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Crystal structures, EPR and magnetic properties of 2-ClC₆H₄CNSSN[•] and 2,5-Cl₂C₆H₃CNSSN[•][†]

Antonio Alberola,^a Emma Carter,^b Christos P. Constantinides,^c Dana J. Eisler,^c Damien M. Murphy^b and Jeremy M. Rawson^{*cd}

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The β -sheet structure associated with chlorinated aromatics $(d_{\text{Cl}\cdots\text{Cl}} \approx 4.0 \text{ Å})$ has been implemented to drive formation of π -stacked structures of dithiadiazolyl radicals. Both title compounds exhibit an increase in paramagnetism above 150 K but solid-state EPR studies indicate that the origin of the paramagnetism in these two systems is different.

There has been considerable interest in thiazyl radicals and their selenium analogues as building blocks for the construction of magnetic materials.¹ One family of radicals whose magnetic properties have attracted some attention are the 1,2,3,5-dithia-diazolyl (DTDA) radicals (1).^{2,3} Previous solution EPR and more recent UV/vis studies on derivatives of 1 have revealed a very favourable dimerisation enthalpy (*ca.* 35 kJ mol⁻¹).⁴ As a consequence the majority of derivatives have been found to adopt one of the $\pi^*-\pi^*$ dimer motifs (Fig. 1, A–D) which effectively quenches their paramagnetism in the solid state.



In a small number of instances dimerisation has been suppressed and can lead to long range magnetic order in some derivatives.² We have been particularly interested in utilising



Fig. 1 $\pi^*-\pi^*$ modes of association in 1,2,3,5-dithiadiazolyl radicals.

crystal-engineering principles to weaken the dimerisation process in the solid state and to probe the resultant effects on the electronic structure. Chlorinated aromatics have a tendency to adopt a π -stacked β -sheet structure in which the shortaxis (corresponding to the π -stacking direction) is ca. 4 Å,⁵ substantially longer than the typical intra-dimer contacts in derivatives of 1 (2.9–3.1 Å).⁶ If the strength of the Cl \cdots Cl interaction is of comparable magnitude to the dimerisation energy then weakening or cleavage of the $\pi^* - \pi^*$ dimer is anticipated. In this communication we report the synthesis, structures and magnetic properties of two chlorinated derivatives, 2 and 3, both of which adopt π -stacked chloro-aryl rings. In both cases SQUID magnetometry reveals the onset of paramagnetism above 150 K and EPR studies reveal two differing microscopic mechanisms for the increase in bulk paramagnetism; thermal population of an excited triplet state associated with the $\pi^*-\pi^*$ dimer (in 3) and breakdown of the $\pi^*-\pi^*$ dimer (in 2) to generate increasing numbers of $S = \frac{1}{2}$ radical centres.

Radicals 2 and 3 were prepared from the corresponding aromatic nitriles according to standard experimental methods² and were purified by vacuum sublimation (100–70 °C, 10⁻¹ Torr) to yield 2 and 3 as black lustrous blocks and needles respectively (see SUP-01).‡ Both 2 and 3 adopt structures in which the chloro-aromatics adopt the anticipated π -stack motif (see SUP-02) with Cl···Cl contacts in the range 3.693(3)–4.100(3) Å. However the packing of the heterocyclic rings is significantly different.

Radical 2 crystallised in the monoclinic space group Pc with four molecules in the asymmetric unit, each of which have

^a Dep. De Quimica Fisica I Analitica-Quimica Fisica,

Universitat Jaume I, Av. De Vicent Sos Baynat s/n,

E-12071 Castello de la Plana, Spain

^b The School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, UK CF10 3AT

^c Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

^d Dept of Chemistry and Biochemistry, The University of Windsor, 401 Sunset Av., Windsor, ON, Canada N9B 3P4. E-mail: jmrawson@uwindsor.ca

[†] Electronic supplementary information (ESI) available: Preparation and crystallographic details for 2 and 3; discussion of the crystallographic studies on 3; figures of the π -stacked structures of 2 and 3; analysis of geometries of cisoid $\pi^*-\pi^*$ dimers; reported Cl···Cl contacts in chlorinated π -conjugated planar organics; representative low T EPR spectrum of 2 illustrating $S = \frac{1}{2}$ defect sites; temperaturedependence of the EPR intensity of 3. CCDC 796396-796397. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc04296j



Fig. 2 The two crystallographically independent molecules in the structure of **2**; (a) conventional cisoid $\pi^*-\pi^*$ dimer; (b) orthogonal $\pi^*-\pi^*$ dimer; and (c) the SOMO–SOMO bonding interaction between radicals in the orthogonal dimer pictured with a contour value of 0.035 au.

conventional intramolecular dimensions. These four molecules associate in the solid state to generate two dimers (Fig. 2a and b); one of type **A** and one containing the unprecedented orthogonal dimerisation mode, **E** (Fig. 1). At 180 K, the S...S distances [3.160(3) Å] in dimer **A** fall at the longer end of the conventional range for type **A** dimers [3.09(6) Å, SUP-03]. The orthogonal dimer **E** has no precedent in DTDA chemistry but still offers the potential for a net $\pi^*-\pi^*$ bonding interaction between singly-occupied MO's (Fig. 2c) with intradimer S...S distances of 3.288(3) and 3.240(3) Å, and S...N distances of 3.274(6) and 3.474(7) Å.

A similar perpendicular $\pi^*-\pi^*$ interaction has been observed in the isoelectronic diselenadiazolyl radicals, albeit with the two heterocycles oriented somewhat differently, *i.e.* with the Se–Se bond bridging the two Se–N bonds rather than Se–Se and N···N edges.⁷

The structure of **3** proved difficult to determine satisfactorily and an ordered structure could only be determined when using a super-cell (see SUP-04). Radical **3** crystallises in the triclinic space group $P\overline{1}$ with two cisoid dimers of type **A** (Fig. 3) in the asymmetric unit. The heterocyclic ring geometry is unexceptional but the intra-dimer S···S distances [3.156(6)–3.268(5) Å] are notably longer than those observed in other cisoid dimers of this type [3.09(6) Å, SUP-03] indicative of some weakening of the $\pi^*-\pi^*$ dimer interaction. The inter-dimer S···S contacts are somewhat longer [4.075(5)–4.185(6) Å] though notably the dichlorophenyl rings are almost evenly spaced [3.619(4)–3.710(4) Å] consistent with the preferred β -sheet structure (3.77–4.02 Å, see SUP-05).

Magnetic studies on both 2 and 3 were undertaken on a Quantum Design SQUID magnetometer in an applied field of 1000 G for radical 2 and 5000 G for radical 3 in the range



Fig. 3 One of the two crystallographically independent cisoid dimers in the asymmetric unit of $(3)_2$.

5–300 K in both warming and cooling modes. Data were corrected for diamagnetism. No significant differences in sample susceptibility were observed between heating or cooling modes. The temperature dependence of $\chi T vs. T$ for **2** and **3** is presented in Fig. 4. Both materials are essentially diamagnetic below 150 K although a small Curie-tail was apparent upon cooling to low temperature. This was assigned to trace defects (0.7% for **2** and 0.22% for **3**) of DTDA radicals in the lattice and confirmed by low temperature EPR studies. On warming from 150 K up to room temperature a steady increase in χT was observed. At 300 K the paramagnetism corresponds to 13% $S = \frac{1}{2}$ Curie spins for **2** and 15% $S = \frac{1}{2}$ Curie spins for **3**.

Variable temperature X-band EPR studies (5–300 K) on polycrystalline solid samples of **2** and **3** revealed a small number of $S = \frac{1}{2}$ radical defect centres in the lattice at low temperatures which were also apparent in the SQUID data. These were readily modelled as isolated DTDA radicals by comparison with previous studies^{4b,8} and analogous spin Hamiltonian parameters were observed ($g_x = 2.002, g_y = 2.008,$ $g_z = 2.021, {}^{N}A_x = 14, {}^{N}A_y > 1, {}^{N}A_z > 1$ G; see SUP-06). However the temperature evolution of their EPR spectra above 150 K is significantly different and reveals alternative pathways for the increase in paramagnetism in these two materials.



Fig. 4 Temperature dependence of χT for 2 (top) and 3 (bottom) in the range 5–300 K. The solid line (bottom) corresponds to a Bleaney–Bowers model (see text).



Fig. 5 Solid state X-band EPR spectra of (a) **2** and (b) **3** at 220 K. Inset shows the half-field resonance associated with the formally spin-forbidden S = 1 term (relative EPR intensities are ×600 for **2** and ×1 for **3**).

In 2 there is a steady increase in intensity of the spectrum in the g = 2 region above 150 K (a double integral of the EPR signal follows the behaviour of the χ vs. T data from SQUID magnetometry; see SUP-07). Whilst there is some dipolar broadening associated with the increase in the number of paramagnetic centres generated, no additional features are observed (Fig. 5a). Conversely the EPR spectrum of 3 above 150 K shows clear evidence for the presence of a triplet state reflected in (i) additional features attributable to zerofield splitting and (ii) the observation of the forbidden $\Delta M_{\rm s} = \pm 2$ transition in the half-field region (Fig 5b). The spin Hamiltonian parameters for this S = 1 species were $g_x = 2.002, g_y = 2.008, g_z = 2.021; |D| = 0.0183,$ $|E| = 0.0008 \text{ cm}^{-1}$. Fig 5b also includes a contribution from a rhombic $S = \frac{1}{2}$ EPR spectrum associated with isolated DTDA radicals (see above). The behaviour of 3 is consistent with an S = 0 ground state with thermally accessible triplet configuration (Fig. 6).⁹ A fit of both the χ vs. T data and EPR signal intensity to the Bleaney-Bowers equation up to 230 K provides an estimate of the singlet-triplet separation $2J/k \approx -1300$ K (comparable with previously reported dithiadiazolyl radicals with $2J/k \approx -2400$ K).⁹ Above 230 K, both γ and the EPR signal intensity rise more steeply than the model predicts, consistent with small thermal expansion of the intradimer $S \cdots S$ distance leading to a weakening of the exchange coupling. An improved fit (up to 280 K) can be achieved using a small temperature-dependence of $J [J = -880 + 0.005T^2$ (Fig. 4)].

The paramagnetism in **2** may be due to the breakdown of the dimer **E**, generating $S = \frac{1}{2}$ radicals. Conversely, whilst both **2** and **3** possess dimers of type A, the shorter mean intradimer S...S contact in **2** (*cf.* the dichlorophenyl derivative **3**) may lead to stronger bonding and a less accessible triplet configuration. Thus the paramagnetism in **2** appears to arise from formation of $S = \frac{1}{2}$ states whereas the paramagnetism in **3** appears due to thermal population of a triplet configuration.

The current studies reveal that partial chlorination of the aromatic substituent is sufficient to weaken the conventional $\pi^*-\pi^*$ dimensiation process associated with DTDA radicals.



Fig. 6 (left) Closed-shell singlet ground state afforded for strongly interacting $\pi^*-\pi^*$ dimers; (right) thermally accessible triplet excited states for weakly bonded $\pi^*-\pi^*$ dimers.

Our EPR studies reveal different microscopic origins for the observed paramagnetism. A detailed study of these and other chlorophenyl derivatives will be the subject of a full paper.

Notes and references

‡ Crystal data for **2**: C₇H₄ClN₂S₂, M = 215.69, monoclinic, Pc, a = 9.5948(19), b = 14.020(3), c = 12.332(3) Å, $\beta = 91.24(3)^\circ$, V = 1658.6(6) Å³, μ (Mo-K α) = 0.899, T = 180(2) K, Z = 8, $D_c = 1.728$ mg m⁻³, F(000) = 872, independent reflections 4388 ($R_{\rm int} = 0.056$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.¹⁰ Non-hydrogen atoms were anisotropically refined. R_1 ($I > 2\sigma$ (I)) = 0.046, w R_2 (all data) = 0.133, S = 1.164 (all data). Crystal data for **3**: C₇H₃Cl₂N₂S₂, M = 250.13, triclinic, $P\bar{1}$, a = 7.3271(2), b = 10.3563(3), c = 24.6666(7) Å, $\alpha = 88.096(2)$, $\beta = 81.458(2)$, $\gamma = 77.0090(10)^\circ$, V = 1803.60(9) Å³, μ (Mo-K α) = 1.127, T = 180(2) K, Z = 8, $D_c = 1.842$ mg m⁻³, F(000) = 1000, independent reflections 5799 ($R_{\rm int} = 0.0395$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.¹⁰ Non-hydrogen atoms were anisotropically refined. R_1 ($I > 2\sigma$ (I)) = 0.046, wR_2 (all data) = 0.122, S = 1.050 (all data).

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