C(2) 1.490(2), C(5)–C(8) 1.439(2), C(8)–N(3) 1.145(3), N(1)–C(1)–C(2) 117.8(2), N(2)–C(1)–C(2) 118.4(2), S(1)–N(1)–C(1) 113.52(13), S(2)–N(2)–C(1) 113.74(13), S(2)–S(1)–N(1) 94.49(8), S(1)–S(2)–N(2) 94.37(8), N(1)–C(1)–N(2) 123.9(2). Symmetry operators: *A* 1 + *x*, −1 + *y*, −1 + *z*; *B* −*x*, 2 − *y*, −*z*; *C* 1 − *x*, 1 − *y*, −*z*.

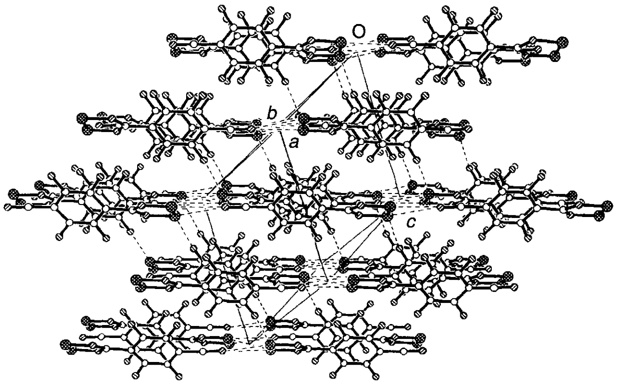

Fig. 2 The stacking of the sheets of radicals with dashed lines for the S···S and S···N interactions within sheets and for the S···F contacts between sheets. The view is perpendicular to that of Fig. 1.

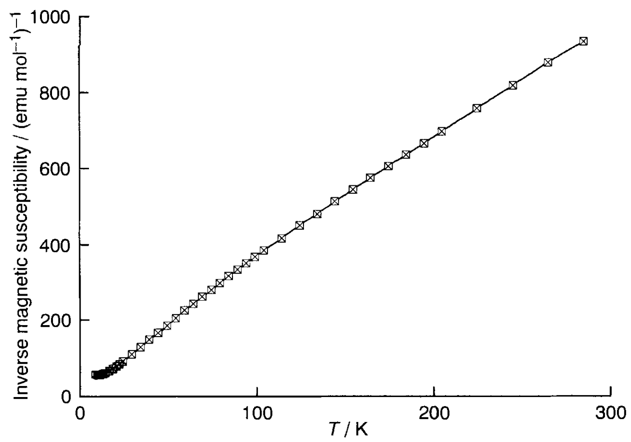

Fig. 3 Plot of the inverse magnetic susceptibility of the α-phase of **3** as a function of temperature

is illustrated in Fig. 3. The Weiss constant of −25 K is indicative of antiferromagnetic behaviour.

The only other 1,2,3,5-dithiadiazolyl radical which is paramagnetic at room temperature is $\mathrm{Bu^tC\overline{NSSN}}\cdot$.[9] Its melting point, which is uncharacteristically low for this class of compound, means that it exists as a liquid at room temperature. However, in the solid state, it is a diamagnetic dimer.[9]

The β-phase of **3** is currently under investigation; preliminary magnetic data show it to be similarly strongly paramagnetic at room temperature, but at low temperature an abrupt magnetic anomaly is observed. Detailed examinations of the variable temperature magnetic behaviour, ESR spectra and full chemical characterisation of both the α and β modifications are currently in progress.

These results further illustrate the rich structural diversity exhibited by dithiadiazolyl radicals. Moreover, the isolation of the first dithiadiazolyl radical which is paramagnetic in the solid state represents a significant departure from the common behaviour in the chemistry of these radicals.

We are grateful to the EPSRC for financial support (N. B., W. C., C. I. G., I. L., J. M. R.), The Royal Society for an equipment grant (W. C.) and Dr G. M. Brooke for a sample of p-$\mathrm{NCC_6F_4CN}$.

Received, 4th November 1994; Com. 4/06760F

Footnote

† *Crystal data* for **3**: $\mathrm{C_8F_4N_3S_2}$, M = 278.23, triclinic, space group $P\bar{1}$, a = 7.574(6), b = 8.065(6), c = 9.509(7) Å, α = 65.73(3), β = 69.17(3), γ = 67.52(3)°, U = 475.5(6) Å^3, Z = 2, D_c = 1.943 g cm^{-3}, $F(000)$ = 274, μ(Mo-Kα) = 0.598 mm^{-1}. 1682 Independent reflections were measured on a Stoe-Siemens diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, $2\theta < 50°$) with ω/θ scans. Data were collected at 160 K using a Cryostream cooler.[10] Structure solution was by direct methods, refinement by full-matrix least squares methods on F^2 for all independent reflections.[11] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]\}^{1/2}$ = 0.0763 for all data, conventional R [on F values for 1510 reflections with $F^2 > 2\sigma(F^2)$] = 0.0273, goodness of fit = 1.105 on F^2 for 155 refined parameters. All atoms were refined anistropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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