

Synthesis and Magnetic Properties of the Novel Dithiadiazolyl Radical, $p\text{-NCC}_6\text{F}_4\text{C}_6\text{F}_4\text{CNSSN}^\bullet$

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Abstract: The dithiadiazolyl radical $p\text{-NCC}_6\text{F}_4\text{C}_6\text{F}_4\text{CNSSN}^\bullet$ (**4**) retains its monomeric nature in the solid state with molecules linked together into chains via supramolecular CN \cdots S interactions. Variable temperature magnetic studies on **4** show that it behaves as a near-ideal Curie paramagnet ($|\theta|$ less than 0.1 K), indicating negligible intermolecular exchange. The effective magnetic moment ($1.78 \mu_B$) is temperature independent and in excellent agreement with the value expected for an $S = \frac{1}{2}$ paramagnet with $g = 2.01$ ($1.74 \mu_B$). The lack of exchange coupling between radicals is attributed to the absence of significant orbital overlap between radical centres.

Keywords: Magnetic properties, dithiadiazolyl, molecular magnetism, organic magnet.

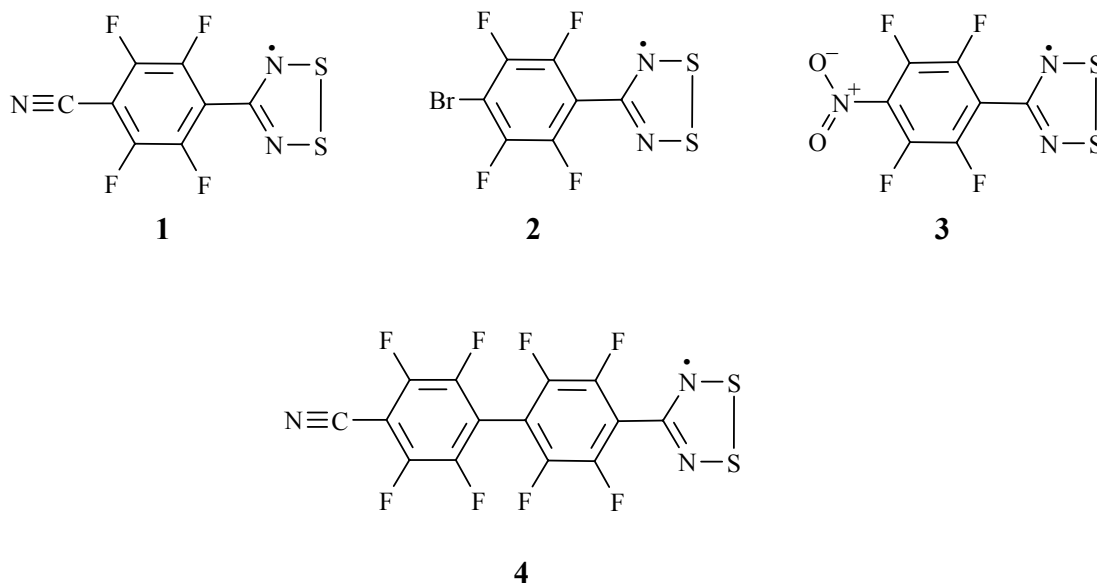
Introduction

The development of organic molecular magnetic materials is a field which is still very much in its infancy. The design of organic molecular magnets is conceptually simple; an organic molecular ferromagnet can be considered as a regular array of organic free radicals in which ferromagnetic interactions propagate throughout the lattice. For the majority of organic radicals the magnetic anisotropy is rather low and, to a good approximation, they can be considered as Heisenberg spin

systems [1]. For bulk magnetic order in a Heisenberg spin system these magnetic interactions must propagate throughout the lattice in three dimensions. The magnetic ordering temperature is dependent on the weakest of these interactions.

The simplicity of these few statements hides some immense synthetic and theoretical challenges and this simple theory becomes extremely complex in its implementation. In the first instance many organic radicals are extremely unstable and considerable efforts have been made to identify stable free radicals which may be isolated in the solid state and which can be used as the primary building blocks in the design of these materials. Secondly we need to understand the nature of the magnetic exchange interaction between organic radicals. This too is a non-trivial task. Whilst there are a number of mechanisms to describe the exchange process [2], most are strongly dependent on the nature of the intermolecular contacts which leads us to a third problem; how to control the solid state structure. This is an area of chemistry which provides many challenges also; approaches to predict the solid state structures of molecular compounds are also in their infancy [3]. Attempts to predict solid state structures based on lattice energy calculations normally reveal multiple minima of comparable energy and success in structure prediction is often fortuitous. Moreover many molecular structures are found to be polymorphic and this may lead to substantial differences in magnetic properties. That any organic ferromagnets have been prepared at all is perhaps not entirely due to improved understanding but merely a reflection of fortuity arising from the persistent efforts made by many groups around the world.

In our own research area we have focused on a group of thermally stable thiazyl radicals known as dithiadiazolyls. Many of these radicals have been isolated in the solid state. Whilst the majority form diamagnetic closed-shell dimers via a $\pi^*-\pi^*$ dimerisation process, [4] a small number of perfluorophenyl derivatives **1-3** have recently been found which retain their paramagnetism in the solid state [5,6,7].

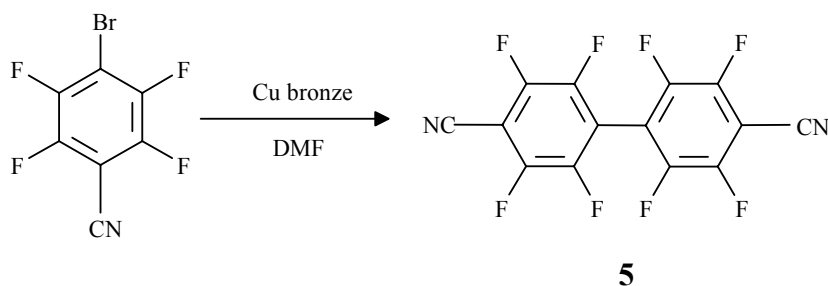


Radical **1** is polymorphic; the α -phase exhibits a maximum in χ around 8 K indicative of antiferromagnetic ordering, [5a] whilst the β -phase undergoes a phase transition to a canted antiferromagnetic phase at 36 K [5b]. Radical **2** also exhibits short range antiferromagnetic interactions, [6] but **3** has recently been reported to order as a ferromagnet at 1.3 K [7]. In both polymorphs of **1** [5], as well as other cyano-functionalised dithiadiazolyl radicals [8], an electrostatically favourable CN \cdots S interaction is persistently observed. This would appear to be a robust supramolecular synthon which may be expected to impart some structural control in the solid state structure of **4**. In this paper we describe the synthesis, crystal structure and magnetic properties of the perfluorobiphenyl derivative **4**, closely related to **1**.

Results

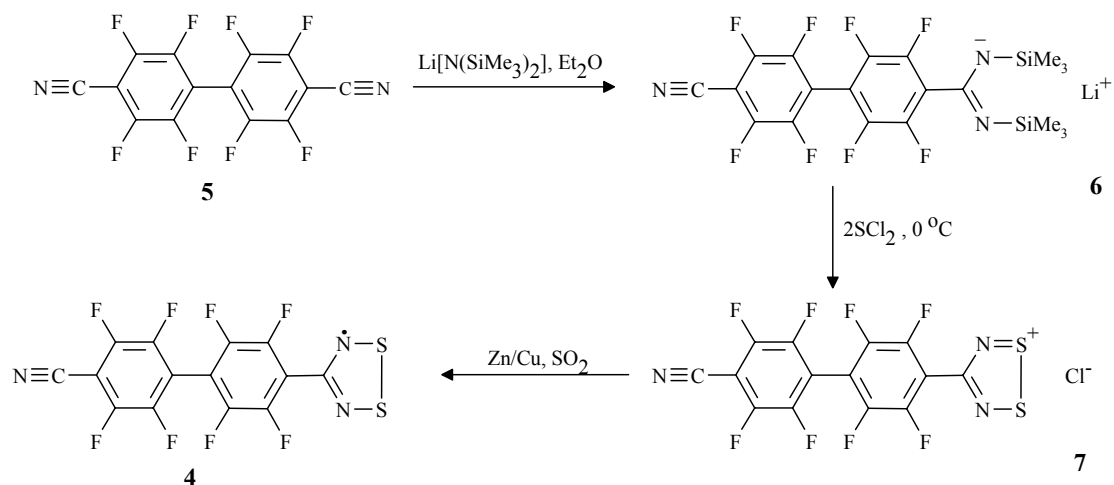
The precursor for the dithiadiazolyl radical **4** is the symmetric perfluorobiphenyl derivative **5**. The dinitrile *p*-NCC₆F₄C₆F₄CN may be isolated as a by-product of the reaction of sodium iodide with pentafluorobenzonitrile in 5% yield [9]. However we found that it could be conveniently prepared in a one-pot reaction (Recovered yield *ca* 20%) via an Ullmann coupling reaction [10], of *p*-BrC₆F₄CN using copper-bronze in refluxing DMF (Scheme 1).

Scheme 1



The dinitrile **5** was readily converted into the target radical **4** using standard synthetic methods (Scheme 2); treatment of **5** with one equivalent of Li[N(SiMe₃)₂] yielded the lithiated amidinate **6**. The salt **6** was not isolated, but treated directly with slightly more than two equivalents of SCl₂ to afford the dithiadiazolylum cation **7** as its chloride salt. Subsequent reduction of **7** with Zn/Cu couple in liquid SO₂ formed **4**. Crystals of **4** suitable for X-ray diffraction experiments were obtained *via* sublimation under dynamic vacuum at 10⁻⁴ to 10⁻⁵ torr (150 °C). The isolated yield for the three step synthesis was 15%.

Scheme 2

*X-ray crystal structure of 4*

Radical **4** is monomeric in the solid state and crystallises in the monoclinic space group $C2/c$ with half a molecule in the asymmetric unit (Figure 1). The geometry of the heterocyclic ring is unremarkable with heterocyclic bond lengths and angles comparable with related dithiadiazolyls (Table 1). The twist angle between the heterocyclic ring and the first perfluorophenyl ring is 42.9° , slightly smaller than seen in the majority of other perfluorophenyl-1,2,3,5-dithiadiazolyl radicals but much larger than their non-fluorinated derivatives in which the two rings are nearly coplanar. The twist angle between the two perfluorophenyl rings is 56.7° , resulting in the dithiadiazolyl ring and the second heterocyclic ring being almost perpendicular with respect to each other (twist angle 80.4°).

Figure 1. Molecular structure of **4** with atom labelling scheme

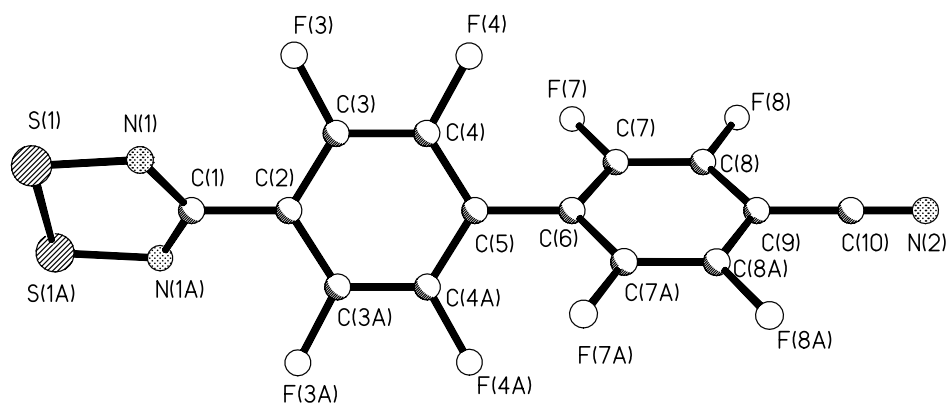
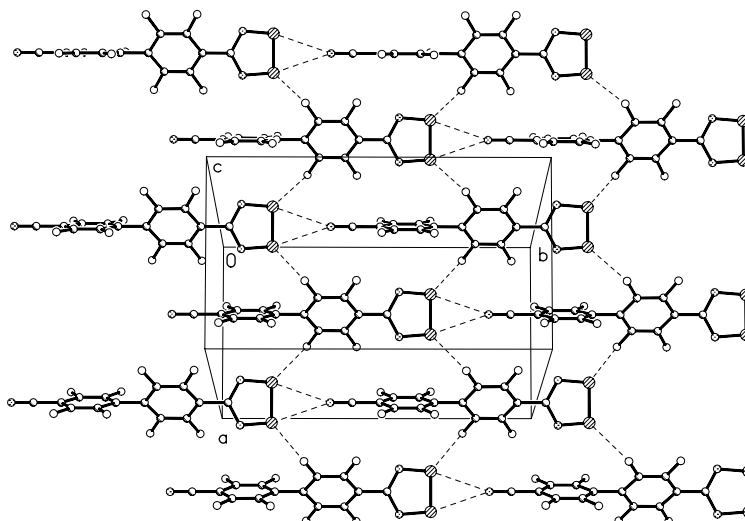


Table 1. Heterocyclic bond lengths and angles for **1-4**. The angle θ represents the angle between CN_2S_2 and C_6F_4 mean planes

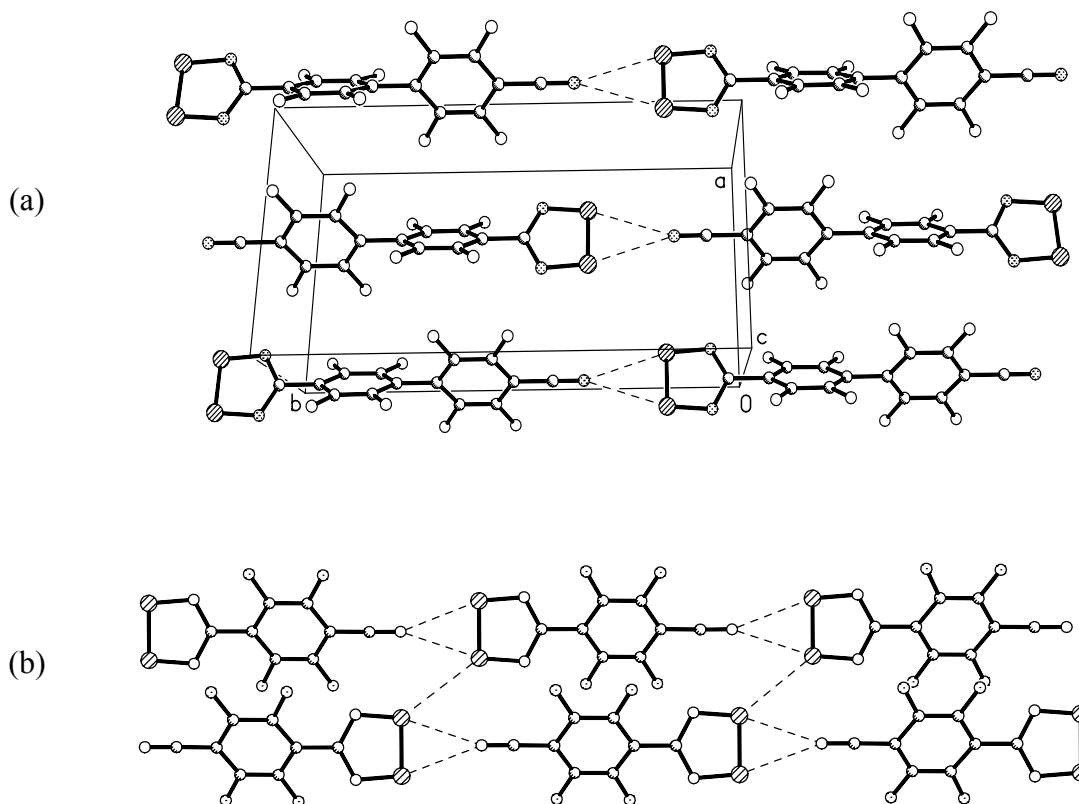
	1α	1β	2	3	4
C-N/Å	1.331(2) 1.324(2)	1.325	1.317(14) 1.327(12)	1.325(2)	1.331(2)
N-S/Å	1.637(2) 1.638(2)	1.638	1.640(8) 1.624(9)	1.635(2)	1.6340(19)
S-S/Å	2.0897(14)	2.082	2.070(4)	2.0815(13)	2.0856(11)
NCN/ $^\circ$	123.9(2)	124.0	124.0(9)	123.9(3)	123.5(3)
CNS/ $^\circ$	113.52(13) 113.74(13)	113.4	113.9(7) 112.8(7)	113.55(17)	113.67(16)
NSS/ $^\circ$	94.49(8) 94.37(8)	94.53	93.7(4) 95.5(3)	94.51(7)	94.57(6)
θ / $^\circ$	32	58	51.8	58.1	42.9
Reference	5a	5b	6	7	This work

Figure 2 Co-parallel chains of **4** with intermolecular $\text{CN}\cdots\text{S}$ and $\text{S}\cdots\text{F}$ contacts.

The solid-state structure of this material is gratifyingly similar to other dithiadiazolyl derivatives bearing cyano-functional groups; the molecules form molecular chains linked through electrostatic $\text{CN}^{\delta-}\cdots\text{S}^{\delta+}$ interactions ($d_{\text{CN}\cdots\text{S}} = 3.213 \text{ \AA}$, Figure 2). Whilst this intermolecular separation is somewhat longer than those observed in other cyano-substituted dithiadiazolyl radicals ($2.986 - 3.075 \text{ \AA}$), [5,8] it is still comparable to the sum of the van der Waals radii for in-plane interactions (3.2 \AA) [11]. In **1** both coparallel (**1 β**) and antiparallel (**1 α**) alignment of molecular chains are observed indicating a fine

energetic balance between centric and polar structures. In the case of **4** these supramolecular chains align co-parallel with S...F contacts at 3.109 Å close to the sum of the van der Waals radii (2.90 Å) (Figure 2). These layers pack so that the chains in adjacent layers run antiparallel to each other (Figure 3a). This antiparallel alignment of molecules exhibits a passing semblance to that seen in **1α** (Figure 3b) [5a]. However, in **1α** the lateral S...NC contacts (3.378 Å) are close to the van der Waals radii (3.2 Å) whereas they are considerably longer in **4** at 5.119 Å. The antiparallel orientation is generally favoured with dipolar materials in order to optimise dipole-dipole interactions [The molecular dipole of **4** determined from *ab initio* DFT calculations using both B3LYP/6-31G* and B3LYP/6-31G** basis sets is 5.06 Debye].

Figure 3. (a) Antiparallel alignment of chains of **4**; and (b) antiparallel alignment of chains of **1α**.

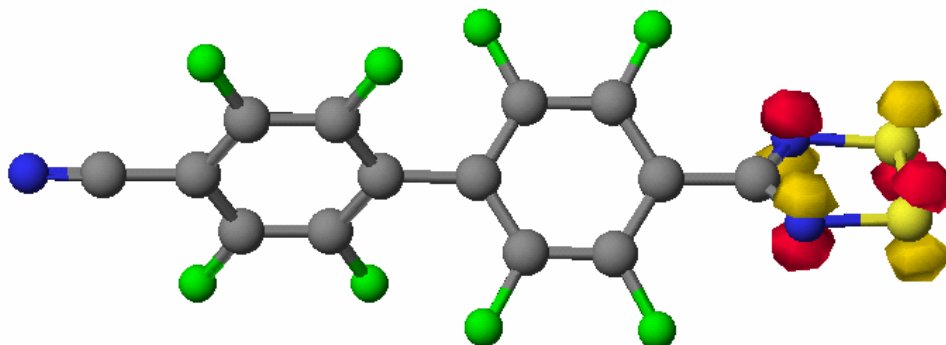


Finally it is worth noting that there are no close intermolecular S...N or S...S contacts between radicals in **4**. The nearest S...N and S...S contacts (at 7.037 Å and 6.163 Å respectively) are considerably longer than the sum of the van der Waals radii.

Theoretical Studies on 4

Previous EPR studies [12,7] on **1** – **3** indicate that the unpaired spin density distribution in these systems is almost invariant of the substituent on the perfluoroaryl group. In addition there is excellent agreement between the spin densities calculated from EPR and *ab initio* calculations. These have recently been supported by polarised neutron diffraction experiments [13] on **3**. *Ab initio* calculations on **4** were determined using DFT theory with the B3LYP/6-31G* and B3LYP/6-31G** basis sets using the crystal geometry. These calculations yielded identical results and confirmed that the unpaired spin density is localised on the heterocyclic ring with a near-equal distribution of spin density on the S and N atoms. The small excess of spin density on these atoms is accommodated by a small negative spin density at the heterocyclic C atom. Very small contributions amounting to less than 1% of the total spin density was detected on the perfluorophenyl rings. The calculated spin density distribution is illustrated in Figure 4.

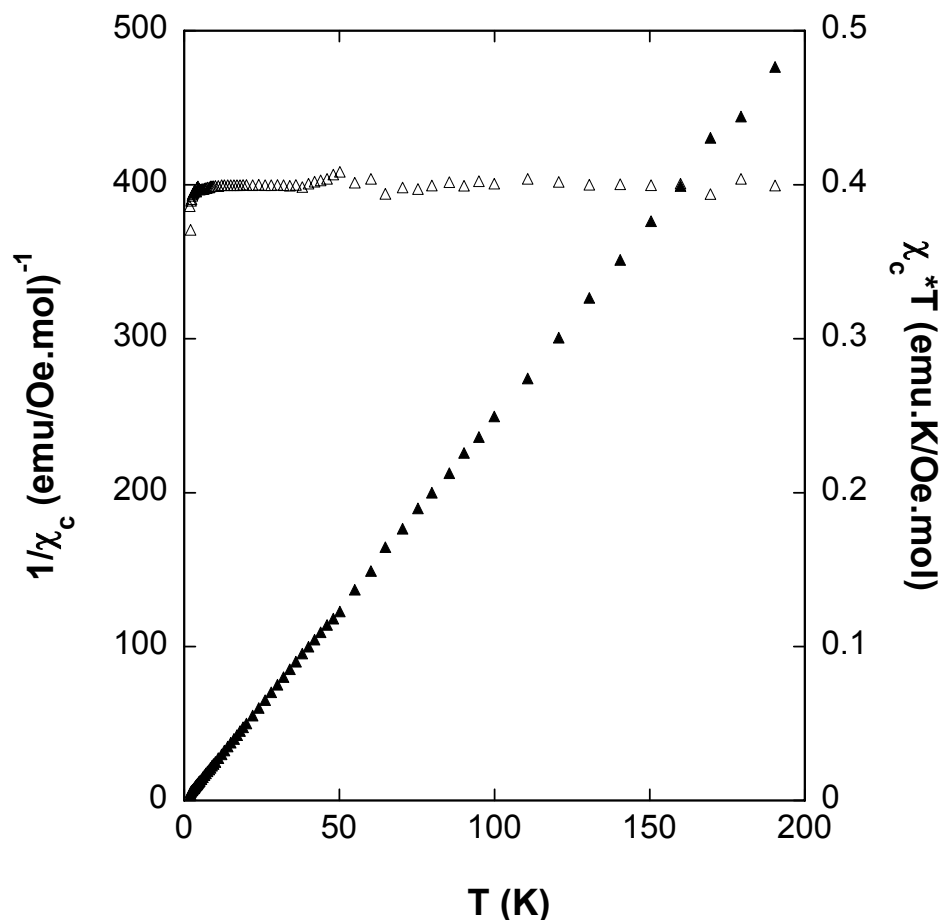
Figure 4: Spin density distribution in **4**, determined from *ab initio* DFT calculations. Spin densities at the heterocyclic ring are: (B3LYP/6-31G**) C -7.5%, N 25.6% and S 28.4%.

*Magnetic Behaviour of 4*

Variable temperature magnetic measurements on a polycrystalline sample of **4** were recorded in an applied field of 1 T between 1.8-300 K on a Quantum Design SQUID magnetometer. Data were corrected for diamagnetism using Pascal's constants [14].

A plot of inverse susceptibility vs temperature for **4** revealed that it behaves as a near-ideal Curie paramagnet (Figure 5); the Curie constant of 0.400 emu.K/Oe.mol is close to the value expected for a classical $S = \frac{1}{2}$ paramagnet ($C = 0.375$) with a Weiss constant, $|\theta|$ less than 0.1 K, indicating negligible intermolecular exchange. Indeed the effective magnetic moment is temperature independent at $1.78\mu_B$ down to *ca* 5 K, in excellent agreement with the value expected for an $S = \frac{1}{2}$ paramagnet with $g = 2.01$ ($1.74\mu_B$). Whilst the downturn in χT at low temperature could be ascribed to weak antiferromagnetic interactions between radicals, it is most likely to arise out of saturation effects induced by the large applied field at low temperature.

Figure 5: Temperature dependence of $1/\chi$ for **4** (\blacktriangle) and temperature dependence of the $\chi_c \cdot T$ product in the low temperature region (Δ).



Discussion

McConnell published several mechanisms in the 1960's to describe magnetic interactions between radicals and these have been utilised as guiding principles for many years to attempt to understand magnetic exchange interactions. The McConnell I mechanism [2a] relies on the direct overlap of orbitals bearing positive and negative spin densities and favours a net ferromagnetic interaction when regions of positive and negative spin density overlap. Recent theoretical studies have made it clear that there are several deficiencies in the McConnell I model [15]. Moreover in the vast majority of nitronyl nitroxide radicals, there are no close N \cdots N, N \cdots O or O \cdots O contacts less than the sum of the van der Waals radii (3.2Å) between nitronyl nitroxide functional groups which bear the majority of the spin density and a direct exchange mechanism would not appear operative in these systems. An alternative approach is to consider direct exchange purely in terms of orbital orthogonality. For systems in which magnetic orbitals are mutually orthogonal then a ferromagnetic interaction is anticipated. Conversely where there is a weak bonding contribution, then the excited closed shell singlet configuration will stabilise the singlet.

Detailed studies on **1β** and the related inclusion complex PHTP-*p*-NCC₆H₄CN₂SSN [16] support a dominant magnetic exchange pathway in **1** via interchain exchange interactions through close intermolecular S...N contacts. In **1β** the geometry supports an antiferromagnetic ground state. In contrast the singly occupied molecular orbitals in **3** are near orthogonal and a ferromagnetic interaction is anticipated. In the current derivative, **4**, there is no significant orbital overlap and no direct exchange mechanism is expected. Moreover, the absence of any magnetic communication between dithiadiazolyl radicals indicates that there is no significant charge-transfer (McConnell-II) mechanism [2b] operative either.

Conclusions

The design of organic molecular magnets requires an ability to understand both the nature of the magnetic exchange pathway and to predict the solid state structure with some accuracy. Given the limited abilities of the synthetic chemist to control the solid state structure with any degree of precision, the synthesis of organic ferromagnets still requires a large degree of serendipity. In the current paper we have highlighted our ability to provide some control of solid state structure of **4** through the use of supramolecular motifs to generate a one-dimensional chain. Yet our inability to fine-tune the intermolecular contacts in the remaining two dimensions has meant a complete lack of control over the magnetic interactions. Further studies, not only to understand the nature of the intermolecular geometry, but also to predict them in a reliable way must be a key objective for the future development of organic magnets.

Experimental

General

Zn/Cu couple, Cu-bronze, *p*-BrC₆F₄CN, SCl₂ and Li[N(SiMe₃)₂] (Aldrich) were used as received. DMF was dried over molecular sieves, Et₂O was distilled off Na wire and SO₂ was freshly distilled off P₄O₁₀ prior to use. All glassware was oven dried at 120°C for a minimum of 3h prior to use. ¹⁹F-NMR spectra were recorded on a Bruker AM-400 MHz or DRX-400 MHz Fourier transform spectrometers, and CFCl₃ was used as reference. Electron impact (EI) mass spectra were recorded on a Kratos Concept instrument.

Synthesis of *p*-NCC₆F₄C₆F₄CN

Cu bronze (275 mg, 4.3 mmol) was added to BrC₆F₄CN (1 g, 3.94 mmol) in dry DMF (50 mL) under a nitrogen atmosphere and the mixture heated under reflux for 3 hours. The mixture was cooled to room temperature and the DMF removed by vacuum distillation to yield a dark green residue. The residue was sublimed under dynamic vacuum (10⁻¹ torr, 150 °C) onto a water cooled cold finger to

yield a white crystalline solid. Yield 260 mg (19 %). Found: C 47.90 % H 0.23 % N 7.94 %. $C_{14}F_8N_2$ requires: C 48.28 % H 0.00 % N 8.05 %; EI^+ m/z : 348 (M^+), 329 (M^+-F), 310 (M^+-2F); ^{19}F NMR ($CDCl_3$) δ /ppm: -129.8 m (4F), -133.7 m (4F).

Synthesis of $p-NCC_6F_4C_6F_4CNSSN^*$ (4)

$p-NCC_6F_4C_6F_4CN$ (696 mg, 2 mmol) was added to a solution of $LiN(SiMe_3)_2$ (334 mg, 2 mmol) in dry ether (20 mL). The reaction mixture turned dark red and was stirred for 4 h at room temperature. The solution was then cooled to 0 °C and SCl_2 (0.3 ml, 389 mg, 3.75 mmol) added. The reaction was warmed to room temperature and stirred for a further 18 h. The resultant orange precipitate of $[p-NCC_6F_4C_6F_4CNSSN]Cl$ (contaminated with $LiCl$) was filtered, washed with dry ether (2 x 10 mL) and dried *in vacuo*. The crude $[p-NCC_6F_4C_6F_4CNSSN]Cl$ solid and Zn/Cu couple (65 mg, 1 mmol) were placed in a two-limbed reaction vessel and SO_2 (8mL) was condensed onto the mixture. The reaction was stirred for 18 h at room temperature and the radical was then isolated by filtration and further radical extracted by repeated washings of the residues with SO_2 until the washings were near colourless. The SO_2 was removed to yield a purple solid which was then sublimed (10^{-4} - 10^{-5} torr, 150 °C) to yield dark crystals of $p-NCC_6F_4C_6F_4CNSSN^*$ suitable for X-ray diffraction. Yield 130 mg (15 %). Found: C 48.39 % H 0.42 % N 7.85 %. $C_{14}F_8N_3S_2$ requires: C 48.48 % H 0 % N 8.05 %; EI^+ m/z : 426 (M^+), 380 (M^+-SN), 348 (M^+-S_2N).

X-ray crystallography

Single crystals of 4 were mounted on the end of a glass fibre with fluoropolymer. X-ray crystal data were collected on a Nonius Kappa CCD diffractometer using monochromatic $Mo-K\alpha$ radiation at 180(2) K. The structure was solved and refined using full matrix least squares on F^2 using SHELXTL. All atoms were refined anisotropically. CCDC 242405 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Samples Availability: Available from the authors.