A bimodal dithiadiazolyl diradical: crystal structure and magnetic properties of the 2,2′-dimethylbiphenylene bridged derivative

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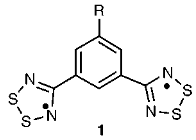
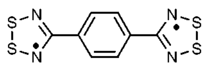
The two termini of the torsionally strained dithiadiazolyl diradical $S_2N_2C{-}C_6H_3Me{-}MeC_6H_3{-}CN_2S_2$ 3 possess different solid state structural environments; the bulk magnetic susceptibility of 3 is interpreted in terms of the distinct properties of the two radical centres.

The potential applications of 1,2,3,5-dithiadiazolyl (DTDA) radicals in molecular magnets,[1] conductors[2] and thin film devices[3] has led to increasing interest in both the diversity and control of the structural features of these systems.[4] Most monofunctional derivatives associate in the solid state to afford diamagnetic dimers, and suppression of this dimerization hence represents a major experimental challenge. Recently, Rawson and co-workers have reported several radicals that are unassociated[1,5] or only very weakly spin paired.[6] Most significantly, the β-phase of *p*-cyanoperfluorophenyl-DTDA is weakly ferromagnetic below 36 K.[1]

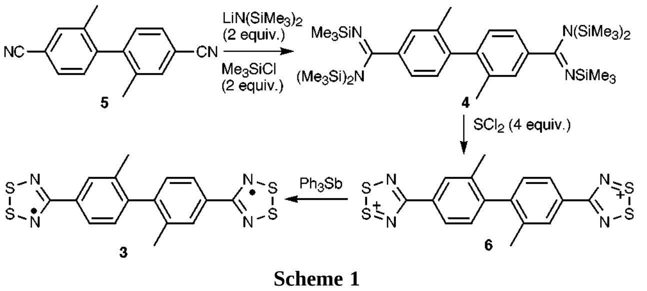
Bifunctional radicals, *e.g.* **1** (R = H, CN, Bu^t)[7,8] and **2**,[3,9] have also been examined, but in the systems studied to date the two termini have been crystallographically equivalent, as a result of which the bulk magnetic properties are a function of a single spin centre. In order to explore the relationship between structure and magnetic behavior in DTDA diradicals we have prepared and characterized the 2,2′-dimethylbiphenylene (DMBP) bridged derivative **3** (Scheme 1). We selected this bridge in the hope that torsion about the central C–C bond of DMBP would inhibit both the π-stacked structures found for **1** and the herringbone arrangement exemplified by **2**. Colourless crystals (mp 142–145 °C) of the necessary bis-amidine **4** [δ_H(CDCl$_3$) 0.065 (s, *Me*$_3$Si, 54 H), 7.34–7.56 (AA′BB′, 8 H)] were prepared in 65% yield from the dinitrile **5**[10] using standard methodology.[11] Reaction of **4** (3.00 g, 4.3 mmol) with SCl$_2$ (2.00 g, 19.3 mmol) in 100 ml of MeCN at reflux gave the crude bis(dithiadiazolylium chloride) **6**, which was reduced with Ph$_3$Sb (2.0 g, 5.7 mmol) to yield **3** (1.36 g, 82%), which was purified by fractional sublimation at 160–100 °C/10^{-3} torr, affording black reflective nodules, mp 242 °C.†



1



2



Scheme 1

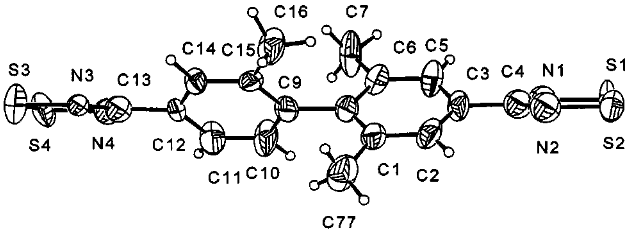


Fig. 1 ORTEP drawing of **3**, illustrating the torsion within the molecule. The C7 (C77) methyl group is disordered.

The molecular structure‡ (Fig. 1) of **3** exhibits a minor disorder in both CN$_2$S$_2$ rings, which were refined as rigid groups, and also in one of the methyl groups, which was refined with 50% occupancy of the two (C7/C77) positions. These imperfections aside, the molecule displays the anticipated torsion (74.0°) about the central C–C bond of the DMBP bridge; in biphenyl itself, for example, the two rings are coplanar,[12] but in 2,2′-dimethyl-4,4′-diaminobiphenyl the torsion angle opens to 86°.[13] The crystal packing of **3** (Fig. 2) represents a significant departure from the two classes of solid state motifs represented by **1** and **2**. Moreover the two DTDA radicals within each molecule are located in very different solid state environments. One end (S3/S4) is essentially undimerized, and the arrangement of these DTDA rings resembles an array of footprints running parallel to the *y* direction. At the other end of the molecule the DTDA ring (S1/S2) is dimerized in a *trans*-

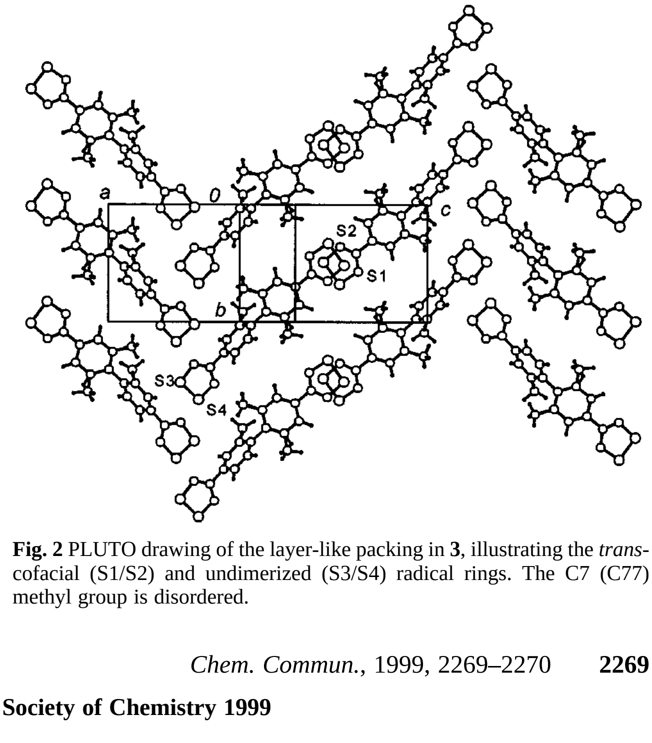


Fig. 2 PLUTO drawing of the layer-like packing in **3**, illustrating the *trans*-cofacial (S1/S2) and undimerized (S3/S4) radical rings. The C7 (C77) methyl group is disordered.

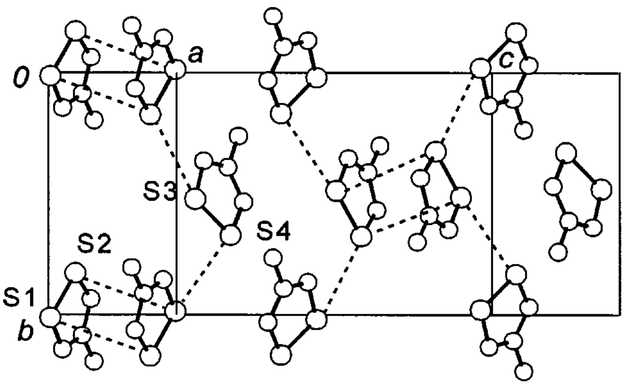


Fig. 3 A single layer of DTDA rings in **3** (DMBP bridges removed), showing close intermolecular contacts.

cofacial manner across an inversion centre to an equivalent radical on a neighbouring molecule. This hitherto unobserved orientation for radical association produces rather long S···S contacts [d(S1···S2′) = 3.68(2) Å], but the separation of the DTDA planes of the dimer is a tight 3.24 Å, easily short enough to effect spin pairing (*vide infra*). We note *en passant* that this mode of dimerization lies near to the proposed transition state for the photochemical isomerization of 1,3,2,4- to 1,2,3,5-DTDAs.[14] Although Fig. 2 suggests the two ends of the molecule are well separated, closer inspection of the packing of the DTDA rings (Fig. 3) reveals two short contacts [d(S1···S4′) = 3.38(2) Å and d(S2···S3′) = 3.38(2) Å]. These dimer/radical bridging interactions may facilitate magnetic exchange between the spins on the S3/S4 rings.

The extent of spin coupling in these two radical environments in **3** has been assessed by magnetic susceptibility measurements over the temperature range 4–400 K. The magnetic behavior (Fig. 4) of the compound can be divided into high (> 200 K), and low (< 200 K) temperature regions, both of which are interpreted in terms of Curie paramagnetism. We associate the low temperature paramagnetism primarily with the undimerized (S3/S4) end of the molecule. On the first scan through this region we find an unpaired spin count of n = 1.11 per molecule. The slight excess paramagnetism over n = 1 may be associated with the high temperature magnetic regime or experimental error. At low temperatures there is a hysteretic phase transition (75–150 K) that quenches some of the molecular spins. The Weiss constant for the ordering transition in all of these states is about −100 K and therefore strongly antiferromagnetic. Thus, at low temperatures, thermal cycling apparently leads to a coupling of some of the radical electrons at this end of the molecule. This may reduce the structural disorder noted above.

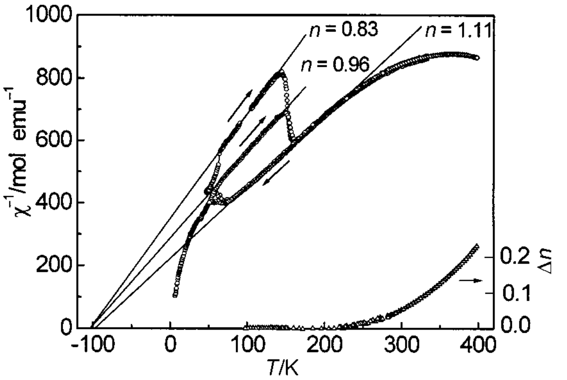


Fig. 4 Plots of $1/\chi$ (χ = magnetic susceptibility) and excess Curie Spins (Δn) of **3** as a function of temperature.

In the high temperature regime the departure from simple n = 1.11 Curie behavior probably arises from the thermal dissociation of the coupled spins at the dimerized (S1/S2) end of the molecule. The excess spins created (Δn) are shown on the right. Similar paramagnetic enhancements at elevated temperatures have been observed in the π-stacked structures of **1**.[7,8]

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Notes and references

† Satisfactory chemical analyses were obtained for compounds **3** and **4**.

‡ *Crystal data* for **3**: Data were collected at 293 K on an Enraf-Nonius automated diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) using θ–2θ scans. The structures were solved by direct methods and refined by full-matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$.$S_4N_4C_{16}H_{12}$, M = 388.5, monoclinic, space group $P2_1/n$, with a = 11.0371(11), b = 8.489(8), c = 18.854(2) Å, β = 103.299(9)° V = 1719.1(16) Å^3, Z = 4, D_c = 1.50 g cm^{-3}, μ = 0.54 mm^{-1}. 202 Parameters were refined using 1349 unique observed reflections [$I > 1\sigma(I)$] to give R = 0.117 and R_w = 0.142. CCDC 182/1434. See http://www.rsc.org/suppdata/cc/1999/2269/ for crystallographic data in .cif format.

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