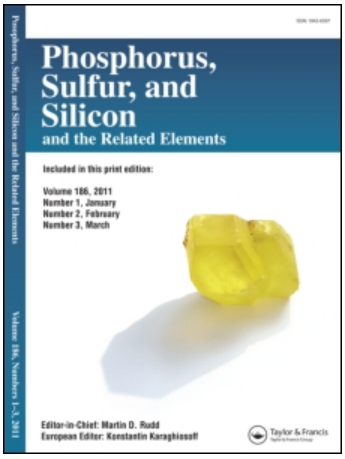

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THE SOLID STATE PACKING OF DIFLUORO-PHENYL-DITHIADIAZOLYL RADICALS

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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,[1] RCNSSN$^{\bullet}$, as building blocks in the construction of magnetic materials.[2] These radicals are usually associated in the solid state through a spin-paired dimerisation at sulfur ($d_{S...S} \sim 3.0$Å). In contrast the fluorinated radical *p*-$NCC_6F_4CNSSN^{\bullet}$ is monomeric and becomes magnetic below 36K.[2] 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.

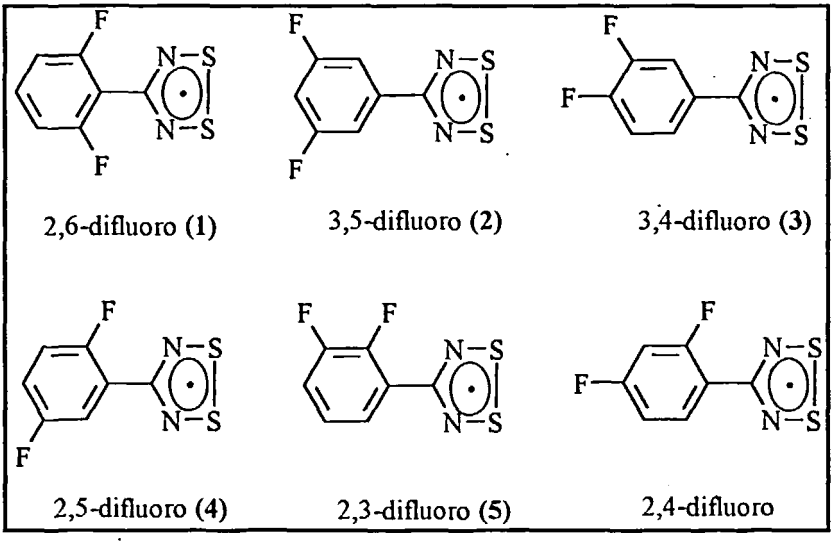

FIGURE 1 difluorophenyl-dithiadiazolyl radicals

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

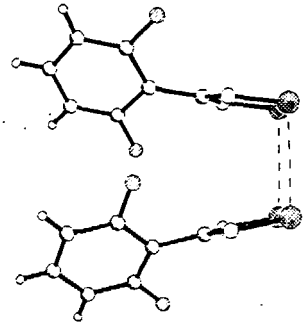

FIGURE 2

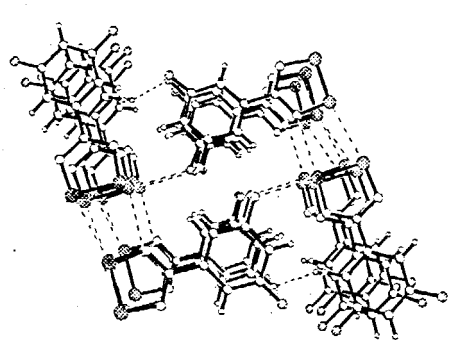

FIGURE 3

and heterocyclic rings (48°), whereas **2** and **3** have no *ortho*-fluorine atoms and the rings are close to co-planar (<12°). In **4** the twist angle is an intermediate 20.1° In **1-3** the intermolecular S...S distances are around 3.0Å whereas the separation in **4** is 3.493(3)Å.[3] 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).

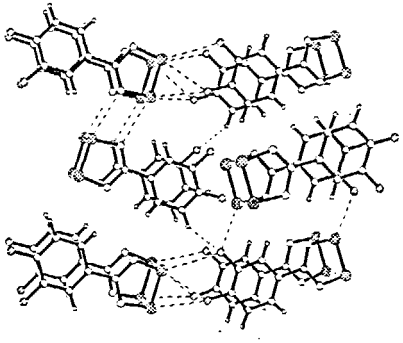

FIGURE 4

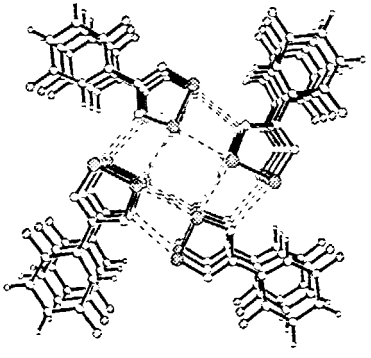

FIGURE 5

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

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

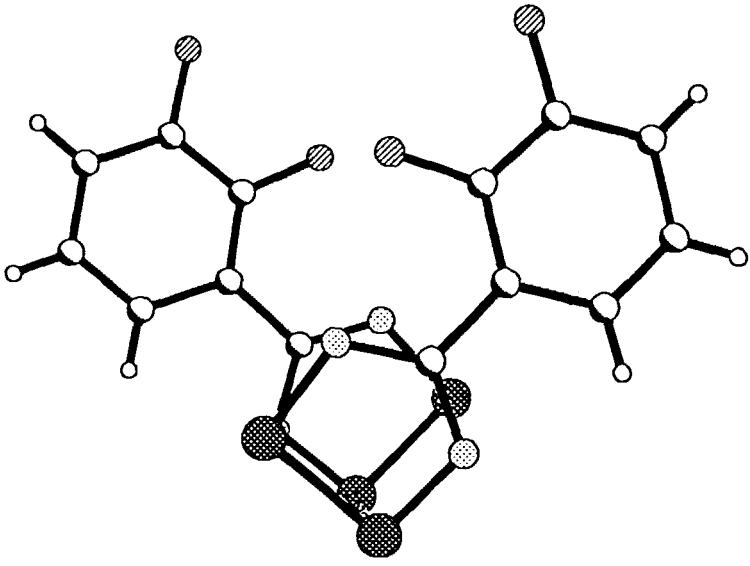

FIGURE 6

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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