A spontaneous magnetic moment in an organic radical: Synthesis and characterization of benzodioxepinyl-1,3,2-dithiazolyl.

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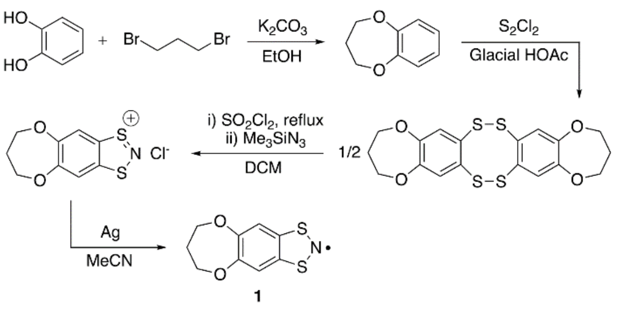
Supporting Information Placeholder

ABSTRACT: The synthesis of the 1,3,2-dithiazolyl radical (**1**) derived from 3,4-dihydro-2H-1,5-benzodioxepine is described. Crystals of **1** were grown by vacuum sublimation and adopt the orthorhombic space group *Pbca*. DC SQUID magnetometry reveals Curie-Weiss behaviour for T > 20 K (C = 0.376 emu K mol^{-1} and θ = +5.7 K) consistent with local ferromagnetic interactions. The presence of weaker antiferromagnetic interactions lead to magnetic ordering as a canted antiferromagnet (T_N = 3.8 K) with a small spontaneous moment (2.5×10^{-4} Nβ) and a small coercivity (*ca.* 8 Oe) at 2 K. Magnetic ordering was reflected in a field dependence of the magnetic susceptibility below 3.8 K and a peak in the low temperature heat capacity data. A canting angle of 0.08° was estimated from *M vs H* data.

The seminal work of Heisenberg on magnetic materials focused on compounds constructed from metals containing unpaired electrons in either *d*- or *f*-orbitals.[1] Although mechanisms for intermolecular magnetic exchange between organic radicals were postulated by McConnell in the 1960s,[2] the emergence of the first organic magnets in which the magnetism derives from unpaired electrons located in *p*-orbitals (or delocalized π-systems), were not reported until the late 1990s: Kinoshita's studies on the β-phase of the *p*-nitrophenyl nitronyl nitroxide radical *p*-NPNN provided the first example of an organic ferromagnet[3] albeit ordering at low temperature (0.6 K). Several other families of organic radicals were soon shown to exhibit spontaneous magnetic moments.[4-6] The incorporation of heavier *p*-block elements, such as sulfur and selenium, with more radially expanded orbitals and greater spin-orbit coupling has afforded examples of radicals not only with higher magnetic ordering temperatures but also greater magnetic anisotropy.[7-15] Despite their favorable magnetic properties, these radicals offer significant challenges due to their hydrolytic instability, the frequent presence of polymorphism,[16-18] and propensity for solid state dimerization *via* a conventional 2*c*,2*e*$^-$ σ-bond[19] or, more commonly, 'pancake bonding'.[20] Both dimerization processes are effective quenchers of radical paramagnetism.

Among the families of group 15/16 radicals, the 1,3,2-dithiazolyl (DTA) radical has attracted attention due to its low dimerization enthalpy.[21] These DTA radicals have been explored both experimentally and computationally as organic equivalents of the 'spin crossover' phenomenon, common to octahedral d^4 – d^7 ions,[22] undergoing solid state phase transitions between diamagnetic (π^*-π^* dimer) and paramagnetic monomer phases at or near ambient temperature.[23-30] Magnetic studies on other neutral DTA radicals reflect the presence of dominant antiferromagnetic interactions between radicals but only the planar benzo-1,3,2-dithiazolyl (BDTA) has been shown to exhibit long range magnetic order. This radical undergoes a phase transition from a diamagnetic π^*-π^* dimer[21] to a paramagnetic monomer phase *via* an unusual melt-recrystallization process.[31] Subsequent supercooling of this paramagnetic phase revealed antiferromagnetic ordering at T_N = 13 K.[31] However, since the structure of the paramagnetic phase is unknown, it is impossible to develop a magnetostructural correlation in this case. In the current paper we describe the synthesis, structural and magnetic characterization of a new DTA radical (**1**, Scheme 1) in which the dominant exchange coupling is ferromagnetic but the presence of weaker antiferromagnetic interactions ultimately lead to magnetic ordering as a canted antiferromagnet at 3.8 K.



Scheme 1: Synthetic route to **1**

Radical **1** was prepared in an analogous fashion to related dialkoxy-benzo-substituted DTA radicals (Scheme 1):[32] 3,4- dihydro-2H-1,5-benzodioxepine was prepared by condensation of catechol and 1,3-dibromopropane (92%).[33] Reaction with S_2Cl_2 formed the intermediate tetrathiocin (81%),[34] which was chlorinated with SO_2Cl_2 to form the bis(sulfenyl chloride) and condensed with Me_3SiN_3 to form [**1**]Cl in 46% yield. The structure of [**1**]Cl was determined by X-ray diffraction (see SI). Subsequent reduction of [**1**]Cl with Ag powder in dry MeCN afforded radical **1** (EPR, DCM: g = 2.006, a_N = 11.1 G, Figure S4) which was isolated by vacuum sublimation (10^{-2} Torr, 110 – 60 °C) to afford **1** as dark red octagonal plates. Radical **1** crystallizes in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit. The benzodithiazolyl fragment and the two O atoms are planar within 0.107 Å (Figure 1), while the C_5O_2 ring adopts a chair conformation with all three saturated C atoms lying 'above' the benzodithiazolyl plane. There are no close face-to-face 'pancake bonding' style S⋯S contacts around 3.1 Å, which are known to render DTA radicals diamagnetic.[20] Instead, radical **1** packs in a herringbone-like motif in the *ab* plane (Figure 1) with each molecule forming three S⋯S contacts less than the sum of the van der Waals radii (3.60 Å). There are two symmetry equivalent S⋯S contacts (S1⋯S2 at 3.5716(7) Å, d_1 in Figure 1) which generate a chain structure parallel to the crystallographic *b*-axis. The third and shortest of the intermolecular S⋯S contacts is a centrosymmetric S…S contact (S2⋯S2 at 3.3007(6) Å, d_2 in Figure 1). The combination of these two sets of S⋯S contacts affords a two-dimensional honeycomb network of contacts in the *ab* plane (Figure S2).

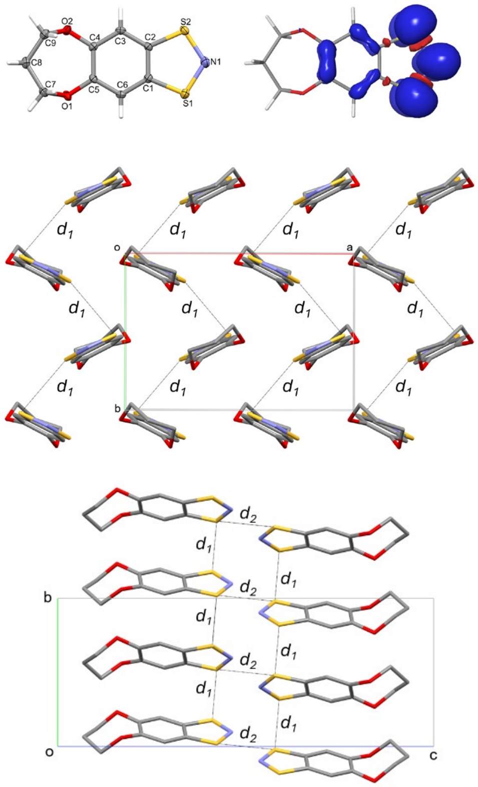


Figure 1. (top) molecular structure of **1** (non-H atoms plotted with thermal ellipsoids drawn at the 50% probability level) along with the computed spin density distribution (UB3LYP/6-311G**++); (middle) packing of **1** in the *ab* plane with S⋯S contacts marked (d_1 = 3.5716(7) Å); (bottom) view in the *bc* plane highlighting both d_1 and d_2 contacts (d_2 = 3.3007(6) Å).

Variable temperature magnetic studies on a sample of **1** (18.2 mg) sealed in a gelatin capsule and immobilized with a little cotton were recorded on a Quantum Design PPMS in the range 2 – 200 K. A correction was applied for sample diamagnetism. A separate batch of the same sample was studied by PXRD to confirm phase purity (see Figure S3).

Above 20 K, the sample follows Curie-Weiss behavior with a Curie constant (C = 0.376 emu K mol^{-1}) typical of an S = ½ spin and a positive Weiss constant (θ = +5.7 K), consistent with local ferromagnetic interactions (Figure 2, inset). A plot of $\chi_m T$ *vs* T reveals an increase in $\chi_m T$ upon cooling, reaching a maximum of 0.6 emu K mol^{-1} at 8 K, consistent with dominant ferromagnetic interactions. Upon further cooling $\chi_m T$ decreases (Figure 2), reflecting the presence of weaker antiferromagnetic interactions becoming significant at low temperature. Below 4 K, the magnetic susceptibility becomes field dependent (Figure 3), marking the onset of magnetic order. The divergence in field-cooled and zero-field cooled susceptibilities reflect the emergence of a spontaneous magnetic moment (Figure S5).

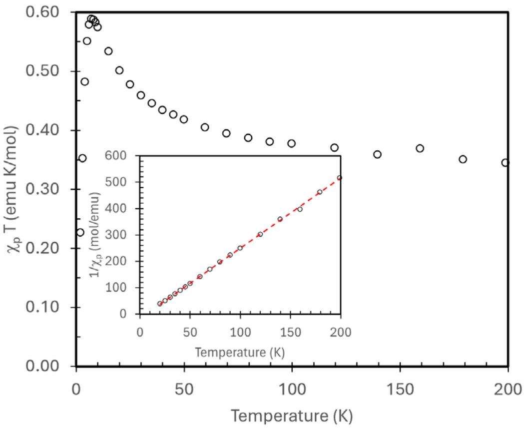


Figure 2. Temperature dependence of $\chi_p T$ for **1** (H = 500 Oe) with (inset) temperature dependence of $1/\chi_p$. The dashed line corresponds to the Curie-Weiss fit to the $1/\chi_p$ *vs* T data.

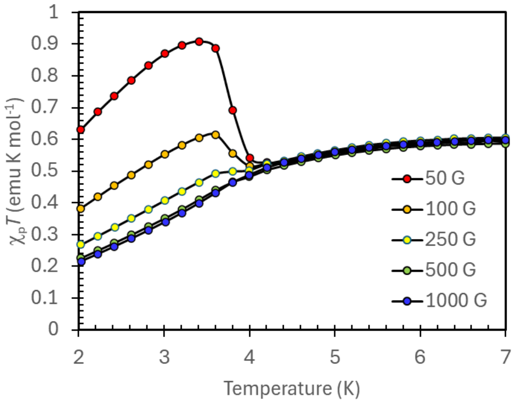


Figure 3. Field dependence of $\chi_p T$ *vs* T for **1** in the low temperature region.

M vs H plots were recorded at 4.5 K and 2.0 K and are presented in Figure 4. At 4.5 K, a little above the magnetic ordering temperature, the *M vs H* plot reflects a typical paramagnetic response ($M = \chi H$), passing through the origin, confirming the absence of possible ferromagnetic impurities. Measurements below 4 K exhibit the emergence of a small magnetic hysteresis loop (M_{rem} = 2.5 × 10^{-4} Nβ and H_{co} = 8 Oe at 3.5 K). The small coercivity is typical of light atom structures where the magnetic anisotropy arising from spin orbit coupling (which scales as Z^4)[35] is small, although incorporation of heavy atom substituents has been implemented to enhance coercivities.[36] The sharpness of the EPR spectra of **1** point towards a system with little g-anisotropy and a g-value (2.006) reflecting negligible spin-orbit coupling effects. For applied fields 30 < H < 10000 Oe, the magnetization does not rapidly saturate (typical of ferromagnets), but follows:

$$M = M_T + \chi H \qquad \text{Eq. 1}$$

where M is the sample magnetization, M_T is the spontaneous magnetization extrapolated to zero field at temperature T, χ is the molar paramagnetic susceptibility and H is the applied field. This response is typical of a canted antiferromagnetic material.[37] Fitting low field M vs H data (50 – 1000 Oe) below the ordering temperature to Eq 1 (Figure S7) permits the spontaneous moment M_T to be determined. The temperature dependence of M_T ideally follows a Bloch $T^{3/2}$ law in the range $T/T_C < 0.85$, but follows critical behavior in the vicinity of T_C, where M is dependent on $(T_C - T)^{\beta}$ and β is the critical exponent.[38] An empirical fit across the entire range from T = 0 to $T = T_C$ can be described by Eq 2:

$$M_T = M_0[1 - (\frac{T}{T_C})^{\alpha}]^{\beta} \qquad \text{Eq 2}$$

A best fit to Eq. 2 (Figure 5) affords M_0 = 0.0015 Nβ, α = 2.11, β = 0.321 and T_C = 3.9 K. The value of β is in good agreement with the critical value expected for a Heisenberg-like ('isotropic') S = ½ spin (β = 0.365), typical for light heteroatom organic radicals. The α parameter is somewhat larger than the theoretical value of $^3/_2$ but aligns well with experimental observations on a range of ordered phases for half-integer spins which follow a T^2 rather than $T^{3/2}$ dependence.[39] Taking the extrapolated value of M_T at T = 0 (M_0 = 0.0015 Nβ), we can estimate a canting angle of 0.08°, based on Eq 3 (using g = 2.006 from EPR studies).

$$\sin\theta = M_0/gS \qquad \text{Eq. 3}$$

The value of the canting angle is comparable with other spin-canted antiferromagnets derived from thiazyl and selenazyl radicals, typically < 0.1°.[8,40]

At 2 K, the magnetization increases monotonically with applied field up to *ca.* 3.0 T whereupon it levels off, approaching saturation at 0.92 Nβ at 7 T (see Figure S6). The saturation value is close to the value expected for an S = ½ spin with g = 2.0 (1.00 Nβ). Similar behavior has been observed in other thiazyl radicals comprising a combination of strong ferromagnetic and weaker antiferromagnetic interactions (*vide infra*) and has been ascribed to a field-induced spin-flop reorientation of the spins.[39] The presence of long-range magnetic order was additionally corroborated by heat capacity measurements, which reveal a lambda-type peak at T_N = 3.8 K, signaling the onset of magnetic order (Figure 6).

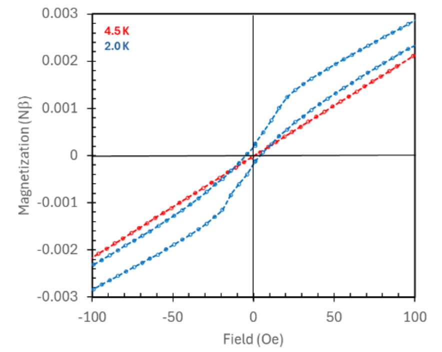


Figure 4. Magnetization *vs* field plots for **1** at 4.5 and 2.0 K.

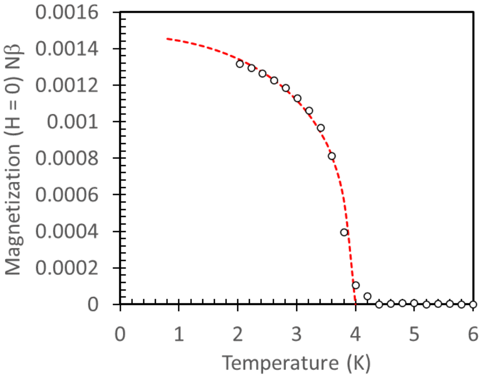


Figure 5. Temperature dependence of the extrapolated zero-field magnetization, $M_S(H = 0)$. The dashed red line corresponds to the best fit to Eq. 2 using the parameters in the text.

DFT calculations (UB3LYP/6-311G**++) reveal that *ca.* 94% of the unpaired spin-density is localized on the SNS fragment of the DTA ring in **1** (Figures 1 and S9). Using a linear correlation between the spin density at N and the hyperfine coupling ($a_N \sim Q_N\rho_N$ where Q_N = 19.1 G),[41] the experimental hyperfine affords an estimated spin density at N of 58% in good agreement with the computed value (55%). Based on this spin distribution, the close S···S contacts likely play an important role in propagating magnetic communication. For **1**, the computed nearest-neighbor exchange couplings reveal a dominant ferromagnetic exchange coupling (J_1 = +10 cm^{-1}) associated with the close S···S contact d_1 (Figure 1). The other near-neighbor S···S interaction (d_2) appears weakly antiferromagnetic (J_2 = −3 cm^{-1}), while other near-neighbor exchange interactions were computed to be ≤ 1 cm^{-1} (Figure S10). Previous computational studies have identified geometric arrangements of coplanar, near-neighbor 1,3,2-dithiazolyl radicals exhibiting ferromagnetic exchange (with J up to +150 cm^{-1}),[27] but the current study is, to our knowledge, the first time in which ferromagnetic exchange is experimentally observed, dominating over weaker antiferro-

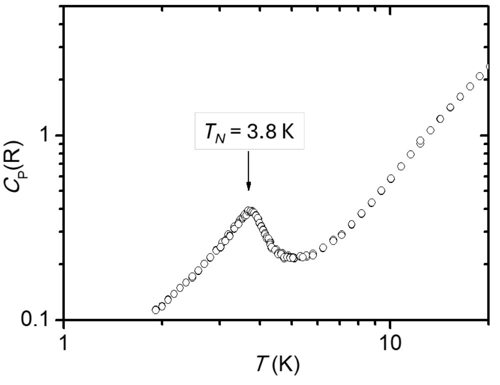
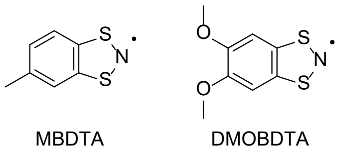


Figure 6. Molar heat capacity C_P/R *vs* temperature for **1**.

magnetic exchange terms. While this dominant ferromagnetic exchange term is consistent with the positive value of the Weiss constant in the high temperature regime, ultimately the presence of the weaker antiferromagnetic interactions rationalize the downturn in $\chi_m T$ below 8 K and eventual (canted) antiferromagnetic ordering at 3.8 K. Since ferromagnetic arrangements are always invariant to both translation and inversion[13] this leads to an unambiguous magnetic structure (magnetic group Pb′c′a) in which the spontaneous moment is parallel to the *c*-axis (Figure S11). Radical **1** is therefore a rare example of an organic radical crystallizing in a centrosymmetric space group which exhibits spin canting.[,40,42]

It is noteworthy that **1**, DMOBDTA[32] and MBDTA[43] (Scheme 2) all crystallize in the orthorhombic space group Pbca with one molecule in the asymmetric unit. Although **1** exhibits Curie-Weiss behavior with $\theta = +5.7$ K consistent with local ferromagnetic interactions, both DMOBDTA and MBDTA exhibit strong antiferromagnetic interactions. An examination of the structures of these three radicals reveal that, despite adopting the same space groups, the relative orientations of the radical in the asymmetric unit leads to very distinct differences in their packing (see Figure S12) and resultant magnetic properties.



Scheme 2: Structures of MBDTA and DMOBDTA

The current study affords a unique example of dominant ferromagnetic exchange in a neutral 1,3,2-dithiazolyl radical. While the presence of additional weak antiferromagnetic interactions in **1** ultimately leads to magnetic ordering as a canted antiferromagnet, the potential to modulate the exchange interactions augers well for the development of ferromagnets based on this family of radicals.

ASSOCIATED CONTENT

Supporting Information

SI comprises experimental details for the synthesis of **1**, a summary of crystallographic data for [**1**]Cl and **1** (at 173 and 296 K), a comparison of the experimental and computed PXRD patterns and EPR spectra for **1** as well as additional magnetic measurements and computational studies on **1.** The Supporting Information is available free of charge on the ACS Publications website.

Accession Codes

CCDC deposition numbers 2371636 - 2371638 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

Synthesis and characterization were undertaken by D.L., M.H., and J.W.; computational studies were undertaken by D.L. and N.M.; magnetic measurements were undertaken by A.A., J.C. and H.B. D.L., J.M.R. and M.P. drafted the initial manuscript with additional input from all authors.

Notes

The authors declare no competing financial interests.

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SYNOPSIS TOC (Word Style “SN_Synopsis_TOC”).

The 3,4-dihydro-2H-1,5-benzodioxepinyl-1,3,2-dithiazolyl radical (**1**) orders as a canted antiferromagnet at 3.8 K.