Preparation and Spectroscopic Characterisation of Dithia-Arsolium and -Stibolium Cations: Evidence for pπ–pπ Bonding of Sulphur with Arsenic and Antimony

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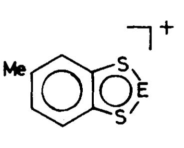
5-Methyl-1,3,2-benzodithiarsolium and 5-methyl-1,3,2-benzodithiastibolium cations have been prepared and the naphthalenic nature of the compounds is strong evidence for the presence of unique pπ–pπ bonding of sulphur to arsenic and antimony.

We have recently described the synthesis and characterisation of the first dithiaphospholium cation (**1a**), which contains a unique example of pπ–pπ bonding between phosphorus and sulphur.[1,2] The thermodynamic stability of the system is principally due to the molecular positive charge, organo-aromatic (Hückel 10π) delocalisation, the low basicity of the anion and the crystal lattice energy of the salt being significantly greater than that of an alternative covalent Lewis adduct structure.[1,2,3] Our interest in the development of new bonding arrangements for the non-metal elements has prompted an investigation of the potential versatility of this specific collection of stabilising features. We now report the synthesis, isolation and spectroscopic characterisation of 5-methyl-1,3,2-benzodithiarsolium (**1b**) tetrachloroaluminate and 5-methyl-1,3,2-benzodithiastibolium (**1c**) tetrachloroaluminate. While the new naphthalenic derivatives represent genuine examples of rare dico-ordinate arsenic and dico-ordinate antimony cations,[4,5] perhaps of greater significance is the identification of unprecedented examples of stable As–S 4pπ–3pπ bonding and Sb–S 5pπ–3pπ bonding.

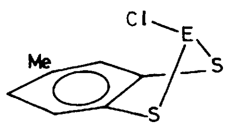
Table 1. ^1H and ^{13}C n.m.r. chemical shifts of derivatives of (**1**), (**2**), and (**3**). Spectra were run on a Nicolet NT-360 spectrometer in CD_2Cl_2, $CDCl_3$, CH_2Cl_2, or $CHCl_3$. Coupling constants (J) are in Hz.

^1H n.m.r.						
(**1a**)[a]	(**1b**)[b]	(**1c**)[b]	(**3**)[c,d]	(**2a**)[b]	(**2b**)[b]	(**2c**)[b]
8.54	8.33	7.44	8.73	7.55	7.48	7.45
8.46	8.26	7.38	8.67	7.49	7.43	7.39
7.92	7.75	6.93	8.00	7.12	7.05	6.93
2.71	2.66	2.33	2.73	2.39	2.37	2.35
$^3J = 8.5$	$^3J = 8.6$	$^3J = 8.0$	$^3J = 8.5$	$^3J = 8.1$	$^3J = 8.1$	$^3J = 8.0$
^{13}C-{^1H} n.m.r.						
(**1a**)[a]	(**1b**)[b]	(**1c**)[e]	(**3**)[b,c]	(**2a**)[b]	(**2b**)[b]	(**2c**)[b]
153	153		146	139	139	140
150	150		144	136	136	137
144	142		143	128	136	136
133	131		134	126	127	130
128	129		127	126	127	130
127	128		127	120	126	127
22	21		22	21	21	21

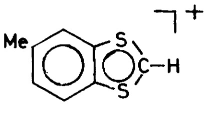
[a] Ref. 2a. [b] This work. [c] Methine signals omitted. [d] Ref. 9. [e] Not available due to low solubility.



(**1**) **a**; E = P
b; E = As
c; E = Sb



(**2**) **a**; E = P
b; E = As
c; E = Sb



(**3**)

Tetrachloroaluminate salts of (**1b**) (m.p. 121—123 °C, 35%) and (**1c**) (m.p. 166—168 °C, 50%)† were obtained by reaction of the corresponding chloropnictoles (**2b**) and (**2c**),[6] respectively, with equimolar quantities of $AlCl_3$ in CH_2Cl_2. The compounds are microcrystalline orange solids, which are significantly more air sensitive than salts of the phospholium analogues.[1,2]

The i.r. spectra of the $AlCl_4^-$ salts of (**1**) are very similar, including the characteristic strong fundamental band of the anion at 485—490 cm^{-1}.[7] In addition, the absence of bands associated with $AlCl_3$ (622, 320 cm^{-1}),[7] and the strong pnictogen-chlorine stretching absorptions present in the spectra of (**2b**) (*ca.* 310 cm^{-1}) and (**2c**) (*ca.* 275 cm^{-1}),[6] is evidence for an essentially ionic structure in the solid state, with a cation containing heteroatom π-bonding as opposed to an alternative σ-bonded Lewis adduct. The mass spectra of all derivatives of (**1**) are essentially identical to those of the precursor chloropnictoles (**2**), indicating a reabstraction process in the spectrometer, common for non-metal cations.[8] Loss of chloride is observed to give a base peak corresponding to (**1**) with minimal fragmentation, implying stability for the cation in the gas phase.

^1H and ^{13}C n.m.r. data for the series of cations (**1**) are presented in Table 1 and are compared with those of the 5-methyl-1,3-benzodithiolium cation (**3**)[9] and the corresponding derivatives of (**2**). The chemical shifts for (**1a**) and (**1b**) are very similar and are significantly deshielded from their neutral relatives (**2a**) and (**2b**). As described for (**3**),[10] the deshielding observed for the benzo nuclei of (**1a**) and (**1b**) can be attributed to the effective delocalisation of the positive charge throughout the molecule by means of the aromatic manifold.[1,2] The increase of the coupling constants observed for (**1a**) and (**1b**) with respect to those found for (**2**) is also consistent with a naphthalenic model for (**1**).[11] Such a bonding arrangement requires the employment of pπ–pπ bonding over the S–P–S and S–As–S moieties. σ-Inductive delocalisation of charge does not affect such dramatic shifts for aromatic nuclei.[12] The ^1H n.m.r. spectrum obtained for the sparingly soluble (**1c**) shows the principal component of the solution to be (**2c**), implying that the salt is in equilibrium with the starting materials, a phenomenon postulated for (**1a**).[2] Signals at 102 p.p.m. in the ^{27}Al n.m.r. spectra of (**1**) support the presence of the $AlCl_4^-$ anion in solution.[13] However, consistent with the ^1H n.m.r. spectrum, the ^{27}Al spectrum of (**1c**) is complex containing two additional peaks.

Dico-ordinate As, Sb, and Bi cations possessing $np\pi$–$2p\pi$ bonding (n = 4, 5, 6) with nitrogen, have recently been reported by Veith.[5] As observed for other phospholium cations,[13] the phosphorus derivative is stabilised by π-donation from the nitrogen centres. The n.m.r. data for (**1a**) and (**1b**) indicates that effective aromatic delocalisation may enhance pπ bonding for phosphorus and arsenic with sulphur. Compound (**1c**) is only stable in the solid state and disproportionates in solution, relying more on intermolecular interaction and less on π-bonding to stabilise the low co-ordination. This is consistent with the observations made by Veith and is possibly a further demonstration of the importance of the

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† *Selected spectroscopic data* for (**1b**) $AlCl_4^-$: I.r. (CsI, Nujol), 1260, 870, 820, 720, 510, 485, 435 cm^{-1}; mass spec. m/z (^{35}Cl): 264 (25%), 229 (100%).

For (**1c**) $AlCl_4^-$: I.r. (CsI, Nujol) 1260, 865, 810, 720, 510, 480, 450 cm^{-1}; mass spec. m/z (^{35}Cl, ^{171}Sb): 310 (47%), 275 (100%).

Elemental analysis for (**1b**) $AlCl_4^-$ was consistent with proposed structure.

Crystals suitable for *X*-ray diffraction have not yet been obtained.

crystal lattice energy in the isolation and identification of such compounds.

The versatility of the stabilising features listed above and the simplicity of the synthetic approach offer the potential for the eventual isolation and characterisation of all possible pπ bonds between atoms of Groups 14—16, a goal recently identified by Schmidt and Gordon.[14] The preparation of the series of compounds (**1**) is a contribution toward the development of general, thermodynamically stable pπ-bonding throughout the main group and therefore has significant consequences for the chemistry of the non-metals.

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