

Synthesis of the Unique 10 π -Electron 1,3,2-Benzodithiaphospholium Cation and a Structural Comparison with the Phenyl Phosphine Derivative

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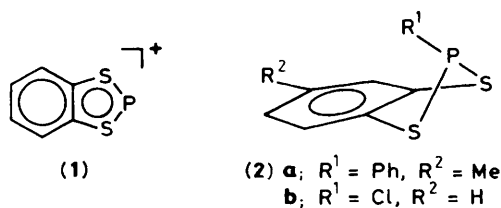
The first example of a dithiaphospholium cation is a 10 π -electron planar heterocycle, which exhibits thermodynamically stable 3p π –3p π bonding between phosphorus and sulphur.

Despite the thermodynamic preference for σ -bonding over π -bonding for the 3rd row and heavier elements of groups 14, 15, 16, and 17, p π –p π bonded systems have been prepared by utilising specific stabilising features. Double-bonded compounds containing elements from groups 14 and 15 can be kinetically stabilised by bulky substituent groups [e.g. Mes₂Si=SiMes₂ and MesP=PMes (Mes = 2,4,6-Me₃C₆H₂)].¹ The prevention of close contact between units avoids multimolecular oligomerisation to fully σ -bonded species. Alternatively, the heavier elements of groups 16 and 17 rely on molecular charge to render p π –p π bonding thermodynamically stable (e.g. Ch₄²⁺, Ch = S, Se, Te; X₂⁺, X = Br, I).² However, the specific nature of the respective stabilising aspects has restricted the generality of p π bonding between non-metals. For instance, multiple bonds between heavier elements of different groups (*i.e.* 14–17) are extremely rare.³ Naturally, the topic has attracted the interest of a number of theoreticians,⁴ who predict the eventual isolation and characterisation of all possible double bonds between the non-metals.^{4a}

As a new experimental contribution, we report the synthesis and X-ray crystal structure of the 1,3,2-benzodithiaphospholium cation (1) as its tetrachloroaluminate salt. The new

bicyclic cation (1) is planar and exhibits a unique example of 3p π –3p π bonding between phosphorus and sulphur. For direct comparison, we also present the crystal structure of a derivative of the parent phosphine system, 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole (2a), which contains the closest related example of a fully σ -bonded phosphorus(III) centre. The isolation of (1) is an important development in the efforts to make p π -bonding between the heavier non-metal elements energetically competitive with σ -bonding.^{4b}

Compound (2b)⁵ (6.3 mmol) reacted rapidly with AlCl₃ (6.3 mmol) in CH₂Cl₂ (55 ml) at room temperature to give a bright yellow solution and a precipitate. The solution was filtered



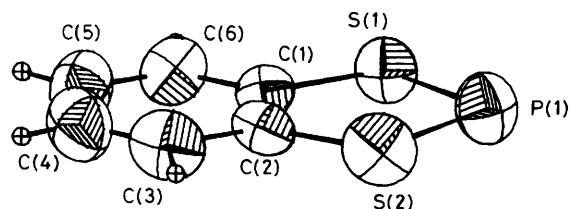


Figure 1. SNOOPI view of the 1,3,2-benzodithiaphospholium cation (1).

Table 1. Selected bond lengths (Å) and angles (°) for (1) and (2a).

	C ₆ H ₄ S ₂ PAiCl ₄ (1)	C ₁₃ H ₁₁ PS ₂ (2a)
P–S(1)	2.016(3)	2.110(2)
P–S(2)	2.015(3)	2.102(2)
S(1)–C(1)	1.728(5)	1.761(5)
S(2)–C(2)	1.711(6)	1.765(6)
C(1)–C(2)	1.383(7)	1.401(6)
C(2)–C(3)	1.411(8)	1.389(7)
C(3)–C(4)	1.350(10)	1.377(8)
C(4)–C(5)	1.351(10)	1.386(7)
C(5)–C(6)	1.374(9)	1.378(8)
C(6)–C(1)	1.407(8)	1.377(8)
S(1)–P–S(2)	97.59(10)	94.9(1)
P–S(1)–C(1)	102.6(2)	99.1(2)
P–S(2)–C(2)	102.5(2)	99.6(2)
S(1)–C(1)–C(2)	117.8(4)	118.8(4)
S(2)–C(2)–C(1)	119.5(4)	118.8(4)

and the solid recrystallised from CH₂Cl₂ to give extremely air-sensitive, yellow, needle-like crystals (5.84 mmol, 93%, decomp. ca. 80 °C), characterised† as 1,3,2-benzodithiaphospholium tetrachloroaluminate. A single crystal suitable for X-ray analysis‡ was selected in a dry box and mounted in a glass capillary. Compound (2a) was prepared by a modified literature procedure⁸ and recrystallised from boiling n-hexane as white needle-like crystals, which were mounted in glass capillaries.

SNOOPI⁹ views of the new phospholium cation (1) and compound (2a) are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are presented for comparison in Table 1. The bicyclic cation (1) is planar with a mean

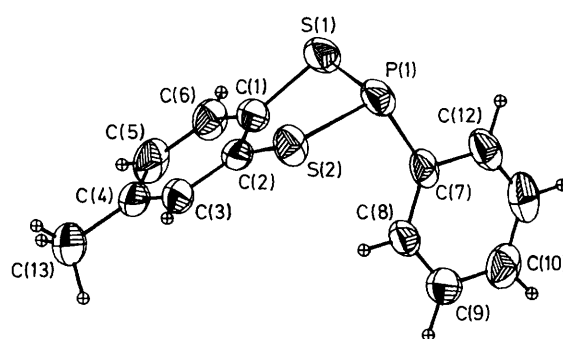


Figure 2. SNOOPI view of 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole (2a).

deviation of 0.013 Å and the maximum deviation at phosphorus from the plane of 0.027 Å. By comparison, compound (2a) is folded at the S–S vector with an angle of 25.2° between the S₂P and C₆S₂ planes (P deviates from the C₆S₂ plane by 0.53 Å).

The P–S bonds in (1) are significantly shorter (4%) than those in P₄S₃ (2.09 Å)¹⁰ and compound (2a). To our knowledge, they are the shortest P–S bonds reported, other than those of the phosphorus(v) sulphides. Similarly, while the C–S bonds in (2a) are only slightly shorter than a normal C–S single bond (1.80 Å in SMe₂),¹⁰ cation (1) shows a 4% shortening. The angles at phosphorus and sulphur are slightly larger in the cation compared with those of (2a), owing to the molecular planarity of (1). Nevertheless, the S–P–S angle is substantially smaller than the corresponding angle observed in the open-chain diaminophosphonium cation (115°).¹¹ The crystal structure of (1) consists of discrete ionic units and the anion is essentially tetrahedral. There are a number of cation–anion Cl⋯P (3.34 Å) and Cl⋯S (3.43 Å) contacts which are comparable to those observed in related chalcogen homopolyatomic cationic systems.¹² The cumulative effect of these interactions may have some bearing on the structure of the cation, and this is presently under investigation.

Chloride ion abstraction from (2b) is favoured over competitive Friedel–Crafts reaction at the benzo moiety involving electrophilic attack by the solvent CH₂Cl₂. However, the yield of this reaction is concentration dependent and best results are obtained at high dilution. A structural adjustment at the tetrahedral phosphorus centre is observed [compound (2b) is presumed to have a similar molecular geometry to that of (2a)], to give a distorted trigonal planar dithiaphospholium cation (1). Essentially, all the isolated phospholium ions feature at least one amino substituent and the stability of the cation is dependent on reliable π-donation of the lone pair from the planar nitrogen atoms into the phosphorus 3p_π orbital.¹¹ The paraelement¹³ (isolobal) relationship between the planar amino nitrogen and the planar dico-ordinate sulphur centre allows for a similar bonding arrangement in compound (1). However, the planarity of the system implies that the heteroatoms are intimately involved in a 10π electron environment, affording an effective delocalisation of the positive charge, and emphasising the isovalent relationship with naphthalene. Although there are numerous examples of P=S double bonds [phosphorus(v) sulphides] which rely on an expanded valence shell at phosphorus and 3d_π–3p_π bonding,¹⁰ the indefinite stability and structure of (1) is strong experimental evidence of 3p_π–3p_π bonding between phosphorus and sulphur.

The thermodynamic stability of (1) is dependent on two main features. (a) The presence of the positive charge

† Compound (1) gave satisfactory elemental analyses; i.r. (CsI plates, Nujol mull) 760, 740, 565, 555, 525, 485, and 460 cm^{−1}.

‡ Crystal data for compound (1): C₆H₄S₂PAiCl₄, *M* = 339.98, monoclinic, space group *P*2₁/*c*, *a* = 6.605(3), *b* = 23.377(4), *c* = 8.666(2) Å, β = 100.28(3)° *U* = 1316.5 Å³, *Z* = 4, *D*_c = 1.713 Mg m^{−3}, μ = 13.4 cm^{−1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-*K*_α radiation (λ = 0.70926 Å) using ω–2θ scans (2θ_{max}, 50°). Absorption corrections were applied and the structure was solved by direct methods⁶ and refined by block-matrix least-squares⁷ (2 blocks) to residuals of *R* = 0.036, *R*_w = 0.037 for 1326 observed reflections with *I* > σ(*I*) and with 144 variables.

Compound (2a): C₁₃H₁₁PS₂, *M* = 262.32, monoclinic, space group *P*2₁/*n*, *a* = 14.691(3), *b* = 6.291(1), *c* = 14.882(3) Å, β = 114.56(2)°, *U* = 1250.9 Å³, *Z* = 4, *D*_c = 1.393 Mg m^{−3}, μ = 5.09 cm^{−1}. Data were collected and the structure solved in a similar manner to that described above. Refinement converged to *R* = 0.037, *R*_w = 0.037 for 1061 observed reflections with *I* > 2σ(*I*) and with 191 variables. Correspondence regarding crystallography should be addressed to T. S. Cameron. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

decreases the diffuse character of the π -orbitals and enhances $3p_{\pi}$ - $3p_{\pi}$ bonding. In addition, charge repulsion prevents multimolecular rearrangement to a σ -bonded alternative.^{2a} (b) The Hückel nature of the ring system provides a substantial resonance stabilisation energy.

Compound (1) represents the first in an extensive series of unsaturated systems containing the heavier elements of groups 15 and 16, that are stabilised by a combination of charge and π -delocalisation. The arsenic and antimony analogues of (1) have been prepared in a similar manner and are presently under investigation. There is clearly potential for the preparation of general $p\pi$ -bonding between heavier non-metals using comparable stabilising features.

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