Molecular materials from 1,3,2-dithiazolyls. Solid-state structures and magnetic properties of 2,3-naphthalene and quinoxaline derivatives
Barclay, T.M.; Cordes, A.W.; George, N.A.; Haddon, R.C.; Oakley, R.T.; Palstra, T.T.M.; Patenaude, G.W.; Reed, R.W.; Richardson, J.F.; Zhang, H.Z.

Published in:
Chemical Communications

DOI:
10.1039/a700310b

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1997

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
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 essentially paramagnetic at ambient temperatures, with 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, relatively little is known of their structural and transport properties. In the solid state the 4,5-dicyano derivative forms the simple cofacial dimer. The pyrazine-based compound (PDTA) also dimerizes cofacially, but the dimers adopt a stacked dimer structure similar to that observed for many dithiadiazolyls. Surprisingly, and despite its structural resemblance to PDTA, the benzo derivative (BDTA) associates in a centrosymmetric manner and does not form π stacks. The trihiaxalazapentalenyl radical (TTTA) represents a sharp contrast to the previous examples, in that dimerization is minimal electronic reorganization. The packing pattern of the ribbons resembles the close-packed herringbone arrangement found many polycyclic aromatics, e.g. naphthalene and anthracene. There is no dimerization of NDTA radicals, and the closest intermolecular S···S contacts (d1−d4) are well outside the van der Waals separation of 3.6 Å.

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 intramolecular contacts associated with the cell repeat [3.7105(8) Å], there is only one S···S contact inside 4.0 Å 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 \(^1\) 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; d₁ = 3.869, d₂ = 3.868, d₃ = 3.821, d₄ = 3.863, d₅ = 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 \( \chi \) vs. \( T \) are shown in Fig. 3. Analysis of the susceptibility data for NDTA indicate that it is essentially paramagnetic above 200 K, with \( \theta = 1.3 \) 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 \( \theta = 10.7 \) K and \( f = 0.53 \) mol \(^{-1}\). In QDTA the low-temperature susceptibility is consistent with a diamagnetic ground state, with 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 \( \pi \)-stack structure nominally fulfills the prescription for a neutral \( \pi \)-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.

We thank the NSERC, the NSF/EPSCOR program and the State of Arkansas for financial support. T. M. B. acknowledges the Department of Education for a doctoral fellowship.

Footnotes
* E-mail: oakley@chembio.ou.edu.ph.ca
† Crystal data for NDTA and QDTA: data were collected (at 293 K) on an Enraf-Nonius CAD-4 automated diffractiometer with graphite-monochromated Mo-K\(\alpha\) radiation, using 2\(\theta\)–2\(\theta\) scans to a 2\(\theta_{\text{max}}\) = 50\(^\circ\). The structures were solved by direct methods and refined by full-matrix least-squares analysis which minimized \( \Sigma (\Delta F^2) \).

NDTA: \( \text{C}_6\text{H}_6\text{NS}_2 \), \( M = 204.28 \), triclinic, space group \( \text{P}\overline{1} \), \( a = 9.4516(18) \), \( b = 9.5167(19) \), \( c = 10.5397(13) \), \( \alpha = 76.911(15) \), \( \beta = 86.139(12) \), \( \gamma = 75.144(15) \), \( \mu = 0.52 \) mm\(^{-1} \), 236 Parameters were refined using 1764 unique observed reflections \( (I > 3\sigma(I)) \) to give \( R = 0.037 \) and \( R_w = 0.058 \).

QDTA: \( \text{C}_8\text{H}_4\text{N}_3\text{S}_2 \), \( M = 206.26 \), monoclinic, space group \( \text{P}2_1 \), \( a = 3.7105(8) \), \( b = 19.009(5) \), \( c = 5.7864(9) \), \( \beta = 95.724(14) \), \( U = 406.10(15) \) \( \text{Å}^2 \), \( Z = 2 \), \( D_{\text{exp}} = 1.69 \) g cm\(^{-3} \), \( \mu = 0.58 \) mm\(^{-1} \). 117 Parameters were refined using 472 unique observed reflections \( (I > 3\sigma(I)) \) to give \( R = 0.041 \) and \( R_w = 0.056 \).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/415.

References

Received in Columbia, MO, USA, 14th January 1997; Com. 700310B