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## THE SOLID STATE PACKING OF DIFLUORO-PHENYL-DITHIADIAZOLYL RADICALS

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The solid state structures of a series of difluorophenyl dithiadiazolyl radicals are presented and the packing described in terms of S...F, S...S and F...F secondary interactions.

**Keywords:** dithiadiazolyl radical; organic magnet; crystal structure

### INTRODUCTION

We have been interested in developing dithiadiazolyl radicals,<sup>[1]</sup>  $\text{RCNSSN}^\bullet$ , as building blocks in the construction of magnetic materials.<sup>[2]</sup> These radicals are usually associated in the solid state through a spin-paired dimerisation at sulfur ( $d_{\text{S...S}} \sim 3.0 \text{ \AA}$ ). In contrast the fluorinated radical  $p\text{-NCC}_6\text{F}_4\text{CNSSN}^\bullet$  is monomeric and becomes magnetic below 36K.<sup>[2]</sup> We now report the influence of the F atoms on the solid state packing, through recent studies on the structures of some difluorophenyl dithiadiazolyls.

### Difluorophenyl-dithiadiazolyl Radicals

Five of the possible six difluorophenyl-dithiadiazolyls (Fig. 1) have been prepared and characterised by X-ray diffraction.

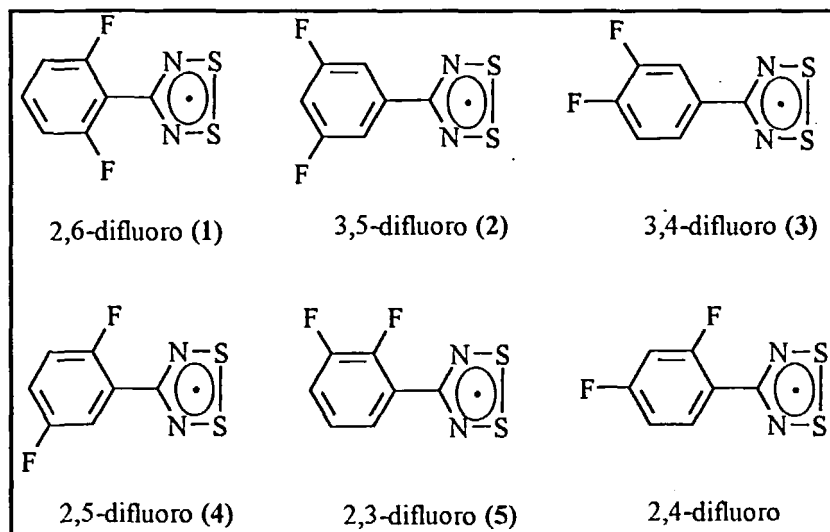


FIGURE 1 difluorophenyl-dithiadiazolyl radicals

The structures of 1 (Fig. 2), 2 and 3 illustrate the head-to-head dimerisation commonly observed<sup>[1]</sup> for dithiadiazolyls. In the case of 1, N...F repulsions induce a large twist angle between aryl

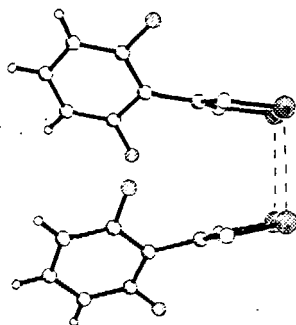


FIGURE 2

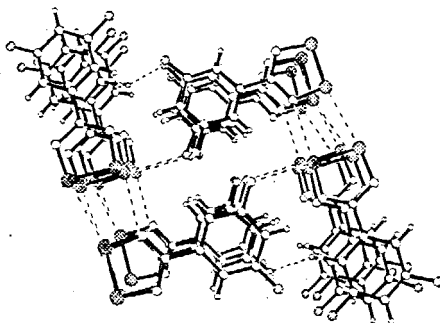


FIGURE 3

and heterocyclic rings ( $48^\circ$ ), whereas **2** and **3** have no *ortho*-fluorine atoms and the rings are close to co-planar ( $<12^\circ$ ). In **4** the twist angle is an intermediate  $20.1^\circ$ . In **1-3** the intermolecular S...S distances are around  $3.0\text{\AA}$  whereas the separation in **4** is  $3.493(3)\text{\AA}$ .<sup>[3]</sup> Although **1-4** all possess head-to-head packing arrangements; the symmetrically substituted derivatives **1** and **2** both form herring-bone motifs (Fig. 3) whereas **3** forms a ribbon-like structure (Fig. 4) and **4** forms a 'pin-wheel' motif (Fig. 5).

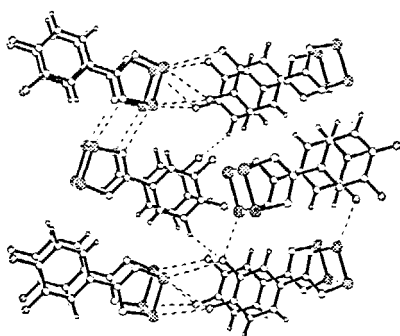


FIGURE 4

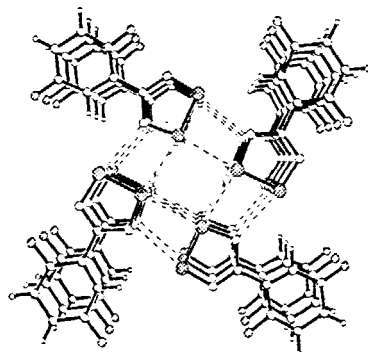


FIGURE 5

The weakness of the non-bonding S...S,  $S^{\delta+} \dots N^{\delta-}$  and  $S^{\delta+} \dots F^{\delta-}$  interactions leads to a diversity of solid state structures.

In contrast to **1-4**, **5** atypically forms a twisted (*ca.*  $90^\circ$ ) dimer (Fig. 6) with an *intra*-dimer separation of *ca.*  $3.1\text{\AA}$ . This unusual conformation can be attributed to the large dipole induced by the asymmetric position of the F atoms and electrostatic  $S^{\delta+} \dots N^{\delta-}$  and  $S^{\delta+} \dots F^{\delta-}$  interactions.<sup>[3]</sup>

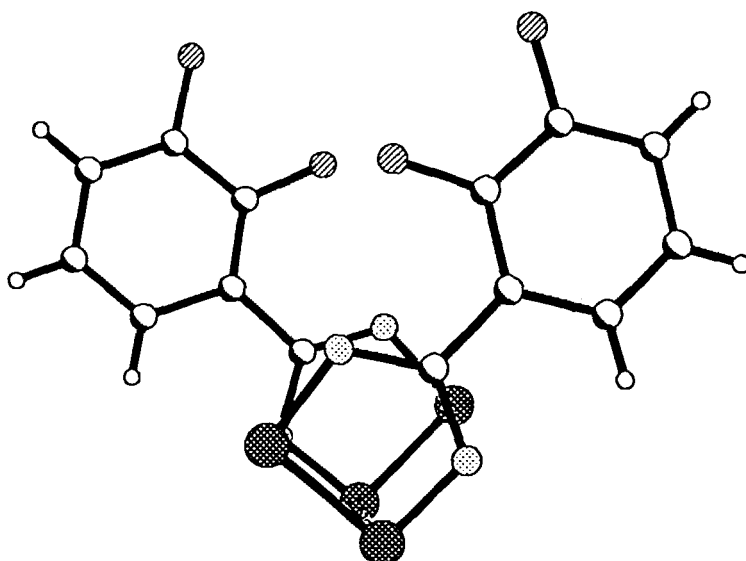


FIGURE 6

Despite the exceptionally long S...S separation in **4**, variable temperature magnetic measurements indicate that it is diamagnetic in the solid-state. **4** however provides the first example of an undistorted dithiadiazolyl stack.

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