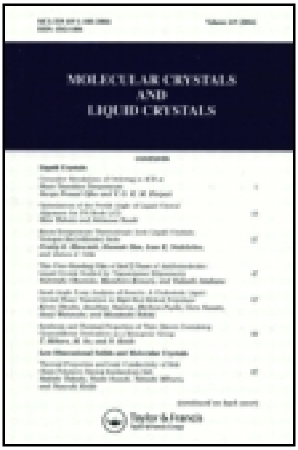


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Multi-Functional Magnetic Materials Based on Dithiadiazolyl Free Radicals

Jeremy M. Rawson [a], Robert J. Less [a], J. Nicholas B. Smith [a], Fernando Palacio [b] & Guillermo Antorrena [b]

[a] Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

[b] Instituto de Ciencia de Materiales de Aragon, CSIC-Universidad de Zaragoza, E-50009, Spain

Version of record first published: 24 Sep 2006

To cite this article: Jeremy M. Rawson, Robert J. Less, J. Nicholas B. Smith, Fernando Palacio & Guillermo Antorrena (1999): Multi-Functional Magnetic Materials Based on Dithiadiazolyl Free Radicals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 275-284

To link to this article: http://dx.doi.org/10.1080/10587259908023325

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 275-284
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Multi-Functional Magnetic Materials Based on Dithiadiazolyl Free Radicals

JEREMY M. RAWSON[a], ROBERT J. LESS[a], J. NICHOLAS B. SMITH[a],
FERNANDO PALACIO[b] and GUILLERMO ANTORRENA[b]

[a]*Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK and* [b]*Instituto de Ciencia de Materiales de Aragon, CSIC-Universidad de Zaragoza, E-50009, Spain*

The crystal structures of a series of dithiadiazolyl free radicals, p-XC_6F_4CNSSN (X=F,Cl,Br and CN) are described in terms of dipolar interactions which induce chain-like motifs in the solid state. When X=CN two morphologies are observed; the β-phase is polar and undergoes a phase transition to a weakly ferromagnetic state at 36K, an unprecedented temperature for an organic radical. The polar structure which gives rise to weak ferromagnetism in β-p-NCC_6F_4CNSSN, also provides a number of other potential solid state properties which may interact independently or cooperatively with the magnetic behaviour.

Keywords: dithiadiazolyl; weak ferromagnet; canted antiferromagnet; piezo-electric; ferro-electric; non-linear optic

INTRODUCTION

The design of organic molecular magnets is, simultaneously, one of the most difficult and rewarding tasks for the synthetic chemist; The design must incorporate stable radical centres which do not dimerise in the soli state.[1] Perhaps more importantly, the synthetic chemist must attempt to control the solid state structure, and hence intermolecular interactions which determine the magnetic communication (ferromagnetic or antiferromagnetic) between neighbouring spin-centres. The latter is a non-trivial task and a number of approaches have been developed using a supramolecular approach, particularly *via* hydrogen-bonded networks.[2]

A SUPRAMOLECULAR VIEW OF MOLECULAR MAGNETISM

The approach we have used to induce ferromagnetic behaviour is one which utilises antisymmetric exchange between radical centres.[3] The so-called Dzyaloshinskii-Moriya interaction minimises the coupling energy when the interacting spins are oriented perpendicular to one another, i.e. away from perfect antiparallel alignment. This leads to a canting of spins and essentially antiferromagnetic materials exhibit a small but observable spontaneous magnetic moment, typically a factor of 10^2 to 10^3 less than that observed for a pure ferromagnet. In order to observe a non-zero antisymmetric exchange term, interacting spins must not be related through an inversion centre. Whilst space groups possessing an inversion centre do not necessarily preclude weak ferromagnetism, polar space groups provide an attractive target for weak ferromagnetism although this is non-trivial since approximately 70% of achiral molecules crystallise in centro-symmetric space groups.[4]

Our research has concentrated[5] on the 1,2,3,5-dithiadiazolyl radical, **1** (Fig. 1) as the molecular building block for the construction of magnetic materials. In **1**, the unpaired spin density is localised on the CN_2S_2 ring (Fig. 1) and the spin-density distribution is essentially unaffected by changes to the substituent group, R. Consequently we may modify R to control molecular structure through steric and electrostatic means without significant modification of the electronic structure. In particular, we have attempted to devise suitable R-substituents to act as supramolecular synthons to promote crystal polarity.[3]

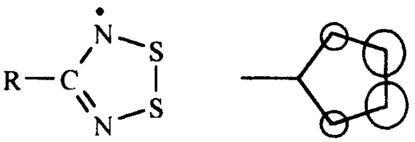
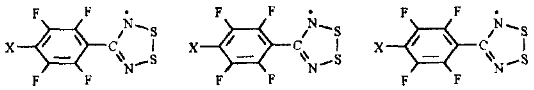


FIGURE 1. The 1,2,3,5-dithiadiazolyl ring and the symmetry of the singly occupied, π-based, molecular orbital. Approximate unpaired spin densities are ~28% and ~22% per S atom and N atom.

These S/N-based radicals exhibit a number of beneficial features; Firstly, there is significant spin-orbit coupling, which gives rise to a greater magnetic anisotropy which favours relatively large canting angles; Secondly the radicals are not sterically hindered and this facilitates close approach of radical centres, leading to stronger exchange interactions which promote high Tc's;[3] Finally, the dithiadiazolyl radicals, **1**, are thermally stable and melt without decomposition.[5] A detrimental feature of these radicals, is their strong tendency to dimerise[5] in the solid state (ΔH_{dim} ~ 35 $kJmol^{-1}$). Whilst this energy term is small in terms of covalent interactions, it is very large in terms of van der Waals forces, the principle instrument of crystal engineering. Recently we have investigated[6] a series of perfluorinated dithiadiazolyl derivatives in which intramolecular N...F interactions lead to a greater steric bulk for the R-group which assists the breakdown of the dimerisation process.

PERFLUORINATED DITHIADIAZOLYL RADICALS

Herein we describe the effect of a substituent X (X=F,Cl, Br and CN) on the molecular structure of *p*-$\mathrm{XC_6F_4CNSSN}$ derivatives. The electronegative group X interacts with the disulfur-bridge of the radical centre, leading to molecular chains (Fig. 2). We discuss how the chain-like motif is modified as a function of the electronegativity of X. The physical properties of β-*p*-$\mathrm{NCC_6F_4CNSSN}$ are briefly reviewed. In addition we describe how the crystal polarity, utilised in this approach to molecular magnetism might yield additional solid state properties required for multi-functional materials.



X	EN
CN (sp N)	5.07
F	3.90
Cl	3.12
Br	2.62
S	2.58
(sp^2 N	4.13)

FIGURE 2. Molecular chains of dithiadiazolyl radicals linked *via* X...S interactions and Pauling electronegativities for selected substituents, X and S. [Orbital electronegativities from reference 7].

The radicals *p*-$\mathrm{XC_6F_4CNSSN}$ were synthesised using standard synthetic methodologies[5] and purified by vacuum sublimation [10^{-2} Torr, ~100°C],

X	space group	*a*	*b*	*c*	α	β	γ
F	*C2/c*	18.044(1)	10.643(4)	10.834(1)	90	123.27(1)	90
Cl	*I2/a*	10.592(3)	11.295(3)	15.570(4)	90	92.850(4)	90
Br	*Aba2*	8.263(2)	20.426(4)	11.556(2)	90	90	90
CN	*P-1*	7.574(6)	8.065(6)	9.509(7)	65.73(3)	69.17(3)	67.52(3)
CN	*Fdd2*	15.105(3)	10.828(2)	11.933(3)	90	90	90

TABLE 1. Unit cell data for p-XC_6F_4CNSSN [X=F,Cl,Br,CN].

yielding crystals suitable for X-ray diffraction studies. Unit cell data are given in Table 1.

For the more electronegative halogens (X= F and Cl) chain-like motifs are observed in the solid state[6,8] (Fig. 3), but the lower electronegativity of Br fails to produce the $S^{\delta+}...X^{\delta-}$ interactions required to form a chain-like structure.[9] Instead, the S forms close contacts to a heterocyclic sp^2 hybrid N and aromatic F atoms. For X=F and X=Cl the structures are dimeric (and consequently diamagnetic), the molecular chains run anti-parallel to one another (Fig. 3) and the structures are non-polar. For X=CN, a chain-like structure is observed also, but the

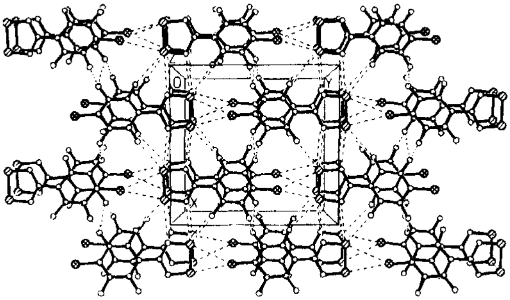


FIGURE 3: Packing diagram of $(p\text{-}ClC_6F_4CNSSN)_2$

compound is monomeric, retaining its paramagnetic nature in the solid state. In this instance, the compound is found to be polymorphic;[3] the α-phase is centrosymmetric with anti-parallel chains (Fig. 4a), but the β-phase is polar, with co-parallel chains (Fig. 4b). In both morphologies the CN...S interactions which lead to a chain-like motif are *ca.* 3.0Å. The different morphologies have profound effects on the magnetic properties; the polar structure, β-*p*-NCC_6F_4CNSSN undergoes a phase transition to a weakly ferromagnetic state at 36K.[5]

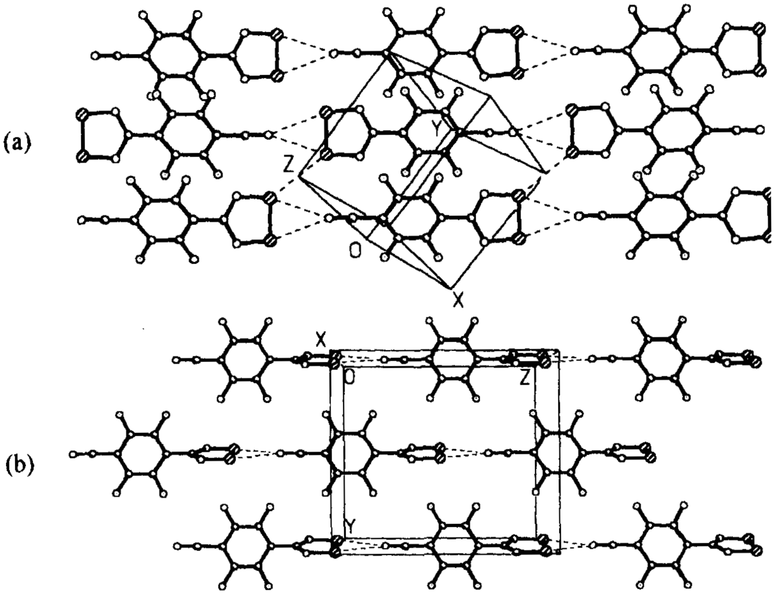


FIGURE 4. Packing diagrams for (a) α- phase, and (b) β-phase of *p*-NCC_6F_4CNSSN

MAGNETIC STUDIES ON β-*p*-NCC_6F_4CNSSN

The magnetic properties of β-*p*-NCC_6F_4CNSSN have been studied extensively.[5] Below 36 K the susceptibility becomes dependent on the applied field (Fig. 5a) and a small spontaneous magnetic moment is observed which saturates at *ca.* 1.5×10^{-3} μ_B as T → 0K. The magnetic ordering temperature of 36K is unprecedented for an organic radical. The data is reproducible (over 20 different samples have been studied on three susceptometers) and trace metal analyses were negative. The intrinsic nature of the magnetism has been confirmed by the frequency independence of the ac susceptibility, and a small maximum in the specific heat capacity at 35.5K corresponding to the weakly ferromagnetic to paramagnetic phase transition.[3] Powder neutron diffraction experiments show no new magnetic reflections below 36K, but magnetic enhancement of selected reflections (Fig.5b);[3] The magnetic space group is **Fd'd2'* in which the spins are fixed in the ab plane (perpendicular to the direction of chain propogation) and the resultant moment is oriented along the a-axis. Having established the origin of the spontaneous magnetic moment and the magnetic structure, we also wished to investigate the magnetic exchange pathway. Two exchange pathways appeared possible (Fig. 6a); either *via* the closest intermolecular contact, the CN...S interaction (~3.0Å) along the chain direction; and/or *via* heterocyclic N...S interactions (~3.5Å). In order to rationalise this dichotomy, an inclusion compound of *p*-NCC_6H_4CNSSN in the diamagnetic host (perhydrotriphenylene) was prepared.[10] In this material, polar chains of radicals are linked together through short CN...S interactions (3.1 Å), but neighbouring chains are magnetically insulated from each other by the host lattice. Variable temperature magnetic studies

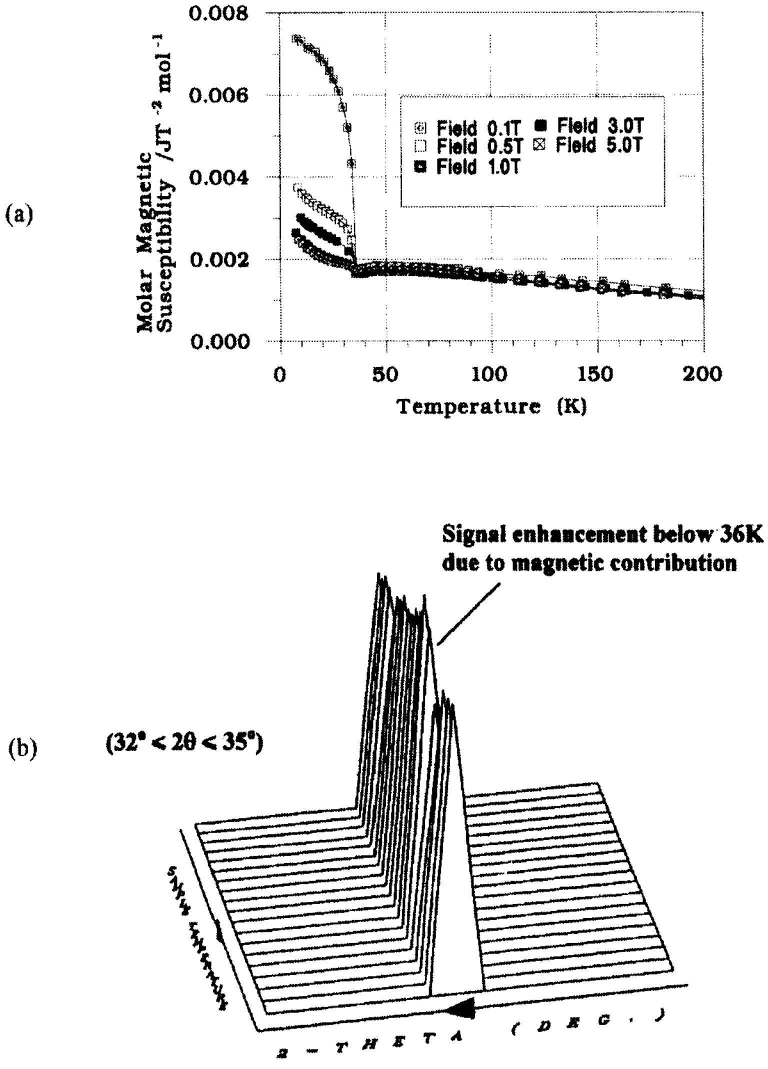
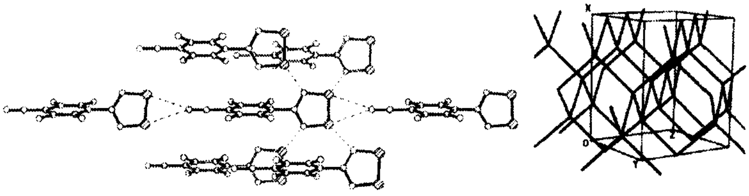


FIGURE 5. (a) Plot of χ vs. T for β-*p*-NCC$_6$F$_4$CNSSN illustrating the field dependence of χ below 36K; (b) Magnetic enhancement of a neutron diffraction reflection of β-*p*-NCC$_6$F$_4$CNSSN below 36K.



(a) (b)

FIGURE 6. (a) Closest intermolecular contacts in β-*p*-NCC_6F_4CNSSN, and (b) diamond-like superexchange pathway.

of this host-guest complex indicate that there is no exchange via the CN...S interaction. Exchange occurs only via the heterocyclic N...S contacts, consistent with the localisation of unpaired spin density on the dithiadiazolyl ring; Each molecule has four nearest neighbours in an approximately tetrahedral arrangement and this generates a diamond-like exchange pathway (Fig. 6b).

TOWARDS NEW MULTI-FUNCTIONAL MATERIALS

The crystal polarity, which is key to the weakly ferromagnetic state of β-*p*-NCC_6F_4CNSSN, is also a key feature for a number of other physical properties such as non-linear optics, piezo-electric and ferro-electric materials;[11] Second harmonic generation in NLO materials leads to frequency doubling;[4] Ferroelectric crystals display a long range order of the molecular dipoles below a critical temperature and these have applications as capacitors. Piezo-electric materials develop an electric polarisation on the application of stress and convert mechanical energy into electrical impulses. We aim to investigate how the magnetic response is modified by these external stimuli.

ACKNOWLEDGEMENTS

We thank Ciba-Geigy, EPSRC and MEC for studentships (JNBS, RJL and GA), the British Council and the EU COST programme for travel. We acknowledge additional financial support from Royal Society (JMR) and CICYT grant no. MAT94-0043 (FP).

References

[1] D. Dougherty in *Research Frontiers in Magnetochemistry* (Ed. C.J. O'Connor), World Scientific, Singapore, 1993.

[2] J. Cirujeda, M. Mas, E. Molins, F.L. de Panthou, J. Laugier, J.G Park, C. Paulsen, P. Rey, C. Rovira and J. *Veciana, J. Chem. Soc. Chem. Commun.*, 1995, 709.

[3] J.M. Rawson, J.N.B. Smith, F. Palacio and G. Antorrena, *J. Mater. Chem.*, 1998, submitted for publication, and references therein.

[4] N.J. Long, *Angew. Chem. Int. Ed.Engl.*, 1995, **34,** 21.

[5] J.M. Rawson, A.J Banister and I. Lavender, *Adv. Heterocycl. Chem.*, 1995, **62,** 137.

[6] C.M. Aherne, A.J Banister, A.S. Batsanov, N. Bricklebank, W. Clegg, M.R.J. Elsegood, J.A.K. Howard, I. Lavender, S.E. Lawrence and J.M. Rawson, manuscript in preparation.

[7] J.E. Huheey, *Inorganic Chemistry,*Third Edition, Harper Intnl, 1983, Chap.3, p. 144–152.

[8] J.M. Rawson, R.J. Less and A.E Goeta, unpublished results.

[9] J.M. Rawson, J.N.B. Smith, N. Feeder, A. Steiner, F. Palacio and G. Antorrena, manuscript in preparation.

[10] P.J. Langley, J.M. Rawson, J.N.B. Smith, M. Schuler, A. Schweiger, F. Palacio, G. Antorrena, C. Hoffman, G. Gescheidt, A. Quintel, P. Rechsteiner, R. Bachmann and J. Hulliger, manuscript in preparation.

[11] *Inorganic Materials Chemistry,* M.T Weller, Oxford Chemistry Primer, Oxford University Press, Oxford, 1994, Chap. 4, p. 42–43.