Modification of molecular packing: crystal structures and magnetic properties of monomeric and dimeric difluorophenyl-1,2,3,5-dithiadiazolyl radicals

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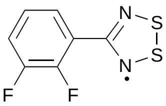
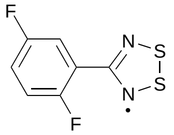
Two dithiadiazolyl radicals of formula $[F_2C_6H_3\overline{CNSSN}]^{\bullet}$ were prepared and characterised by X-ray crystallography; in the solid state the 2′,3′-difluoro isomer forms discrete twisted dimers through a spin-paired singly occupied–singly occupied molecular orbital interaction with an intra-dimer S · · · S distance of 3.020(4) Å, whereas the 2′,5′-isomer is composed of uniform stacks with unexpectedly long intra-stack S · · · S contacts [3.544(3) Å].

The majority of dithiadiazolyl radicals, $[R\overline{CNSSN}]^{\bullet}$, lose their paramagnetic nature in the solid state through an out-of-plane, spin-paired, dimerisation process in which the separation of the heterocyclic rings within the dimeric unit is typically 2.99–3.14 Å;[1] intermediate between twice the covalent radii[2] (2.10 Å) and twice the sum of the van der Waals radii[3] (4.06 Å). The energy of this interaction (*ca.* 35 kJ mol^{-1})[4] is much less than that for a covalent bond (*cf.* 265 kJ mol^{-1} for S–S)[5] but is extremely large on the scale of intermolecular interactions. Therefore counteracting this dimerisation process by means of weak van der Waals forces (the principle instrument of 'crystal engineering') is a difficult task. Other workers have shown that hydrogen-bonding interactions can be successfully used to control molecular packing[6] (*e.g.* in hydroxy-substituted nitronyl–nitroxide radicals[7]), but such an approach is impossible in these compounds because dithiadiazolyl radicals readily react with acidic protons.†,[8] Recently we found the first dithiadiazolyl radical, $[p\text{-}NCC_6F_4\overline{CNSSN}]^{\bullet}$, which retains its monomeric nature in the solid state.[9,10] This radical has been found in two morphologies,[9,10] both of which are paramagnetic. The β-phase is exceptional because it undergoes a phase transition to a weakly ferromagnetic state at 36 K.[10] We believe that the F · · · F repulsions in a head-to-head dimer diminish energy gain on dimerisation to such an extent that the favourable in-plane CN · · · S interactions in $[NCC_6F_4\overline{CNSSN}]^{\bullet}$ can overcome it.[9] These results illustrate that we are able to overcome the spin-paired dimerisation process to produce radicals exhibiting long-range magnetic order, and that fluorinated aryl substituents appear to play a prominent role in determining the solid-state structure. Herein we report the structures of two novel difluorinated dithiadiazolyl radicals; $[2',3'\text{-}F_2C_6H_3\overline{CNSSN}]^{\bullet}$ **I** and $[2',5'\text{-}F_2\text{-}C_6H_3\overline{CNSSN}]^{\bullet}$, **II**, each of which possesses an unusual solid-state architecture.



I



II

Compounds **I** and **II** were prepared from 2,3- or 2,5-difluorobenzonitrile respectively, using standard synthetic procedures[11] and crystals suitable for X-ray diffraction studies‡ were grown by vacuum sublimation [10^{-2} Torr (Torr ≈ 133.322 Pa), 80–120 °C].

Molecules **I** and **II** both contain planar dithiadiazolyl rings of unexceptional geometry. The asymmetric unit of **I** comprises two molecules. Within each molecule the dithiadiazolyl and benzene rings are nearly coplanar with a torsion angle around the C(1)–C(7) bond of 6°. Unexpectedly, the two molecules are associated in the solid state as a twisted dimer (Fig. 1) with a mean intra-dimer separation of *ca.* 3.1 Å between nearly coplanar dithiadiazolyl rings (dihedral angle 3.4°) and with the closest intra-dimer contact S(2A) · · · S(2B) of 3.020(4) Å. Previously such twisted conformations have only been observed in

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† Recently the crystal structures of some dithiadiazolyl–metal complexes have shown ring protonation.[8b,c]

‡ Crystal data: $C_7H_3F_2N_2S_2$ **1**, $M = 217.23$, triclinic, space group $P\bar{1}$, $a = 6.637(6)$, $b = 8.768(11)$, $c = 13.546(5)$ Å, $\alpha = 88.79(6)$, $\beta = 86.37(5)$, $\gamma = 80.40(9)°$, $U = 776(1)$ Å^3, $\mu = 6.14$ mm^{-1}, $Z = 4$, $D_c = 1.86$ g cm^{-3}, $T = 150(2)$ K. Crystal data: $C_7H_3F_2N_2S_2$ **2**, $M = 217.23$, tetragonal, space group $P4_2/n$,$a = 21.28(1)$, $c = 3.544(3)$ Å, $U = 1604(3)$ Å^3, $\mu = 5.94$ mm^{-1}, $Z = 8$, $D_c = 1.80$ g cm^{-3}, $T = 150(2)$ K. Data for **I** and **II** were collected on a Rigaku AFC6S four-circle diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.541 84 Å) in an ω scan mode. For **I**, 2365 reflections were measured ($32 < 2\theta < 40°$) of which 2365 data were unique. For **II**, 2457 reflections were measured ($30 < 2\theta < 38°$) of which 1438 were unique. Both structures were solved by direct methods and refined using full-matrix least-squares refinements on F^2 values of all data using SHELXTL software.[12] At convergence; for **I**, $R1 = 0.070$ [$F > 2\sigma(F)$], $wR2 = 0.197$ and the goodness of fit = 1.11 for all data and 236 parameters; for **II**, R1 = 0.090 [$F > 2\sigma(F)$], $wR2 = 0.281$ and the goodness of fit = 1.09 for all data and 136 parameters. All non-H atoms were refined anisotropically and H atoms were treated as 'riding'. The aryl group in **II** was found to be disordered over two orientations differing by a 180° rotation about the C(1)–C(7) axis; the site occupancies were refined to approximately 2 : 1. Maximum and minimum residual electron densities were within ±0.9 for **I** and ±0.7 e Å^{-3} for **II**. CCDC reference number 186/584.

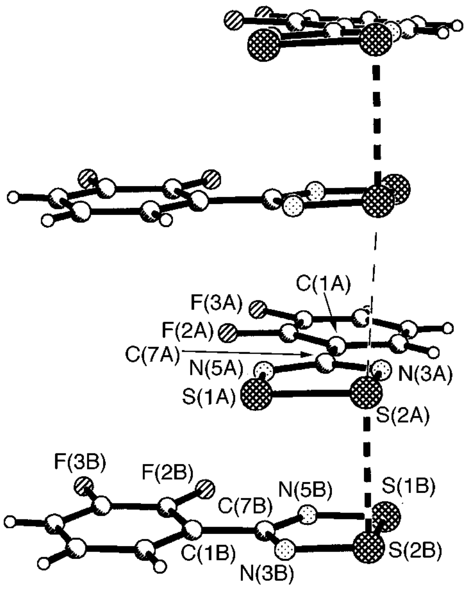

Fig. 1 The asymmetric unit of compound **I** and its translational (along *x* axis) equivalent, showing the shortest S · · · S contacts. Selected bond lengths (Å) and angles (°): S(1A)–S(2) 2.105(3), S(1B)–S(2B) 2.095(3), S(1A)–N(5A) 1.636(6), S(1B)–N(5B) 1.634(7), S(2A)–N(3A) 1.617(6), S(2B)–N(3B) 1.163(7), N(3A)–C(7A) 1.36(1), N(3B)–C(7B) 1.35(1), N(5A)–C(7A) 1.32(1), N(5B)–C(7B) 1.32(1); N(5A)–S(1A)–S(2A) 93.4(2), N(5B)–S(1B)–S(2B) 93.6(2), S(1A)–S(2A)–N(3A) 95.2(3), S(1B)–S(2B)–N(3B) 95.0(2), S(2A)–N(3A)–C(7A) 113.6(5), S(2B)–N(3B)–C(7B) 114.3(5), S(1A)–N(5A)–C(7A) 115.3(5), S(1B)–N(5B)–C(7B) 115.2(6), N(3A)–C(7A)–N(5A) 122.4(6), N(3B)–C(7B)–N(5B) 121.8(7)

derivatives with sterically demanding substituents (Me, CF_3 or NMe_2)[13–15] whereas planar aromatic substituents normally favour eclipsed (cisoid) configurations.[1] The driving force behind the twist in **I** is probably due to the asymmetric positions of the fluorine atoms which induce a comparatively large molecular dipole across the aromatic substituent, coupled with the intermolecular electrostatic interactions between the main centres of positive (sulfur) and negative (fluorine) charges [S(2A) · · · F(3B) and S(2B) · · · F(3A) at 3.03 and 3.07 Å respectively]. These intermolecular interactions occur between adjacent stacks of molecules and are close to the dithiadiazolyl ring plane.

Neighbouring dimers, related by the lattice translation *a*, pack so as to produce an infinite stack of dithiadiazolyl rings running parallel to the crystallographic *x* axis (Fig. 1). The mean inter-dimer separation (*ca.* 3.5 Å) and inter-dimer S · · · S contact 3.628(4) Å are considerably larger than the intra-dimer distances. The Peierls distortion which gives rise to this set of alternating short and long contacts between molecules is a common feature of the dithiadiazolyl ring system[16] and leads to a dimeric structure which is correspondingly diamagnetic.

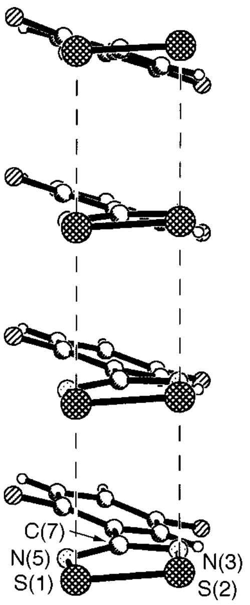

Fig. 2 Molecular packing of compound **II** viewed down the [1 1 0] line, showing the uniform packing arrangement. Selected bond lengths (Å) and angles (°): S(1)–S(2) 2.087(3), S(1)–N(5) 1.627(7), S(2)–N(3) 1.633(7), N(3)–C(7) 1.361(9), N(5)–C(7) 1.314(11); N(5)–S(1)–S(2) 93.7(3), S(1)–S(2)–N(3) 95.3(2), S(2)–N(3)–C(7) 112.9(6), S(1)–N(5)–C(7) 115.7(5), N(3)–C(7)–N(5) 122.3(7)

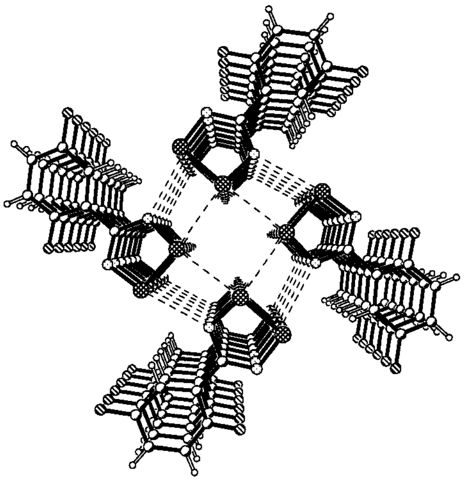

Fig. 3 'Pin-wheel' packing of compound **II** viewed down the 4_2 screw axis (*z* axis)

In comparison, molecule **II** exhibits a unique molecular packing arrangement for dithiadiazolyls. The tetragonal lattice consists of stacks of uniformly spaced dithiadiazolyl radicals (Fig. 2). The radical separation in **II** [equal to the length of the crystallographic *c* axis, *i.e.* 3.544(3) Å] is considerably larger than that normally observed[1] for dithiadiazolyl radicals ($d_{S\cdots S}$ 2.99–3.14 Å) although still less than twice the van der Waals radius of sulfur (4.06 Å when perpendicular to the bonds).[3] Structurally, the radicals remain comparatively isolated and the capacity for sulfur atoms to undergo secondary interactions is compensated through strong inter-stack interactions. Four of these stacks are located around a 4_2 screw-axis in a 'pin-wheel' fashion, with the heterocyclic rings inclined by 8° to the screw axis (Fig. 3). At the centre of the pin-wheel, there are inter-stack S · · · S interactions [$d_{S\cdots S}$ 3.493(3) Å] linking each molecule to its two nearest neighbours (above and below its own ring plane) in each of the two adjacent stacks. Further from the centre of the pin-wheel there is a set of S(1) · · · N(3) and S(1) · · · F(6) contacts at 2.95 and 3.17 Å respectively (*cf.* corresponding sums of van der Waals radii[3] at 3.20–3.63 and 2.90–3.38 Å).

Compound **II** provides the first example of an intrinsic, undistorted dithiadiazolyl stack; all other dithiadiazolyls reported to date undergo a Peierls distortion to form discrete dimer pairs (as in compound **I**). Peierls distortions in one-dimensional systems tend to be suppressed by increasing the dimensionality of the system through the presence of significant inter-stack interactions[16,17] (as in compound **II**). Oakley and co-workers[18] have shown that this process can also be suppressed through iodine doping in $[\mathrm{H}\overline{\mathrm{CNSSN}}]\cdot 0.18\mathrm{I}_2$ **III**.

A few striking similarities between radicals **II** and **III** are worthy of further comment. In both structures the period of identity of the dithiadiazolyl stack coincides with that of the crystal lattice in the direction of the stack [3.544(3) and 3.352(5) Å for **II** and **III** respectively], *i.e.* the unit cell dimension (*c*) coincides with the intra-stack S · · · S separations. In both structures the stacks of dithiadiazolyl radicals are arranged around a high-order screw-axis in a pin-wheel motif (four-fold for **II** and six-fold for **III**) which is clearly favourable for creating a three-dimensional network of inter-stack interactions. The six-fold arrangement in **III** forms a large channel (internal diameter 7.40 Å, twice the distance from the inner sulfur to the 6_1 axis) at the centre of the pin-wheel which is filled with randomly disordered I_2 molecules.[18] In the case of **II**, the corresponding cavity is substantially smaller (internal diameter 4.26 Å, twice the distance from the inner sulfur to the 4_2 axis) and so it may be able to accommodate a lithium atom.

With the abnormally large intra-stack separation of dithiadiazolyl rings (*ca.* 0.5 Å greater than that normally observed for dimeric dithiadiazolyl radicals, and even larger than that observed in **III**), we suspected that **II** might be paramagnetic in the solid state. However, variable-temperature (5–300 K) magnetic measurements on **II** indicated that it was diamagnetic (diamagnetic susceptibility, $\chi_d = -5.55 \times 10^{-9}$ m^3 kg^{-1}) with a small paramagnetic contribution at low temperature equivalent to less than 0.1% of molecules with an unpaired spin.§

These results illustrate how small changes in molecular structure can lead to large changes in solid-state structure. Compound **I** provides the first example of electronically (rather than sterically) directed control of the dimeric structure normally associated with dithiadiazolyl radicals. Compound **II** is the first example of an undoped dithiadiazolyl radical which forms a uniform stack which does not suffer a Peierls distortion. Despite the unexpectedly long S···S contacts, **II** remains diamagnetic in the solid state. Further investigations are needed to determine at what point the separation of dithiadiazolyl rings becomes sufficient to induce paramagnetic behaviour.

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§ Oakley and co-workers have recently reported[19,20] several examples of dithiazolyl radicals in which the molecules form uniformly stacked structures with separations of *ca.* 3.5 and 3.7 Å. When the separation is around 3.5 Å the compound is essentially diamagnetic[19] at room temperature (fraction of Curie spins at 300 K ≈ 0.01) whereas with the larger intermolecular separation,[20] the fraction of Curie spins at room temperature is ≈0.3. The essential diamagnetism in the former case is associated with a band gap of *ca.* 0.4 eV (eV ≈ 1.602 18 × 10^{-19} J) which gives rise to a filled valence band.

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