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Supramolecular aggregation in dithia-arsoles: chlorides, cations and N-centred paddlewheels†

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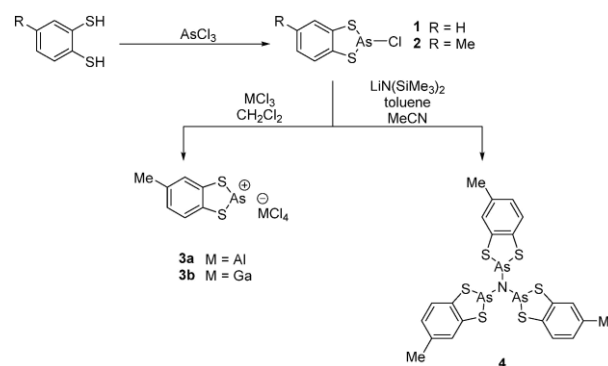
The benzo-fused dithia-chloro-arsole derivative $C_6H_4S_2AsCl$ (**1**) is found to crystallise in the triclinic space group $P\bar{1}$ with 17 molecules in the asymmetric unit whereas the tolyl derivative, $MeC_6H_3S_2AsCl$ (**2**) is polymorphic with the α -phase crystallising in the monoclinic space group $P2_1/c$ with a single molecule in the asymmetric unit and the β -phase adopting a triclinic structure with two molecules in the asymmetric unit. Reaction of these dithia-chloro-arsole derivatives with $LiNiSiMe_3)_2$ in a 3 : 1 mole ratio afforded the unique paddlewheel structure $(MeC_6H_4S_2As)_3N$ (**4**).

The first two-coordinate Lewis acidic phosphorus(III) cation was reported by Dimroth and Hoffmann in 1964.¹ Since then the field of phosphonium chemistry has considerably grown, in part due to the use of these complexes as ligands to coordinate to transition metals.^{2–7} On the other hand, examples of analogous arsenium compounds are less common in the literature,^{8,9} although a number of examples are known $([R_2E]ijX)$, $E = P, As, Sb$.^{10–13} Due to the simultaneous presence of a lone pair and a vacant p-orbital, the chemistry of these cations resembles that of comparable group 14 persistent carbenes, albeit with stronger π -acceptor and poorer σ -donor character associated with the net positive charge.¹⁴ Despite the poorer donor ability, a number of examples of metal-arsenium complexes have been reported affording structures homologous to Fischer carbenes.^{15,16} One of the earliest dithia-arsolidinium cations (**3a**, Scheme 1) to be described was reported by Burford in 1989 but its solid-state structure was never elucidated.¹⁷ Whilst dithia-arsolidinium cations have been shown to exhibit Lewis acidic properties towards both pyridine and triphenylphosphine,^{8,18} more recent studies into arsenic-

containing heterocycles have investigated dithia-chloro-arsole derivatives as potential diagnostic and therapeutic pharmaceuticals for positron emission tomography (PET).¹⁹

In the current report we describe a series of structural studies on the dithia-chloro-arsoles, **1** and **2** (Scheme 1). Compound **1** is unusual in exhibiting 17 molecules in the asymmetric unit and can be categorised amongst the small number of molecules with particularly high Z' numbers.²⁰ While there are relatively large numbers of structures with $Z' > 4$, the numbers decrease significantly for $Z' > 8$ and are very rare for $Z' > 16$ with just 7 reported structures.²¹ In addition, we find **2** is polymorphic and compare the structures of **2 α** , initially reported by Kisenyi et al.,²² with the new polymorph **2 β** in relation to **1** and other dithia-chloro-arsoles. Treatment of **2** with the Lewis acids MCl_3 ($M = Al, Ga$) affords the isomorphous pair of dithia-arsolidinium cations $[3]ij[MCl_4]$ (**3a** $M = Al$, **3b** $M = Ga$) in which the cations are located on a crystallographic mirror plane. Addition of **2** to $LiNiSiMe_3)_2$ in a 3 : 1 ratio leads to formation of the paddlewheel complex **4** (Scheme 1) which exhibits supramolecular aggregation through close $S \cdots S$ contacts.

Combining benzene-dithiol or 4-methyl-benzene-1,2-dithiol with $AsCl_3$ afforded 2-chloro-benzo-1,3,2-dithia-arsole **1** and the 2-chloro-4'-methyl-benzo-1,3,2-dithia-arsole, **2** in good



Scheme 1 Synthesis of arsenic heterocycles 1–4.

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yields (up to 82%) according to the literature method (lit. 85%).²² Single crystals of **1** suitable for X-ray diffraction were grown from a saturated solution of THF whereas **2** could be grown as either of two polymorphs from MeOH (**2α**) or MeCN (**2β**). Recrystallised yields were not optimised for these structural studies.

Compound **1** crystallises in the triclinic space group $P\bar{1}$ with 17 molecules in the asymmetric unit. The molecular geometries of these 17 crystallographically independent molecules are essentially identical and, with no torsional flexibility, this large Z' structure essentially arises through subtle differences in chemical environment. The molecular structure of **1** reveals the C_2S_2As ring plane adopts an envelope structure with fold angles about the $S\cdots S$ vector in the range 8.65 – 20.30° (mean = 14.28°). All 17 molecules of **1** form dimers through a four-centre As_2Cl_2 interaction with $As\cdots Cl$ contacts ($3.360(17)$ – $3.580(18)$ Å) that are shorter than the sum of the van der Waals radii (3.60 Å). These comprise 8 crystallographically independent dimers and one dimer (containing $As11$) located about a crystallographic inversion centre (Fig. 1).

This $[As-Cl]_2$ dimer motif has also been observed in the closely related thiazarsole, $C_6H_4I(NH)SAsCl$.²³ A number of other structures in the CSD also exhibit such $[As-Cl]_2$ motifs.²⁴ These dimers are then linked via additional $As\cdots Cl$ contacts ($3.453(17)$ – $3.951(18)$ Å) generating a chain motif. This intermolecular interaction comprises a combination of electrostatically favourable $As^{\delta+}\cdots Cl^{\delta-}$ interactions, combined with significant dispersion forces. Computational studies support the presence of strong electrostatic and dispersion contributions to bonding (see ESI†). We also examined the potential for a σ -hole interaction but found no evident σ -hole at arsenic but the presence of a σ -hole on chlorine (see ESI†). The latter appears to form a number of contacts to the π -system of the benzo-ring, although the majority of such $C\cdots Cl$ contacts fall beyond the sum of the van der Waals radii.

Recrystallisation of **2** from MeOH afforded crystals of **2α** whose structure was the same as that previously reported (DAXLOD).²² A second polymorph **2β** was isolated from MeCN. **2α** crystallises in the space group $P2_1/c$ with $Z' = 1$

whereas **2β** adopts the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. The molecular structures of **2α** and **2β** are essentially identical and also show an envelope conformation of the heterocyclic ring analogous to **1**. For **2α** the fold angle is 23.60° whereas they are 19.44 and 21.51° for the two crystallographically independent molecules in **2β**. In the case of **2α** there are no $As\cdots Cl$ contacts analogous to those observed in **1**. Instead the packing appears to be directed by $As\cdots \pi$ interactions to the benzo ring ($As\cdots \pi_{\text{centroid}} = 3.251$ Å). These contacts link molecules parallel to the crystallographic c -axis via a 2_1 screw axis (Fig. 2). Such $As\cdots \pi$ interactions from three-coordinate arsenic have been observed in other systems with $As\cdots \pi$ contacts in the range 3.14 – 3.47 Å.²⁵ Conversely **2β** exhibits $As\cdots Cl$ contacts more reminiscent of the dimers formed in **1**. In the first crystallographically independent dimer the intra-dimer $As1\cdots Cl1$ contact ($3.8154(9)$ Å) falls beyond the sum of the van der Waals radii (3.80 Å), and is longer than those observed in **1**. In the second dimer the corresponding intradimer $As2\cdots Cl2$ contact ($3.5025(9)$ Å) falls within the range observed in **1**.

Notably both structures now offer additional $S\cdots Cl$ intra-dimer contacts of ($3.5327(12)$ and $3.4724(12)$ Å for $S2\cdots Cl1$ and $S4\cdots Cl2$ respectively) which are less than the sum of the van der Waals radii of 3.55 Å (Fig. 2 and ESI†). Additionally, a slight fold of the $S-As-S$ fragment out of the plane of the aromatic backbone is noted to form an 'envelope' geometry with fold angles of $23.60(14)^\circ$ and $21.51(14)^\circ$ for **2α** and **2β** respectively. The melting point of **2α** (81 – 82 °C) is higher than that of **2β** (67 – 69 °C) suggesting it has the higher lattice energy. This is also in agreement with the density rule which infers that structures with higher densities are enthalpically more favourable (densities of **2α** and **2β** are 1.920 and 1.910 g cm⁻³ respectively).²⁶

The synthesis of benzo-fused dithia-arsolidinium cations has previously been reported,¹⁷ but structural studies are notably absent. The closely related $[(CH_2)_2S_2As]^+$ cation has been structurally characterised as both $AlCl_4^-$ and $GaCl_4^-$ salts but forms centrosymmetric dimers, $[(CH_2)_2S_2As]_2[MCl_4]_2$ ($M = Al, Ga$). Within these structures, the intra-dimer $As\cdots S$ contacts ($2.423(2)$ Å) are comparable with the heterocyclic $As-S$ bonds

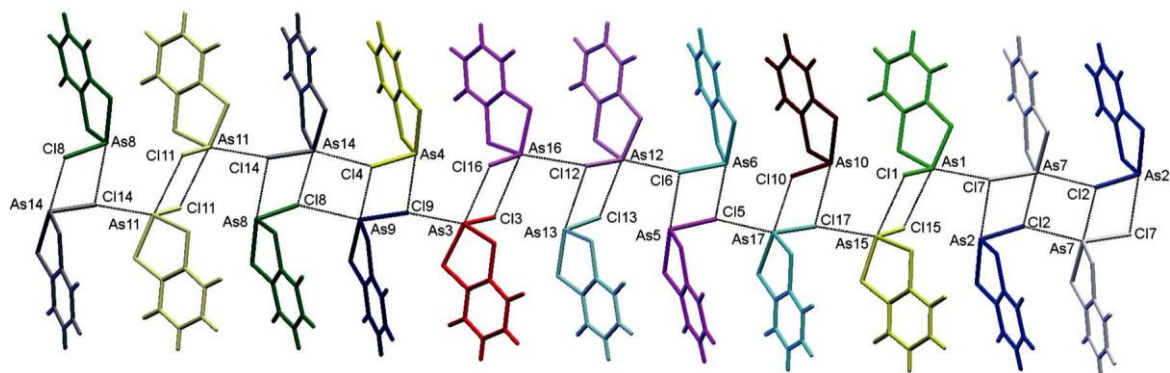


Fig. 1 Dimeric chain-motif of **1** depicting $As\cdots Cl$ close contacts. Molecules are colour coded to highlight the 17 crystallographically independent molecules in the asymmetric unit. Crystallographic inversion centers are located within the second dimer from the left and between the last two dimers shown to the right.

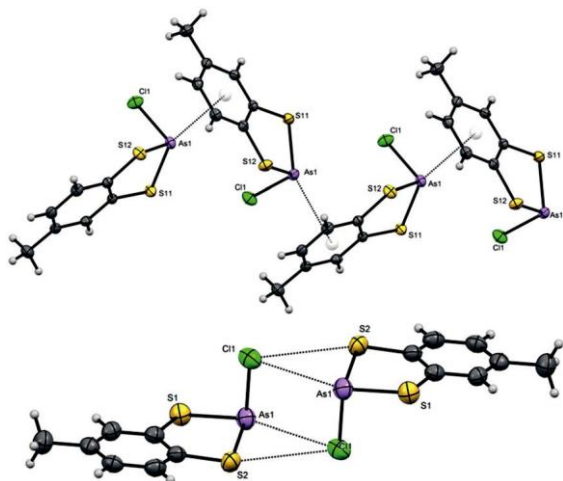


Fig. 2 Solid-state packing of 2 showing As \cdots π centroid contacts within 2 α (top) and one of the two crystallographically independent centrosymmetric dimers of 2 β with As \cdots Cl contacts (bottom).

(2.181(1)–2.326(1) Å) and substantially shorter than the sum of the van der Waals radii (3.65 Å).²⁷ Contrary to these findings, we observed the corresponding salts [MeC₆H₃S₂As] \cdot iJ[MeCl₄] 3a and 3b which were prepared according to the literature method could be recrystallised by slow evaporation from CH₂Cl₂. They were found to be isostructural with two crystallographically independent cation–anion pairs in the asymmetric unit with each sitting on a crystallographic mirror plane such that the cations are rigorously planar (see ESI†). The As–S bonds in 3a and 3b (2.1417(1)–2.1611(1) Å) are shorter than those in the corresponding chloride polymorphs, 1 and 2 (2.188(1)–2.233(1) Å) as well as the previously reported cation dimer, [(CH₂)₂S₂As]₂[GaCl₄] (2.181(3) and 2.326(3) Å). The shortening of this bond in related phosphonium cations has previously been ascribed to π -bonding within the formally 10 π aromatic fused ring system.¹⁷ In addition to bond length changes, the S–As–S bond angle expanded upon generating the cation, increasing from 92.448(1)° in 2 to 94.38(1)–94.81(1)° in 3b. Unlike the chloride salts which show a distinct folding of the heterocyclic ring, both 3a and 3b are rigorously planar with the cation and the anion located on a crystallographic mirror plane. In contrast to the previously reported cation in this series which dimerises, [(CH₂)₂S₂As]₂[GaCl₄]₂, there are no close As \cdots S contacts evident in 3a or 3b. Instead the two-coordinate arsenic centre forms a range of close cation \cdots anion As \cdots Cl contacts (3.2946(1)–3.5376(1) Å), less than the sum of the van der Waals radii (3.60 Å).

Substitution chemistry on the chloro-arsoles has been investigated and condensation of ammonium carboxylates has permitted carboxylate derivatives to be prepared.²⁸ Related substitution with ammonium and sodium salts has led to dithiocarbamate complexes,²⁹ and thiolates.³⁰ Reaction of 2 with lithium bis(trimethylsilyl)amide in toluene afforded (MeC₆H₃S₂As)N[SiMe₃]₂ when undertaken in a 1 : 1 molar ratio but addition of further 2 in molar ratio. Subsequent addition of two equivalents of compound 2 in MeCN afforded the

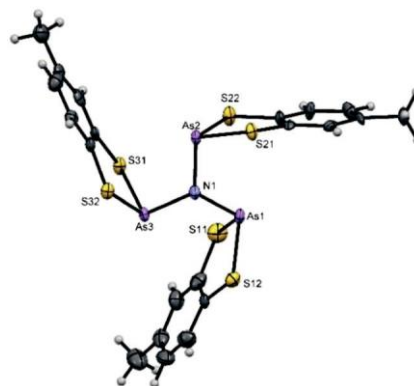


Fig. 3 Solid-state structure of 4. Thermal ellipsoids drawn at 50% probability.

paddlewheel complex (MeC₆H₃S₂As)₃N (4) (Scheme 1). Crystals of 4 suitable for X-ray diffraction were obtained through cooling a saturated CH₂Cl₂ solution to –20 °C, and were found to crystallise in the triclinic space group P 1 (Fig. 3). The crystal structure revealed that the envelope geometry of the five-membered ring as seen in 2 is still preserved, although the fold angle is significantly reduced, from 21.51(4)° to 13.8(1)° for 2 β and 4 respectively.

Slight lengthening of the As–S bonds was also found to occur, from 2.099(1)–2.221(1) Å in 2 β to 2.215(1)–2.252(1) Å in 4. This increase in the bond length gives a corresponding decrease in the S–As–S bond angle, although this does not directly correlate to the decreased fold angle. Typical As–N bond distances were found in the solid-state structure (1.843(1)–1.862(1) Å) with all three As–N–As bond angles being ca. 120°, reflecting an sp² hybridised nitrogen centre with the nitrogen atom close to being coplanar with the three arsenic atoms with the N atom displaced just 0.317(9) Å from the As₃ plane. The unit cell contains two molecules of 4 related about a crystallographic inversion center. These molecules form a dimer with a series of S \cdots S intermolecular interactions (3.428(1)–3.568(1) Å) which are within the sum of the van der Waals radii (3.60 Å) (Fig. 4).

These intermolecular contacts are significantly longer than the intramolecular S \cdots S contacts in S₄N₄ and S₄As₄ which exhibit particularly short S \cdots S distances of 2.580 Å and 2.595 Å respectively.³¹ They are however comparable with the

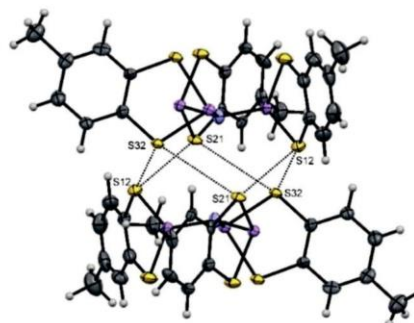


Fig. 4 Solid-state structure of 4 showing intermolecular S \cdots S contacts.

intermolecular S...S contacts in S₈ (orthorhombic α -phase 3.37591J4)–3.50231J5) Å; monoclinic β -phase 3.2751J5)–3.6001J4) and monoclinic γ -phase 3.40121J7)–3.56041J7) Å).³²

Conclusions

In this work we have shown that the 3-chloro-benzo-fused 1,3,2-dithia-arsoles exhibit a rich structural chemistry. For ex-ample, **1** contains a rare high Z' structure with 17 molecules in the asymmetric unit and compound **2** is polymorphic. The melting point and the density rule suggest **2 α** is the enthalpically preferred polymorph. Structural analyses of the first monomeric dithia-arsolidinium complexes [MeC₆H₃S₂As]-ijAlCl₄ and [MeC₆H₃S₂As]ijGaCl₄ have shown them to exhibit a rigorously planar 10 π aromatic system. Finally, the first ex-ample of an arsenic flanked N-centred paddlewheel structure has been revealed through the addition of 3 equivalents of the tolyl-derived arsole to lithium bis(trimethylsilyl)amide.

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