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Thermal hysteresis in dithiadiazolyl and dithiazolyl radicals induced by supercooling of paramagnetic liquids close to room temperature: a study of $F_3C\overline{CNSSN}$ and an interpretation of the behaviour of $F_3C\overline{CSNSC}CF_3$†

Hongbin Du,[a] Robert C. Haddon,[b] Ingo Krossing,[a] Jack Passmore,*[a] Jeremy M. Rawson*[c] and Melbourne J. Schriver[a]

[a] *Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2. E-mail: passmore@unb.ca*

[b] *Department of Chemistry and Physics, and, Advanced Carbon Materials Center, University of Kentucky, Lexington, KY 40506, USA*

[c] *Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: jmr31@cus.am.ac.uk*

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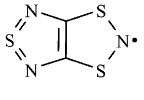
The trifluoromethyl-substituted dithiadiazolyl and dithiazolyl radicals, $F_3C\overline{CNSSN}$ (1) and $F_3C\overline{CSNSC}CF_3$ (2) associate through π*–π* covalent and electrostatic $S^{\delta+}...N^{\delta-}$ interactions in the solid state, but melt with a dramatic volume increase to generate paramagnetic liquids; these radicals exhibit thermal hysteresis, which arises through a meta-stable super-cooled liquid state, close to room temperature.

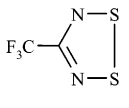
The dithiazolyl radical TTTA has recently been shown[1] to exhibit room temperature bistability with thermal hysteresis between 234 and 317 K. The behaviour arises through a solid–solid transformation between a low temperature diamagnetic phase and a high temperature paramagnetic phase.[1] Other examples of this behaviour have been reported in related thiazyl radicals.[2] In this paper we report the observation of thermal hysteresis in the magnetic properties of the dithiadiazolyl radical (**1**) and the dithiazolyl radical (**2**). In both cases the meta-stable state arises through super-cooling of the liquid phase.

Samples of **1** and **2** were prepared according to literature methods (ESI SUP-01†).[3,4] The structures of **1** and **2** have been reported previously,[4,5] but are worthy of some comment. The structure of **1** comprises twisted cofacial dimers (Fig. 1a) with intradimer S…S contacts of 2.997(2) and 2.978(2) Å. This π*–π* association leads to spin-pairing, generating a closed shell, diamagnetic, ground state. The electrostatic $S^{\delta+}...N^{\delta-}$ interdimer interactions (Fig. 1a) propagate through the crystal structure (ESI SUP-02†) and give rise to an extended network.

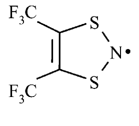
The isoelectronic radical **2** exists as a diamagnetic tetramer in the solid state linked *via* electrostatic contacts and π*–π* interactions[4] [3.097(50), 3.239(36) Å] (Fig. 1b). Theoretical calculations (ESI SUP-03†) on **2** show that the enthalpy of dimer formation *via* either of the closed-shell interactions **2α** or **2β**, is not favourable, in agreement with solution EPR studies,[4] but predict that the planar electrostatic dimer **2γ** *cf.* **1γ** (below) is thermodynamically favoured. The π*–π* interaction observed in the crystal structure of **2** arises through the additional electrostatic stabilisation (2 dimers → tetramer: $\Delta H \approx -50$ kJ mol^{-1}). These energies are in qualitative agreement with a simple electrostatic model using point charges (ESI SUP-03†).



TTTA



1



2

The melting of **1** (35 °C) is associated with an abrupt increase in paramagnetism (Fig. 2a) and an extraordinarily large increase in volume. The volume of **1** is increased by *ca.* 30% on melting [ρ(liquid, 60 °C) = 1.41 g cm^{-3}; ρ(solid, 283–303 K[6]) = 2.00 g cm^{-3}] *cf.* hydrocarbons 5–20%.[7] Larger values are often associated with dramatic changes of structure on melting *e.g.* $AlCl_3$ (83%).[7] The melting of **2** is also accompanied by a large volume increase of 22%, attributed[4] to the breakdown of the π*–π* bonding interaction and an increase in intermolecular contact to the sum of the van der Waals radii (the expected increases are *ca.* 36% for **1** and 28% for **2**).

The abrupt change in susceptibility at the phase transition can be modelled using the domain model of Sorai.[8] Attempts to model the liquid phase behaviour of **1** as either an $S = \frac{1}{2}$ Curie–Weiss paramagnet or as a pure open-shell dimer, (*e.g.* **1γ**) proved unsuccessful (ESI SUP-05†).

The magnetic data clearly indicate some degree of association in the melt either as a π*–π* covalently-bonded dimer such as **1α** (as found in the solid state, see Fig. 1a) or as an electrostatic dimer *e.g.* **1γ**. The large increase in volume implies that the dimer is the electrostatically bound, planar, **1**, rather than the π*–π* bonded **1α** or **1β**. However, B86P86/SVP calculations give favourable dimerisation enthalpies for all three isomers, but with stability of the dimers increasing in the order **1γ**, **1α** ≈ **1β** (ESI SUP-02†). Other isomers are also possible.[9]

The simplest, adequate model, involves an equilibrium between paramagnetic monomers and an open-shell exchange-coupled dimer ($J = -260$ K) in the liquid phase. The curve-fit is a little insensitive to the values of ΔH_{eqm} and ΔS_{eqm} (required

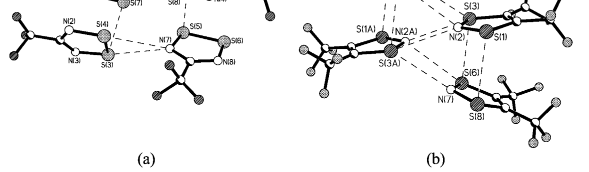


Fig. 1 (a) Asymmetric unit of **1** illustrating the tetrameric motif with dimers linked *via* electrostatic S…N interactions: (b) structure of **2** illustrating the tetrameric motif with dimers linked *via* electrostatic S…N interactions.

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† Electronic supplementary information (ESI) available: Synthesis of **1**; packing diagrams of **1** and **2**; *ab initio* calculations on the association modes of **1** and **2**; estimates of the energy of association of **2** based on a simple electrostatic model; molecular electrostatic potential maps of **1** and **2** and a comparison of the charge distribution in **1** and **2** from semi-empirical and *ab initio* calculations; curve-fits of the magnetic data of **1** utilising a Curie–Weiss, exchange-coupled dimer and monomer–dimer equilibrium models for the liquid phase. See http://www.rsc.org/suppdata/cc/b2/b202627a/

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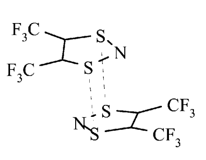
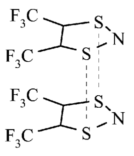
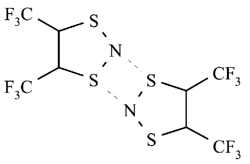


2α



2β



2γ

to determine ΔG_{eqm} and hence the equilibrium constant, K) but in all cases the value of $T\Delta S_{\mathrm{eqm}}$ needed to be close to ΔH_{eqm} at room temperature for a satisfactory fit. The model implies that at 310 K, the liquid consists of 25% monomeric **1** in equilibrium with 63% singlet dimer and 12% triplet dimer.

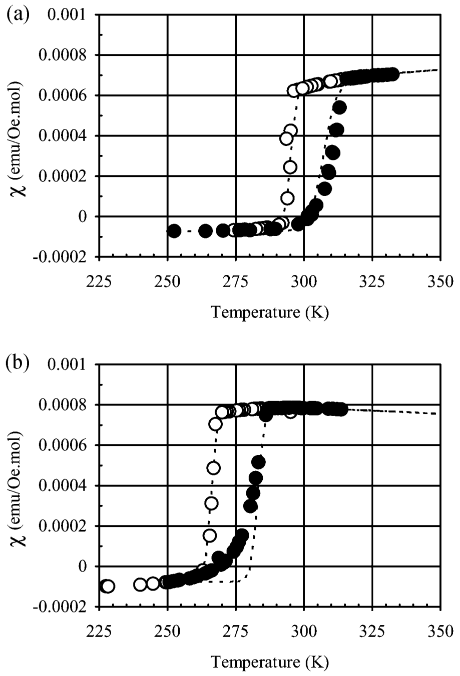
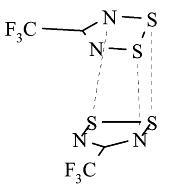
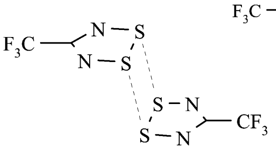


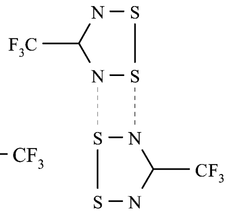
Fig. 2 Variation in χ *vs.* T for (a) **1** and (b) **2**. Full circles (●) and clear circles (○) represent data recorded on warming and cooling respectively. The dotted lines correspond to the curve-fit using the parameters listed in the supplementary data.†



1α



1β



1γ

On cooling, samples of **1** remain paramagnetic below the melting point until undergoing an abrupt transition at 295 K to a diamagnetic state. We attribute this to a meta-stable liquid, or glassy, state which is consistent with its appearance.

The magnetic behaviour of **2** (Fig. 2b) is similar to that of **1**, but with a more marked increase in susceptibility prior to melting, and can be fitted using the same model, but required smaller values of ΔH_{eqm} and ΔS_{eqm} and a weaker exchange interaction ($J = -196$ K).

We propose that the behaviour observed for both **1** and **2** is representative[2b] of many dithiadiazolyl and dithiazolyl radicals at their solid–liquid phase transition. The volume increases coupled with the magnetic behaviour of both **1** and **2** on melting are consistent with the presence of planar, electrostatically-bonded dimers **1γ** and **2γ** in equilibrium with radical monomers in the liquid phase. The observation of thermal hysteresis in the magnetic susceptibility arises from the formation of a meta-stable, super-cooled phase below T_{mp}. The temperature range of thermal hysteresis should be tunable through modification of the substituent(s). More detailed studies of the thermal hysteresis in **1**, **2** and related systems are underway.

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