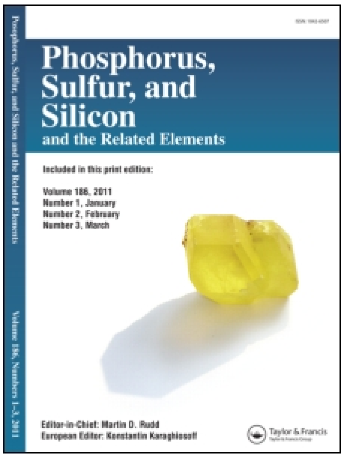

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Synthesis and Magnetic Behaviour of p-$O_2NC_6F_4CNSSN$

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The structure and magnetic properties of the dithiadiazolyl (DTDA) radical p-$O_2NC_6F_4CNSSN$, **1**, is described.

Keywords: dithiadiazolyl; ferromagnet

INTRODUCTION

We have been interested for some time in studying DTDA radicals as molecular magnetic materials. One of the long term goals of metal-free (organic) magnets is the design of materials which may have specialist uses in the electronics industry.

Unfortunately, most DTDA's exist as spin-paired dimers in the solid state, rendering them diamagnetic. The dimerisation energy is considerable (ca. 35 kJ mol^{-1}) and only two monomeric DTDA derivatives have been reported; p-NCC_6F_4CNSSN [1] and p-BrC_6F_4CNSSN. [2]

Here we report the design and characterisation of p-$O_2NC_6F_4CNSSN$, 1. [3]

DESIGN OF 1

There exists a strong correlation between the Hammett parameter (σ_p) of the *para* substituent of the aromatic ring and the redox behaviour of the radical. [4]

Previously reported monomeric DTDA derivatives of formula p-XC_6F_4CNSSN (X = CN, Br) have high σ_p values, while those that form dimers (X = Me_2N, MeO, F, Cl) have low or negative σ_p values. It was on the basis of this that the nitro derivative, **1**, was chosen as a molecule which would remain monomeric in the solid state.

STRUCTURE OF 1

p-$O_2NC_6F_4CNSSN$, **1**, may be prepared from p-$O_2NC_6F_4CN$ following standard synthetic techniques. [4]

As stated earlier, **1**, is monomeric in the solid state with molecules linked into chains *via* electrostatic $NO_2^{\delta-}...S^{\delta+}$ interactions (Fig. 1). There are no close S...N interactions between heterocyclic rings.

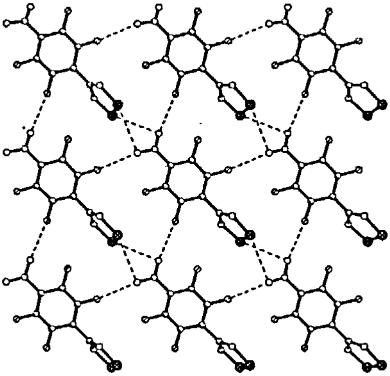

FIGURE 1: Crystal structure of 1 viewed down z axis

MAGNETIC PROPERTIES OF 1

1 is found to be paramagnetic in the solid state and a plot of inverse susceptibility against temperature (Fig. 2) indicates that it exhibits

Curie-Weiss behaviour with a Weiss constant of +1.59 K, indicating local ferromagnetic exchange.

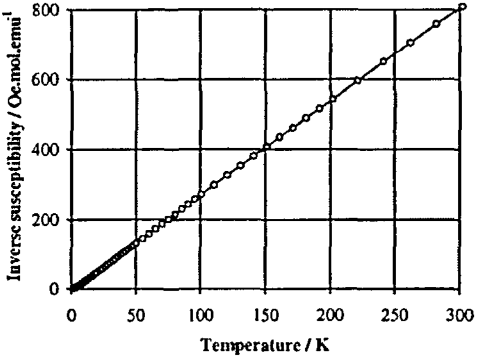

FIGURE 2: Inverse susceptibility plot for **3**

The Curie-Weiss law fails at low temperature, possibly due to short range interactions among magnetic moments.

The effective magnetic moment of **1** is found to be $1.73\mu_B$ (except at low temperature), consistent with an $S = ½$ paramagnet. The slight increase in magnetic moment at low temperature is due to the ferromagnetic interactions between radical centres. On cooling below 5.5 K the magnetic moment drops rapidly indicative of antiferromagnetic exchange interactions occurring between ferromagnetic sublattices.

DISCUSSION

The solid state structure of **1** suggests that the magnetic behaviour may be low dimensional. Preliminary studies find that the fit to a one-dimensional Heisenberg system requires an antiferromagnetic inter-chain term of similar magnitude to the intra-chain term, indicating **1** is not a good one-dimensional system. A better fit may be obtained using a two-dimensional Heisenberg model with a single exchange parameter, J = 1.2 K.

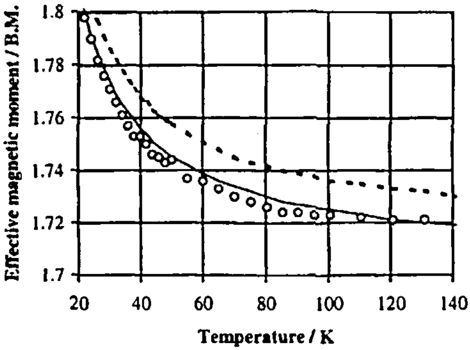

FIGURE 3: Modelling of magnetic behaviour of 1
-- = 1-D model, —— = 2-D model, o = magnetic data

CONCLUSION

The first rationally designed monomeric DTDA radical is reported. Preliminary magnetic measurements indicate local ferromagnetic interactions between molecules. Further studies are planned.

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