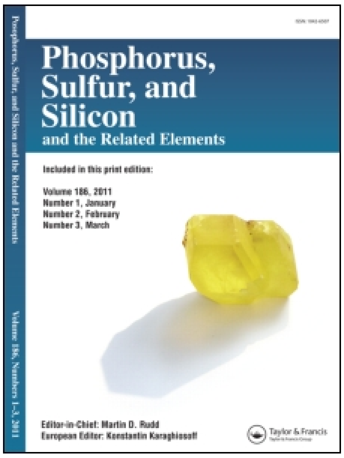

Phosphorus, Sulfur, and Silicon and the Related Elements

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Arsolidinium Cations

Neil Burford[a]; Trenton M. Parks[a]; Bruce W. Royan[a]; T. Stanley Cameron[a]; John F. Richardson[b]; Eric J. Gabe[c]; Rosemary Hynes[c]
[a] Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, CANADA [b] Department of Chemistry, University of Louisville, Louisville, KY, USA [c] National Research Council, Division of Chemistry, Ottawa, Ontario, CANADA

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ARSOLIDINIUM CATIONS

NEIL BURFORD*, TRENTON M. PARKS, BRUCE W. ROYAN and
T. STANLEY CAMERON
Department of Chemistry, Dalhousie University, Halifax,
Nova Scotia, CANADA.

JOHN F. RICHARDSON
Department of Chemistry, University of Louisville, Louisville,
KY, USA.

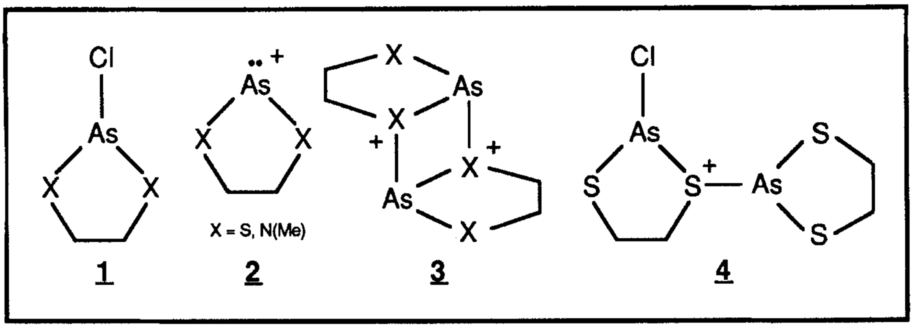
ERIC J. GABE and ROSEMARY HYNES
National Research Council, Division of Chemistry, Ottawa,
Ontario, CANADA

Abstract A series of cyclic thia- and amino- arsenium cations have been prepared and structurally characterised and represent rare examples of cationic environments for arsenic (III). Novel structural arrangements are observed, which illustrate the instability of di-coordinate environments for arsenic. The 1,3-dimethyl-1,3-diaza-2-arsolidinium cation and the 1,3-dithia-2-arsolidinium cation both exist as dimers in the solid state. The dithiaarsolidinium cation is also observed as a component of an unusual bicyclic cationic complex. A genuine dicoordinate environment for arsenic has been isolated as a heteronaphthalenic system, which relies on Huckel features for stabilisation.

INTRODUCTION

Coordinatively unsaturated atomic centres are rare for the non-metal elements. However, their electron deficient nature as well as their synthetic significance have attracted attention and systems containing such units represent an important direction in the development of p-block chemistry. Most familiar are the carbenes, which are viewed as unstable intermediates, but more recently examples have been isolated[1] and structurally characterised,[2] confirming their coordinative unsaturation. The isovalent cationic phosphorus analogs (phosphenium cations)[3] are the only well known carbene-like systems. Studies into the corresponding arsenium cations (dicoordinate arsenic cation) reveal diverse and novel features. For example, a distorted π-sandwich complex structure was observed for the unique $(Cp^*)_2As^+$ cation.[4]

We have begun a systematic study of the dicoordinate cationic arsenic centre by exploiting the halide ion abstraction reaction from simple chloroarsole derivatives, and have identified the first examples of coordinatively unsaturated arsenic.



1 2 3 4

DIAZARSOLIDINIUM CATION

The thermally unstable 2-chloro-1,3,-dimethyl-1,3-diaza-2-arsolidine **1a** (X = NMe) reacts rapidly with $AlCl_3$ or $GaCl_3$ to give pale yellow crystalline solids, which have been characterised as salts of the arsolidinium cation **2a** (ECl_4^-) (X = NMe). The crystal structures reveal a dimeric arrangement **3a** for the cation, with the five-membered heterocycles bound together by a four-membered As_2N_2 ring, as shown in FIGURE 1(a). Although the arsenic environment appears arsine-like, the three As-N bonds differ considerably, with As-N(1) [1.763(8) Å] shorter than expected for a single bond [1.832(3) Å][5], and As-N(2)' [2.103(8) Å] substantially longer and indicative of a weak link between the two rings. The spectroscopically charaterised acyclic $(Et_2N)_2As^+$ [6] is believed to be monomeric in solution, however, variable temperature ^1H NMR studies on salts of **3a** suggests that the dimer structure is maintained in solution.

DITHIARSOLIDINIUM CATIONS

Reaction of 2-chloro-1,3-dithia-2-arsolidine **1b** (X = S) with $GaCl_3$ is stoichiometrically sensitive. An excess of Lewis acid produces the arsolidinium salt in high yield. The cation adopts a dimeric structure **3b** (X = S), FIGURE 1(b)[7], analogous to that of the diaza- derivative, and consistent with the isolobal relationship between an amino nitrogen centre and a dicoordinate sulphur centre.

An excess of arsolidine results in the immediate precipitation of a fine pale yellow crystalline powder, almost identical in appearance to the dicationic **3b** salt. However, structural characterisation reveals a bicyclic monocationic unit **4**, which can be viewed as a Lewis acid-base complex between the chloroarsolidine and a arsolidinium cation.

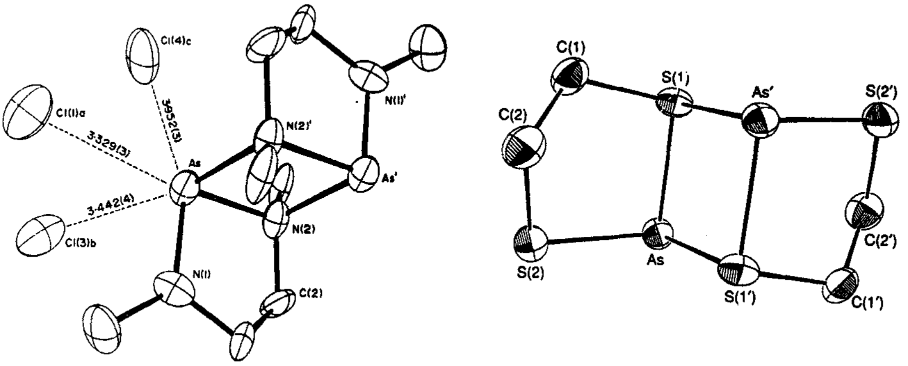


FIGURE 1 Crystallographic views of the dimeric dicationic units of (a) $[C_2H_4(NMe)_2As]_2$ $[GaCl_4]_2$ and (b) $[C_2H_4S_2As]_2$ $[GaCl_4]_2$

THIAZARSOLIUM CATION

Aluminum trichloride readily cleaves the As-Cl bond of 2-chlorobenzo-1,3,2-thiazarsole to give the corresponding cation, which is a planar monomeric unit with short As-N [1.776(4) Å] and As-S [2.1536(15) Å] bonds, FIGURE 2.[8] As such, this cation contains a genuine example of a dicoordinate arsenic centre as a member of a 10π-electron heteronaphthalenic framework, and satisfies the coordinative unsaturation by means of a π-interaction with the sulphur and nitrogen centres. This is the first example of stable pπ bonding between arsenic and sulphur, and evidence for comparable strength with the As-N π-bond.

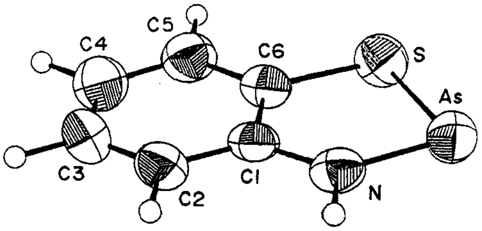


FIGURE 2 View of the benzo-1,3,2-thiazarsolium cation.

These preliminary results illustrate a flexibility in the accommodation of coordinative unsaturation for arsenic. The requirement for supplemental stabilising influences, such as a Huckel electron count is again evident[9], but the unusual weak association complexes indicate a potentially diverse and novel chemistry for the cationic arsenic centre.

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