Molecular materials from 1,3,2-dithiazolyls. Solid-state structures and magnetic properties of 2,3-naphthalene and quinoxaline derivatives

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In the solid state, at room temperature, the radicals 2,3-naphthalene-1,3,2-dithiazolyl (NDTA) and quinoxaline-1,3,2-dithiazolyl (QDTA) are not dimerized; discrete molecules of NDTA are packed in a herringbone fashion, while those of QDTA adopt a slipped π-stack motif; NDTA is essentially paramagnetic at ambient temperatures, with weak antiferromagnetism developing below 190 K; QDTA is diamagnetic at low temperature, but limited paramagnetism sets in above 120 K.

While derivatives of the 1,3,2-dithiazolyl ring (DTA) have been known for well over a decade,[1,2] relatively little is known of their structural and transport properties. In the solid state the 4,5-dicyano derivative forms the simple cofacial dimer.[3] The pyrazine-based compound (PDTA) also dimerizes cofacially,[4] but the dimers adopt a stacked dimer structure similar to that observed for many dithiadiazolyls.[5] Surprisingly, and despite its structural resemblance to PDTA, the benzo derivative (BDTA)[6] associates in a centrosymmetric manner and does not form π stacks. The trithiatriazapentalenyl radical (TTTA) represents a sharp contrast to the previous examples, in that dimerization is not observed.[7] Instead the crystal structure consists of evenly spaced slipped π stacks. Transport properties, however, have not been reported for this compound. In order to explore the architectural issues behind these diverse structural patterns we have examined the solid-state structures and transport properties of the 2,3-naphthalene- and quinoxaline-based 1,3,2-dithiazolyl radicals NDTA **1** and QDTA **2**.

The two radicals were prepared by standard methods. 2,3-Naphthalenedithiol[8] was oxidized with iodobenzene dichloride to give 2,3-naphthalene-bis(sulfenyl chloride), which was condensed with trimethylsilyl azide in CH_2Cl_2 solution to afford 2,3-naphthalene-1,3,2-dithiazolylium chloride. Reduction of this salt with triphenylantimony in acetonitrile afforded NDTA, which was separated by filtration and fractionally sublimed at 80–50 °C (10^{-2} Torr) to give purple plates, mp 149–151 °C. QDTA was prepared by a modification of the literature procedure.[3] Black rod-like crystals of QDTA, mp 137–140 °C, were grown by fractional vacuum sublimation at 70–40 °C (10^{-2} Torr).

The crystal structure of NDTA† consists of discrete molecules of NDTA, with two molecules per asymmetric unit. The internal bond lengths of the two heterocyclic rings [mean d(S–N) = 1.645 Å, mean d(C–S) = 1.748 Å] are typical of those seen in dimeric derivatives[3,6] and indicative of the fact that dimerization effects minimal electronic reorganization. The crystal structure consists of antiparallel ribbons of radicals running in the *z* direction. Viewed down the *z* direction (Fig. 1)

the packing pattern of the ribbons resembles the close-packed herringbone arrangement found many polycyclic aromatics,[9] *e.g.* naphthalene[10] and anthracene.[11] There is no dimerization of NDTA radicals, and the closest intermolecular S⋯S contacts (d_1–d_5) are well outside the van der Waals separation of 3.6 Å.[12]

The crystal structure of QDTA† also consists of undimerized radicals. Here too the internal bond lengths of the heterocyclic ring [mean d(S–N) = 1.649 Å, mean d(C–S) = 1.736 Å] are typical of those seen in simple dimers. As in the case of NDTA, the molecules lie in ribbon-like chains, but the packing of the ribbons (Fig. 2) takes on a slipped π-stack pattern similar to that observed for TTTA. Apart from intermolecular contacts associated with the cell repeat [3.7105(8) Å], there is only one S⋯S contact inside 4.0 Å (d_1) linking radicals in adjacent stacks.

The structural dichotomy observed between NDTA and QDTA is intriguing. The similarity of the NDTA structure to those of simple polycyclic aromatics suggests a similar cause.[9,13] Presumably, when the structure-making CH⋯ring interactions[14] which favour the herringbone arrangement are reduced by the replacement of peripheral CH groups by N atoms, as in QDTA, the preference for close-packing is diminished, and a slipped stack structure prevails. That dimerization does not occur, as it does in the smaller molecule PDTA, is probably a manifestation of a slightly weakened dimerization enthalpy coupled with the greater tendency for the
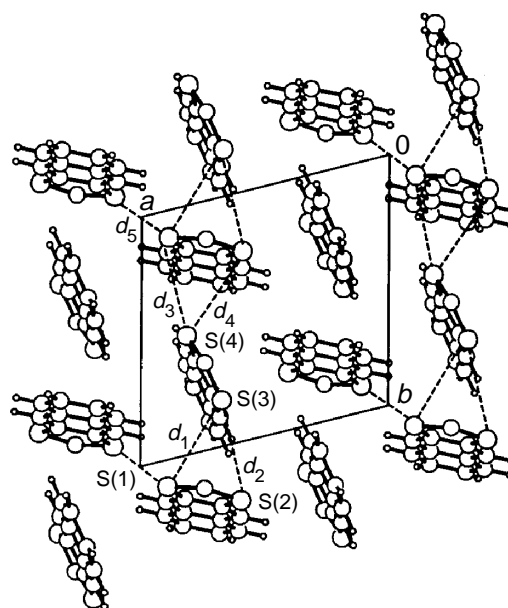
Fig. 1 Herringbone packing of NDTA. Intermolecular S⋯S contacts are shown with dashed lines; d_1 = 3.869, d_2 = 3.868, d_3 = 3.821, d_4 = 3.863, d_5 = 3.602 Å.

crystal structure to be determined by general packing forces rather than local (intermolecular S···S) interactions.

The bulk magnetic susceptibilities of both NDTA and QDTA have been measured over the temperature range 5–400 K on a SQUID magnetometer; plots of χ *vs. T* are shown in Fig. 3. Analysis of the susceptibility data for NDTA indicate that it is essentially paramagnetic above 200 K, with θ = 1.3 K and the fraction of the Curie spins per molecule, f = 0.80 mol^{-1}. Below 200 K there is a phase transition to a more strongly antiferromagnetically coupled state with θ = 10.7 K and f = 0.53 mol^{-1}. In QDTA the low-temperature susceptibility is consistent with a diamagnetic ground state, with $\chi_0 = -99 \times 10^{-6}$ emu mol^{-1}, θ = −0.1 K and f = 0.003 mol^{-1}. Above 120 K the susceptibility slowly rises and, at room temperature, f is *ca.* 0.3 mol^{-1}. Pressed pellet measurements indicate room temperature conductivities of $< 10^{-6}$ S cm^{-1} for both compounds.

The low conductivity of QDTA at room temperature is at first surprising, given the large fraction of unpaired spins and the fact that its evenly spaced π-stack structure nominally fulfils the prescription for a neutral π-radical conductor.[15] We conclude that, as in the case of stacked dithiadiazolyls,[5,16] the bandwidth associated with the half-filled energy band in QDTA is insufficient to overcome the large Coulombic barrier to charge transfer associated with the high electronegativity of the dithiazolyl ring. Accordingly the material is a Mott insulator.
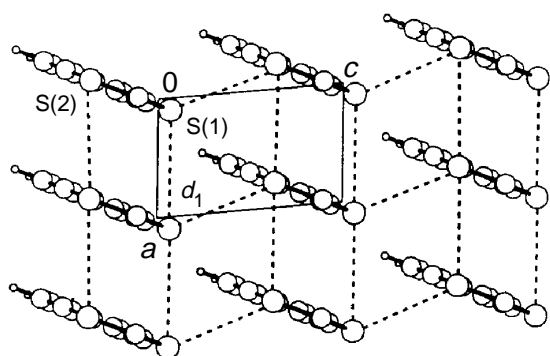

Fig. 2 Slipped π-stack structure of QDTA. Intermolecular S···S contacts are shown with dashed lines; d_1 = 3.840 Å.
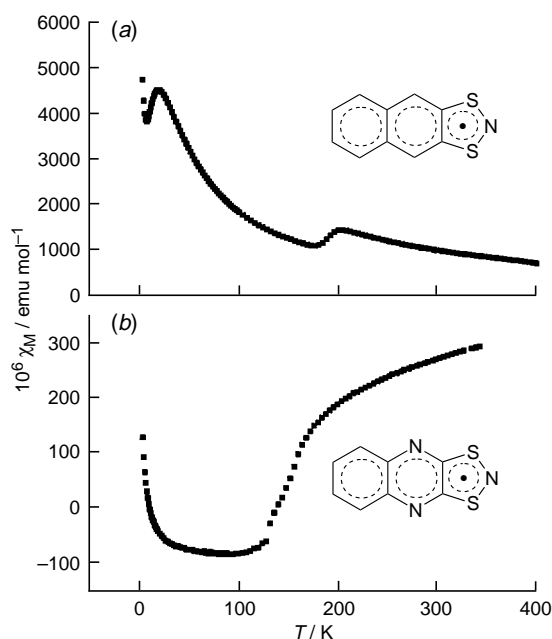

Fig. 3 Magnetic susceptibility χ of NDTA (*a*) and QDTA (*b*), as a function of temperature

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