Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 2743–2749
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

New synthetic pathways into dithiazolyl radicals: Preparation and characterisation of 3′-methyl-benzo-1,3,2-dithiazolyl, M'BDTA

Antonio Alberola *, Rebecca J. Collis, Robert J. Less, Jeremy M. Rawson

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

Received 14 October 2006; received in revised form 20 November 2006; accepted 20 November 2006
Available online 8 December 2006

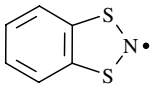
Abstract

A general three-step synthesis to a range of benzo-fused-1,3,2-dithiazolylium salts bearing both electron-withdrawing (CN) and electron-donating (Me) groups is described. This methodology has also been extended to pyridyl derivatives and offers a potential route to a diversity of 1,3,2-dithiazolylium rings and their corresponding 1,3,2-dithiazolyl free radicals. The key steps in the reaction are treatment of a substituted 1,2,-dichlorobenzene with two equivalents of [^{t}BuS]Na, followed by chlorination to yield the corresponding bis(sulfenyl chloride). Subsequent ring closure with Me_3SiN_3 yields the target 1,3,2-dithiazolylium ring system in good yield. The preparation and crystal structures of 3′-methyl-benzo-1,3,2-dithiazolylium chloride and 3′-methyl-benzo-1,3,2-dithiazolyl are described and the electronic properties of the radical examined through EPR spectroscopy, DFT calculations and variable temperature magnetic susceptibility measurements.

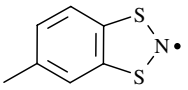
Keywords: Dithiazolyl; Less reagent; Thiazyl ring; Radical

1. Introduction

Despite the successful isolation of the first 1,3,2-dithiazolyl radicals BDTA and MBDTA in the 1980s by Wölmershauser, dithiazolyl radicals have received little attention in comparison with the substantial body of work which has been undertaken on the conducting [2,3] and magnetic [4] properties of 1,2,3,5-dithiadiazolyl derivatives.



BDTA



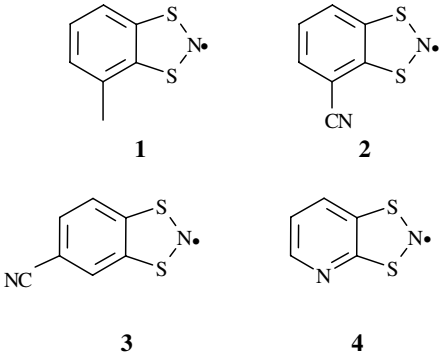
MBDTA

However, in the last few years the physical properties of 1,3,2-DTA radicals have attracted considerable attention as building blocks for the construction of both conducting and magnetic materials [5]. One of the problems encountered when attempting to synthesize 1,3,2-DTA radicals is that, as Wölmershauser noted [6], a variety of preparative routes to these radicals have been developed, however there is no single method that serves for all systems, with most methods having restricted applications. One of the most general synthetic methods to synthesise 1,3,2-dithiazolylium ring systems is the cycloaddition chemistry of SNS^+ salts with alkynes, pioneered by Passmore [7]. Whilst this has recently been extended to the formation of more complex fused-ring structures [8], its approach to the formation of benzo-fused derivatives and related analogues appears limited. One of the aspects of our current work is to develop a synthetic approach which may have some broad application to the synthesis of a wider range of dithiazolyl radicals. Here we report the use of 'the Less Reagent', [^{t}BuS]Na, as a convenient method to prepare dithiazolylium ring systems and illustrate its application to the synthesis of benzo-dithiazolylium rings bearing both electron-withdrawing (CN) and electron-donating (Me) groups as well as heteroatom substituted rings exemplified by the preparation of $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$ and $\mathbf{4}^+$. The structures and

* Corresponding author. Tel./fax: +441223336319.
E-mail address: aa323@cam.ac.uk (A. Alberola).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.11.048

properties of radicals **2**• and **3**• have been reported recently elsewhere [5f,9]. The crystal and electronic structure of **1**• is described in the current contribution.



1 **2** **3** **4**

2. Experimental

2.1. 3′-Methyl-benzo-1,3,2-dithiazolyl (*1*)

To 1.44 g (8.9 mmol) of 2,3-dichlorotoluene dissolved in 30 ml of 1,3-dimethyl-2-imidazolidinone, sodium butylthiolate, 5 g (45 mmol) was added and the reaction mixture heated to 100 °C for a week. After allowing the reaction mixture to cool down to room temperature, water (100 ml) was poured in and the mixture extracted with diethyl ether (3 × 75 ml). The organic extracts were combined and washed with water and brine, and the solvent removed *in vacuo*. The product was purified *via* column chromatography (Silica, hexane) to afford pure $C_6H_3(CH_3)(S^tBu)_2$. Yield: 1.85 g, 78%. Analysis found: C, 67.59; H, 9.26; $C_{15}H_{24}S_2$ requires: C, 67.10; H, 9.01%. δ^H ($CDCl_3$) 1.26 (s, 18H), 2.50 (s, 3H), 6.9 (dq, 1H), 7.06 (d,1H), 7.13 (d, 1H). *m*/*z* (EI) 268.1 (M^+, 100%).

Chlorination of $C_6H_3(CH_3)(S^tBu)_2$ (1.3 g, 3.5 mmol) with Cl_2 (g) in CCl_4 (20 ml) under ambient conditions yielded an orange solution of $C_6H_3(CH_3)(SCl)_2$. The solvent was removed *in vacuo* and the oily residue redissolved in CH_2Cl_2. This was treated with Me_3SiN_3 (0.4 ml, 5 mmol) to yield the salt $[C_6H_3(CH_3)S_2N]Cl$, [**1**]Cl. Reduction of [**1**]Cl with Ag powder in acetonitrile yielded **1** which was purified by vacuum sublimation. Yield: 0.36 g, 45%. Analysis found: C, 49.32; H, 3.12; N, 8.21; $C_7H_6S_2N$ requires: C, 49.97; H, 3.59; N, 8.324%.

2.2. 3′-Cyano-benzo-1,3,2-dithiazolyl (*2*)

To 2 g (11.6 mmol) of 2,3-dichlorobenzonitrile dissolved in 20 ml of 1,3-dimethyl-2-imidazolidinone, sodium butylthiolate 4.7 g (43 mmol) was added and the reaction mixture was heated to 60 °C for 24 h. After allowing the reaction mixture to cool down to room temperature, water (100 ml) was poured in and the mixture extracted with diethyl ether (3 × 75 ml). The organic extracts were combined and washed with water and brine, and the solvent removed *in vacuo*. The product was recrystallised from diethylether to afford pure $C_6H_3(CN)(S^tBu)_2$. Yield: 1.9 g, 57%. Analysis found: C, 67.43; H, 7.58; N, 5.04. $C_{15}H_{21}S_2N$ requires: C, 64.47; H, 7.57; N, 5.01%. δH ($CDCl_3$) 1.32 (s, 18H), 7.41 (t, 1H), 7.70 (dd, 1H), 7.95 (dd, 1H). *m*/*z* (EI) 279.1 (M^+, 100%).

Chlorination of $C_6H_3(CN)(S^tBu)_2$ (1.0 g, 3.5 mmol) with Cl_2 (g) in CCl_4 (20 ml) under ambient conditions yielded an orange solution of $C_6H_3(CN)(SCl)_2$. The solvent was removed *in vacuo* and the oily residue redissolved in CH_2Cl_2.This was treated with Me_3SiN_3 (0.4 ml, 5 mmol) to yield the salt $[C_6H_3(CN)S_2N]Cl$, [**2**]Cl. Reduction of [**2**]Cl with Ag powder in acetonitrile yielded **2** which was purified by vacuum sublimation. Yield: 0.236 g, 35%. Analysis found: C, 49.46; H, 1.73; N, 15.24. $C_7H_3S_2N_2$ requires: C, 49.91; H, 1.68; N, 15.63%.

2.3. 4′-Cyano-benzo-1,3,2-dithiazolyl (*3*)

To 2 g (11.6 mmol) of 3,4-dichlorobenzonitrile dissolved in 20 ml of 1,3-dimethyl-2-imidazolidinone, sodium butylthiolate 4.7 g (43 mmol) was added and the reaction mixture was heated to 60 °C for 24 h. After allowing the reaction mixture to cool down to room temperature, water (100 ml) was poured in and the mixture extracted with diethyl ether (3 × 75 ml). The organic extracts were combined and washed with water and brine, and the solvent removed *in vacuo*. The product was recrystallised from diethylether to afford pure $C_6H_3(CN)(S^tBu)_2$. Yield: 2 g, 61%. Analysis found: C, 64.81; H, 7.63; N, 4.98. $C_{15}H_{21}S_2N$ requires: C, 64.47; H, 7.57; N, 5.01%. δH ($CDCl_3$) 1.41 (s, 18H), 7.47 (dd, 1H), 7.68 (d, 1H), 7.85 (d, 1H). *m*/*z* (EI) 279.1 (M^+, 100%).

Chlorination of $C_6H_3(CN)(S^tBu)_2$ (1.0 g, 3.5 mmol) with Cl_2 (g) in CCl_4 (20 ml) under ambient conditions yielded an orange solution of $C_6H_3(CN)(SCl)_2$. The solvent was removed *in vacuo* and the oily residue redissolved in CH_2Cl_2.This was treated with Me_3SiN_3 (0.4 ml, 5 mmol) to yield the salt $[C_6H_3(CN)S_2N]Cl$, [**3**]Cl. Reduction of [**3**]Cl with Ag powder in acetonitrile yielded **3** which was purified by vacuum sublimation. Yield: 0.314 g, 46%. Analysis found: C, 46.91; H, 1.70; N, 15.62. $C_7H_3S_2N_2$ requires: C, 49.91; H, 1.68; N, 15.63%.

2.4. Pyridine-1,3,2-dithiazolyl (*4*)

To 1.5 g (11 mmol) of 2,3-dichloropyridine dissolved in 20 ml of 1,3-dimethyl-2-imidazolidinone, sodium butylthiolate 4.7 g (43 mmol) was added and the reaction mixture heated to 75 °C for 24 h. After allowing the reaction mixture to cool down to room temperature, water (100 ml) was poured in and the mixture extracted with diethyl ether (3 × 75 ml). The organic extracts were combined and washed with water and brine, and the solvent removed *in vacuo*. The product was recrystallised from diethylether to afford pure $C_5H_3N(S^tBu)_2$. Yield: 2.3 g, 82%. Analysis

found: C, 62.23; H, 8.71; N, 5.27. $C_{13}H_{21}S_2N$ requires: C, 61.13; H, 8.29; N, 5.48%. δH ($CDCl_3$) 1.6 (s, 18H), 7.25 (d, 1H), 7.50 (dd, 1H), 8.35 (dd, 1H). *m/z* (EI) 255.1 (M^+, 100%).

Chlorination of $C_5H_3N(S^tBu)_2$ (1 g, 3.5 mmol) with Cl_2 (g) in CCl_4 (20 ml) under ambient conditions yielded an orange solution of $C_5H_3N(SCl)_2$. The solvent was removed *in vacuo* and the oily residue redissolved in CH_2Cl_2.This was treated with Me_3SiN_3 (0.4 ml, 5 mmol) to yield the salt $[C_5H_3NS_2N]Cl$, [**4**]Cl. Reduction of [**4**]Cl with Ag powder in acetonitrile yielded **4** which was purified by vacuum sublimation. Yield: 0.45 g, 34%. Analysis found: C, 38.31; H, 2.09; N, 17.19. $C_5H_3S_2N_2$ requires: C, 38.71; H, 1.96; N, 18.13%.

3. Discussion

The most universal route to fused 1,3,2-dithiazolyl radicals so far reported involves the chlorination of a 1,2-dithiol, followed by ring closure with trimethylsilyl azide to yield the corresponding 1,3,2-dithiazolylium salt (Scheme 1).

Few 1,2,-dithiols are commercially available and whilst the synthesis of these precursors is well established (Scheme 2), the reductive deprotection of thiolates to generate the corresponding 1,2-dithiols typically requires harsh reaction conditions, e.g. Birch reduction with Na/*l*.NH_3 which may not always support chemically sensitive functional groups. Alternatively more complex multi-step pathways are required [10]. Moreover the 1,2-dithiols are often particularly malodorous, low melting point solids or liquids with limited chemical stability, often decomposing to the corresponding disulfide bridged dimer over time when exposed to atmospheric oxygen.

In order to avoid these complications, we targeted a new synthetic pathway to the 1,2-bis(sulfenyl chloride) which avoided the isolation of the corresponding 1,2-dithiol and thus allowed the synthesis of the radical species avoiding the Birch reduction step. In addition a wide range of suitable precursors should be commercially available.

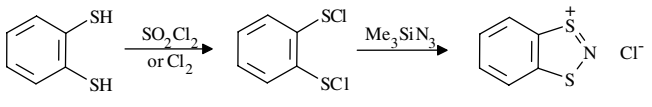
We found that the key benzo-substituted bis(sulfenyl chloride) could be prepared under mild conditions in two steps from an appropriate 1,2-dichlorobenzene and ''Less' reagent'', [^{t}BuS]Na. For example treatment of 2,3-dichlorotoluene with two equivalents of [^{t}BuS]Na in DMI led to the dithiolate under mild conditions (Scheme 3). This nucleophilic substitution can also be achieved using difluoro or dibromo precursors. These dithiolate derivatives are generally solids which can be purified by recrystallisation and stored for months without appreciable decomposition. However the steric bulk of the *tert*-butyl derivative allows the thiolate to be readily deprotected by chlorination with Cl_2 in CCl_4 at 0 °C to generate the bis(sulfenyl chloride). This methodology appears well-suited to a range of electron-withdrawing (e.g. CN and CF_3) groups as well as mildly electron-donating groups (Me) in both ortho and meta positions to the dithiolate group. The same methodology has been successfully employed in the synthesis of heterocyclic derivatives such as the pyridyl compound, **4**. Subsequent ring-closure with Me_3SiN_3 produces the target dithiazolylium cations in good yield.

Despite the range of carbocyclic and heterocyclic derivatives available through this route, it is worth noting some limitations to this methodology. For example nitro groups do not appear accessible since both NO_2^- and Cl^- are both good leaving groups upon treatment with ^{t}BuS$^-$.

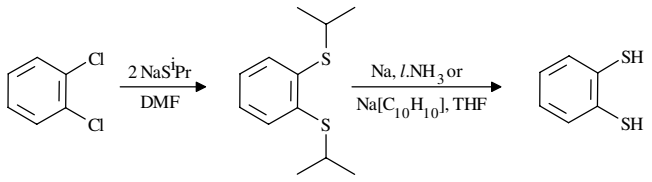
Since compounds **2**–**4** have been described elsewhere recently [5f,11], we will focus on the properties of **1**.

3.1. Crystal structure of [1]Cl

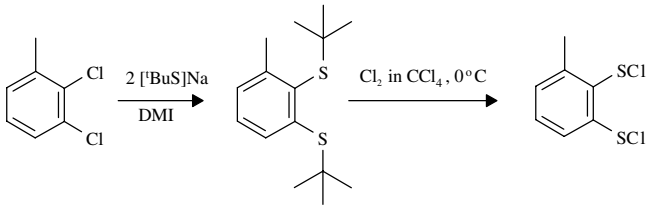
The salt [**1**]Cl crystallises in the triclinic space group $P-1$ with one cation-anion pair in the asymmetric unit. Selected heterocyclic bond lengths and angles in [**1**]Cl are presented in Table 1 (along with data for the radical **1** *vide infra*). The C–C, C–S and S–N bond lengths and angles are comparable with those in [BDTA]Cl. The bicyclic framework is essentially planar and nearly coincident with the [2 1 0] plane (angle between molecular plane and [2 1 0] plane = 2.9°). Indeed there are a web of close contacts close to this plane between cations and anions. These comprise a set of short S···Cl [3.011 Å] and C–H···Cl [2.620–2.784 Å] contacts. A representation of these contacts projected on the *bc* plane is presented in Fig. 1. The bifurcated C–H···Cl···S contact made between a single dithiazolylium cation and the chloride anion is similar to that seen in $[BDTA]Cl\cdot SO_2$ [S···Cl = 3.244 Å and C–H···Cl = 2.719 Å] [13].



Scheme 1.



Scheme 2.



Scheme 3.

Table 1
Selected heterocyclic bond lengths and angles in [**1**]Cl, **1** along with the corresponding distances for [BDTA]Cl.SO_2 and BDTA

	[**1**]Cl	**1**	[BDTA]Cl · SO_2	BDTA
Bond length (Å)				
C–C	1.413(4)	1.385(4), 1.390(4)	1.411(5)	1.394(3)
C–S	1.711(2), 1.730(3)	1.739(3), 1.739(3), 1.754(2),1.756(3)	1.708(2)	1.741(2), 1.746(2)
S–N	1.595(2), 1.617(2)	1.648(3), 1.652(3), 1.652(3), 1.658(3)	1.598(2)	1.644(2), 1.648(2)
S···S	–	3.199, 3.323	–	3.175
Bond angle (°)				
CCS	112.17(19), 112.9(2)	112.9(2), 113.16(19), 113.59(19), 113.69(19)	112.6(2)	112.9(2), 113.1(2)
CSN	98.73(12), 99.57(12)	99.13(12), 99.14(13), 99.69(13), 100.12(13)	99.1(1)	99.1(1), 99.4(1)
SNS	116.59(13)	113.76(14), 114.23(14)	116.6(2)	113.9(1)
Reference	This work	This work	[13]	[13]

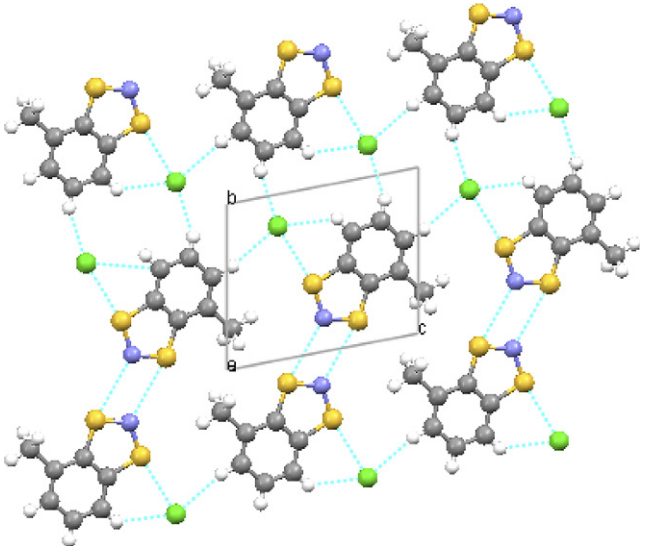


Fig. 1. View of [**1**]Cl in the *bc* plane.

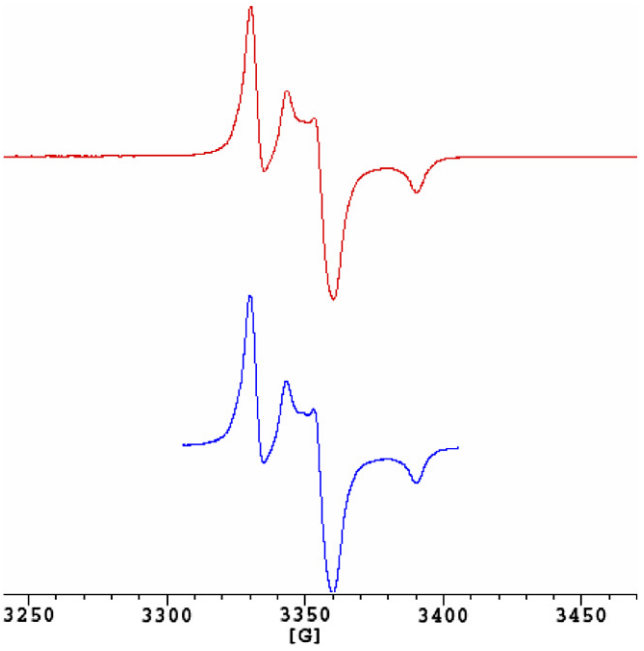


Fig. 2. Frozen solution EPR spectrum (top) and simulation (bottom) using parameters in Table 1.

Additional out-of-plane contacts to Cl and S are also present but are markedly longer; S···Cl [3.449 Å] and C–H···Cl [2.838–2.895 Å]. Whilst one of the S atoms of the dithiazolyl ring is involved in forming S···Cl contacts the second S atom is involved in a centrosymmetric set of in-plane S···N contacts [S...N = 3.260 Å]. These contacts are similar to but slightly longer than those observed in a number of dithiazolyl radicals which span the range 3.123–3.302 Å [5a,5b,12]. The effect of these two sets of in-plane S interactions is to generate chains of $\mathbf{1}^+$ cations parallel to the *c* axis and which are linked together by alternate sets of S···Cl···H and S···N contacts.

3.2. Electronic structure of *1*

Frozen solution EPR spectra were recorded on a solution of **1** in dichloromethane containing a few drops of toluene to improve the glass. The frozen solution spectrum (Fig. 2) exhibited a rhombic EPR pattern ($g_1 \neq g_2 \neq g_3$). Hyperfine coupling to the unique heterocyclic N atom could be observed to one of the principal axes ($a_1^N = 29.4G$) but was not resolved to either g_2 or g_3. However these were estimated to be no greater than 2*G* from the simulation and linewidth. The anisotropic *g*-values and hyperfine couplings as well as isotropic solution values (recorded on a solution of **1** in dichloromethane) are presented in Table 2. The averages of the anisotropic *g*-values and hyperfine couplings ($\langle g \rangle$ and $\langle a^N \rangle$) are in reasonable agreement with those observed in solution and comparable with those previously reported for both BDTA and MBDTA [14,15].

These results are consistent with previous data on 1,3,2-dithiazolyl radicals in which the unpaired electron occupies a π-type orbital with g_1 and g_2 lying in the molecular plane and g_3 lying perpendicular to the plane [14].

3.3. Spin density calculations

The size of the hyperfine coupling constant in the isotropic EPR spectrum depends on the amount of unpaired

Table 2
Isotropic and anisotropic EPR parameters for BDTA, MBDTA and **1**

Compound	BDTA	MBDTA	**1**
g_1	2.0134	2.0129	2.0104
g_2	2.0058	2.0051	2.0033
g_3	2.0021	2.0017	2.0001
$\langle g \rangle$	2.0071	2.0066	2.0046
g_{iso}	2.0067	2.0068	2.0032
a_1^N	2.40	2.25	2.0
a_2^N	3.00	2.45	2.0
a_3^N	29.60	28.95	29.4
$\langle a^N \rangle$	11.67	11.22	11.13
a_{iso}^N	11.00	11.33	11.38
Solvent and temperature (K) for frozen solution spectra	THF/toluene 96 K	Toluene-d^8 152 K	CH_2Cl_2/toluene 140 K
Solvent and temperature (K) for isotropic spectra	$CFCl_3$ 195 K	CH_2Cl_2 293 K	CH_2Cl_2 293 K
Reference	[14]	[15]	This work

electron density in the (isotropic) s-orbital, and a sensitivity factor, **A**, specific for each nuclear type. This relation can be used to estimate the unpaired spin-density in an s-orbital (ρ_s) by comparison of the observed hyperfine coupling constants (in MHz) with the theoretical parameter A, the coupling constant expected for a 100% s-electron density, as obtained by Morton and Preston [16], according to Eq. (1).

$$\rho s = \frac{aiso \times 100}{A} \tag{1}$$

Conversely frozen solution spectra reveal information on the anisotropy in the system which reflects some anisotropic p or d character. An analysis of the anisotropy provides a method of determining the percentage of p (or d) character. In conjunction with the s electron spin density calculated from the isotropic coupling, this provides an excellent mapping of the unpaired spin density distribution. For a system with axial anisotropy, this is estimated from $a_{\|} - a_{\perp}$. For a rhombic system (as in the case of **1**) the axial anisotropy can be estimated as $a_3 - 1/2(a_1 + a_2)$. This can be converted into an appropriate π-electron density by comparison with the corresponding theoretical parameter, P taking into account the orbital reduction factor (2/5) for p orbitals.

$$\rho\pi = \frac{\frac{1}{3}[a_3 - 1/2(a_2 + a_1)] \times 100}{\frac{2}{5}P} \tag{2}$$

The s and π spin densities as well as the total spin density at N for BDTA, MBDTA and **1** were calculated from the isotropic and anisotropic spectra and presented in Table 3.

The electronic structure of the three radicals BDTA, MBDTA and M'BDTA were investigated using pure DFT methods with the PB86 density functional and DN* basis set [17]. The calculations confirm that the inclusion of the electron-donating methyl group in either meta or ortho positions of the BDTA molecule does not affect the heterocyclic spin density distribution significantly.

Table 3
s, π and total electron densities at N determined from the EPR parameters presented in Table 2 along with DFT calculated total spin densities (calculated s-electron density in parentheses)

Compound	BDTA	MBDTA	**1**
s electron density (%)	1.71	1.76	1.76
π electron density (%)	45.24	44.72	46.04
Total electron density (%)	46.95	46.48	47.80
Calculated	47.3	46.9	47.1
	(0.9)	(0.9)	(0.9)

3.4. Crystal structure of *1*

Radical **1** crystallises in the polar space group $P2_1$ with two molecules in the asymmetric unit which form a *cis*-oid dimer with methyl groups adopting an eclipsed geometry. A comparison of the heterocyclic bond lengths in **1**$^{\cdot}$ and [**1**]Cl reveal that addition of an electron into the π^* orbital leads to a marked increase in S–N bond length with smaller increases in C–S and a modest shortening of the C–C bond in line with the bonding characteristics of the π^* orbital. The decrease in bond angle at N upon reduction is counterbalanced by increases in bond angles at C in order retain planarity. The changes in bond angle at S are minimal reflecting the resistance of S to deformation of geometry. Similar behaviour has been seen in the increasing bond angles at the 'softer' C and N hinges in dithiadiazolyl radicals during their ring-opening coordination to metal ions. These changes in bond length and angle upon reduction of **1**$^+$ to generate **1**$^{\cdot}$ mimic those previously observed in BDTA$^+$ and BDTA$^{\cdot}$ (Table 1).

The eclipsed nature of the methyl groups forces a slight asymmetry in the π-bonding between the two crystallographically independent molecules which make up the dimer. This is reflected in short and long intra-dimer S···S distances of 3.199 and 3.323 Å and an angle between molecular planes of 3.5°. Intradimer S···S distances in dithiazolyl radicals fall in a window ranging from 3.097 to 3.511 Å for $F_3CCSNSCCF_3$ and TDP–DTA, respectively. Whilst the former is diamagnetic up to 325 K, the latter exhibits some paramagnetism upon warming above 250 K indicative of a weaker dimerisation process. In the case of $[\mathbf{1}]_2$ the intra-dimer S···S contacts are comparatively short and are expected to be associated with a diamagnetic ground state (see Section 3.3) see Fig. 3.

Analysis has shown [18] that dithiazolyl radicals bearing simple aromatic/aliphatic derivatives tend to adopt herringbone motifs whereas those favouring in-plane electrostatic contacts tend to adopt lamellar structures in the solid state. In the case of $[\mathbf{1}]_2$ the herring-bone motif is manifested as a sandwich herringbone structure with π^*–π^* dimers forming the repeat motif (Fig. 4). The closest interdimer contacts between heterocyclic rings are S···S at 3.589 Å with a range of shorter contacts to aromatic or aliphatic C–H bonds; S···H–C at 2.867 Å and N···H–C at 2.662 Å.

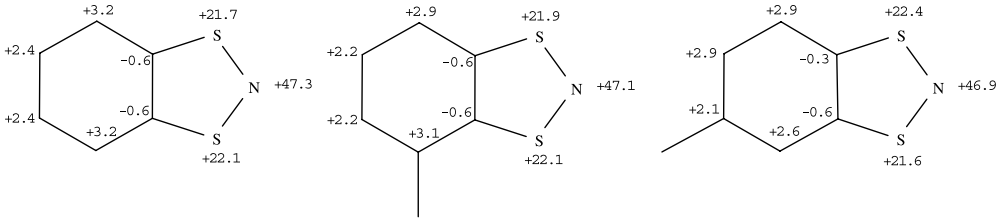


Fig. 3. Calculated spin densities.

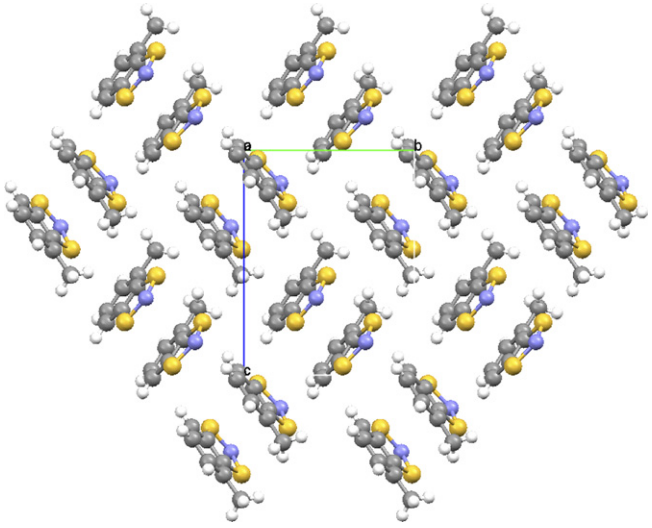


Fig. 4. Crystal packing of $[\mathbf{1}]_2$ viewed in the *bc* plane illustrating the sandwich herringbone pattern.

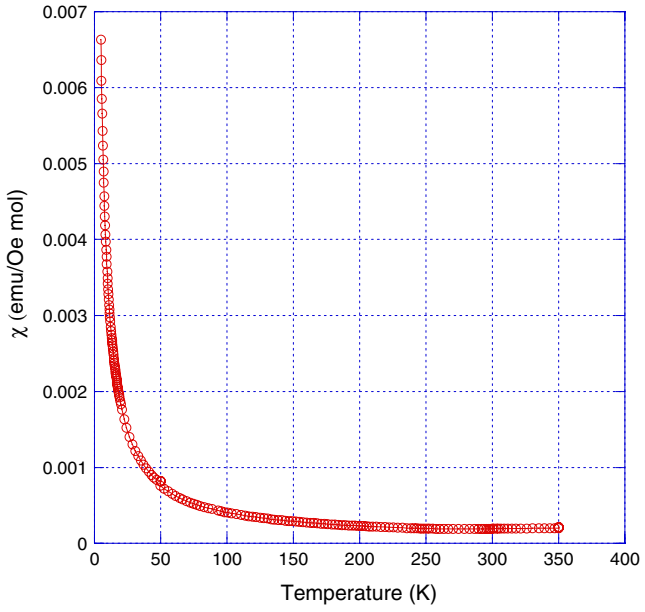


Fig. 5. Temperature dependence of the molar magnetic susceptibility of **1**.The solid line represents the fit to 5% contamination with $S = 1/2$ Curie paramagnetism.

3.5. Magnetic measurements

The magnetic properties of MBDTA and BDTA have received some attention in recent years; the crystal structure of MBDTA reveals a herringbone motif of radicals with close intermolecular S···S contacts. The temperature dependence of the susceptibility of MBDTA exhibited a broad maximum in χ indicative of a low-dimensional network of exchange interactions [19]. Preliminary modelling indicated a satisfactory fit to a two-dimensional square lattice although more recent theoretical calculations indicate a more complex spin topology [20]. Single-crystal X-ray diffraction studies by Passmore and co-workers on BDTA revealed that it forms a sandwich herringbone motif of dimeric π^*–π^* dimers (broadly comparable with **1**, although adopting a transcofacial rather than cis conformation). BDTA is diamagnetic up to 260 K [13]. However recent studies by Awaga indicated a complex phase transition with a new structurally uncharacterised phase growing from the melt of BDTA [21]. Quenching of this new phase reveals that it orders as an antiferromagnet at 11 K. As a consequence we were intrigued to establish the behaviour of **1** in relation to BDTA and MBDTA.

Magnetic susceptibility measurements on **1** were made on a Quantum Design SQUID magnetometer in an applied field of 5000 G between 5 and 350 K. Data were corrected for both sample diamagnetism (Pascal's constants) and the sample holder.

The sample appeared essentially diamagnetic throughout the range 2–350 K, consistent with the short intradimer S···S contacts in $[\mathbf{1}]_2$ which is expected to lead to spin-pairing. The increase in χ upon cooling (Fig. 5) is associated with the presence of a small number of Curie paramagnet defect sites. Indeed the data throughout the entire temperature range can be satisfactorily modelled as arising from 5% of an $S = 1/2$ Curie paramagnet. Unlike BDTA which exhibits an unusual melting and re-solidification process upon heating above 275 K, heating samples of **1** showed no evidence for any melting or phase transition up to the maximum temperature studied, 350 K.

4. Conclusions

The current synthetic methodology provides access to a range of benzo-fused-1,3,2-dithiazolylium salts bearing both electron-withdrawing and electron-donating functional groups which avoids the isolation of the parent 1,2-dithiol. An X-ray structure of 3'-methylbenzo-1,3,2-dithiazolyl reveals a π^*–π^* dimeric structure in the solid state which

has a closed shell configuration evidenced by variable temperature magnetic susceptibility measurements up to 350 K.

Acknowledgements

We thank the EPSRC for financial support for a studentship (R.J.C.) and Homerton College for a Research Fellowship (A.A.) JMR would like to thank Prof. Sanders for generous access to Spartan Prosoftware.

References

[1] G. Wölmershauser, M. Schnauber, T. Wilhelm, J. Chem. Soc., Chem. Commun. (1984) 573.
[2] R.C. Haddon, Nature 256 (1975) 394.
[3] (a) A.W. Cordes, R.C. Haddon, R.T. Oakley, L.F. Schneemeyer, J.V. Waszczak, K.M. Young, N.M. Zimmerman, J. Am. Chem. Soc. 113 (1991) 582;
(b) C.D. Bryan, A.W. Cordes, R.M. Fleming, N.A. George, S.H. Glarum, R.C. Haddon, C.D. MacKinnon, R.T. Oakley, T.T.M. Palstra, A.S. Perel, J. Am. Chem. Soc. 117 (1995) 6880.
[4] A.J. Banister, N. Bricklebank, I. Lavender, J.M. Rawson, C.I. Gregory, B.K. Tanner, W. Clegg, M.R.J. Elsegood, F. Palacio, Angew. Chem. Int. Ed. 35 (1996) 2533.
[5] (a) W. Fujita, K. Awaga, Science 286 (1999) 281;
(b) G.D. McManus, J.M. Rawson, N. Feeder, E.J.L. McInnes, J.J. Novoa, R. Burriel, F. Palacio, P. Oliete, J. Mater. Chem. 11 (2001) 1992;
(c) W. Fujita, K. Awaga, Y. Nakazawa, K. Saito, M. Sorai, Chem. Phys. Lett. 352 (2002) 348;
(d) T.M. Barclay, A.W. Cordes, R.H. deLaat, J.D. Goddard, R.C. Haddon, D.Y. Jeter, R.C. Mawhinney, R.T. Oakley, T.T.M. Palstra, G.W. Patenaude, R.W. Reed, N.P.C. Wetwood, J. Am. Chem. Soc. 119 (1997) 2633;
(e) J.L. Brusso, O.P. Clements, R.C. Haddon, M.E. Itkis, A.A. Leitch, R.T. Oakley, R.W. Reed, J.F. Richardson, J. Am. Chem. Soc. 126 (2004) 8256;
(f) A. Alberola, R.J. Collis, S.M. Humphrey, R.J. Less, J.M. Rawson, Inorg. Chem. 45 (2006) 1903.
[6] G. Heckmann, R. Johann, G. Kraft, G. Wölmershauser, Synth. Met. 41 (1991) 3287.
[7] G.K. MacLean, J. Passmore, M.N.S. Rao, M.J. Schriver, P.S. White, D. Bethell, R.S. Pilkington, L.H. Sutcliffe, J. Chem. Soc., Dalton Trans. (1985) 1405.
[8] A. Decken, A. Mailman, S.M. Mattar, J. Passmore, Chem. Commun. 18 (2005) 2366.
[9] R.T. Oakley, J.M. Rawson, et. al. (in preparation).
[10] T.M. Barclay, A.W. Cordes, R.H. deLaat, J.D. Goddard, R.C. Haddon, D.Y. Jeter, R.C. Mawhinney, R.T. Oakley, T.T.M. Palstra, G.W. Patenaude, R.W. Reed, N.P.C. Westwood, J. Am. Chem. Soc. 119 (1997) 2633.
[11] R.J.Collis, PhD Thesis, Cambridge University, 2007.
[12] J.L. Brusso, O.P. Clements, R.C. Haddon, M.E. Itkis, A.A. Leitch, R.T. Oakley, R.W. Reed, J.F. Richardson, J. Am. Chem. Soc. 126 (2004) 14692.
[13] E.G. Awere, N. Burford, R.C. Haddon, S. Parsons, J. Passmore, J.V. Waszczak, P.S. White, Inorg. Chem. 29 (1990) 4821.
[14] K.F. Preston, J.P.B. Sandall, L.H. Sutcliffe, Magn. Reson. Chem. 26 (1988) 755.
[15] S.R. Harrison, R.S. Pilkington, L.H. Sutcliffe, J. Chem.Soc., Faraday Trans I 80 (1984) 669.
[16] J.R. Morton, K.F. Preston, J. Magn. Reson. 30 (1978) 577.
[17] Spartan Pro. Wavefunction, Inc., Irvine, CA, 2000.
[18] A. Alberola, J.M. Rawson, R. Collis, J. Burley, R. Less, J. Organomet. Chem. 2007, in press.
[19] G.D. McManus, J.M. Rawson, N. Feeder, F. Palacio, P. Oliete, J. Mater. Chem. 9 (2000) 2001.
[20] J. Luzon, PhD Thesis, Universidad de Zaragoza, 2005.
[21] W. Fujita, K. Awaga, Y. Nakazawa, K. Saito, M. Sorai, Chem. Phys. Lett. (2002) 348.