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Phosphorus, Sulfur, and Silicon and the Related Elements

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$\rho\pi$ - $\rho\pi$ Bonding Between Sulfur and the Heavier Elements of Group 15

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$p\pi-p\pi$ BONDING BETWEEN SULFUR AND THE HEAVIER ELEMENTS OF GROUP 15.

NEIL BURFORD^{*} and BRUCE W. ROYAN

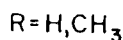
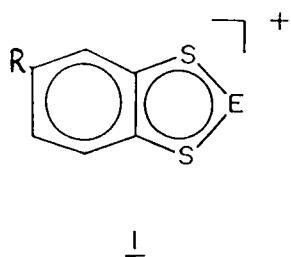
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Abstract As a contribution to the development of general stable $p\pi-p\pi$ bonding throughout the p-block, the first dithiaphosphenium cation 1a has been prepared. Stable dicoordinate phosphorus without the presence of at least one nitrogen or carbon ligand is unique. Moreover, this compound contains an unprecedented example of thermodynamically stable $p\pi-p\pi$ bonding between phosphorus and sulfur. In addition, cation 1a contains a rare example of $p\pi-p\pi$ bonding between the heavier elements of different groups of the Periodic Table. The analogous arsenic and antimony derivatives have been prepared, demonstrating that the system offers potential generality for genuine $p\pi-p\pi$ bonding between all heavy ($n > 2$) non-metal elements.

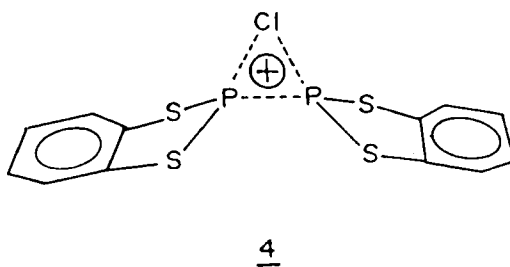
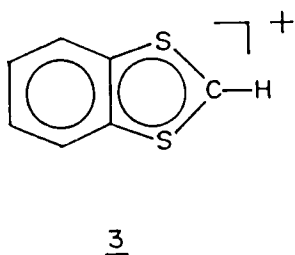
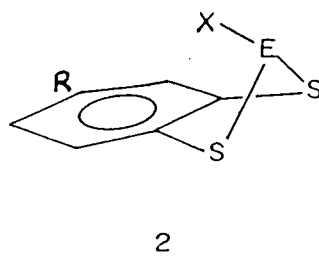
INTRODUCTION

The diversity and extent of organic chemistry can be attributed to a combination of features collectively unique to carbon. While many of the individual properties are common for other elements of the main group, an entirely unique feature of carbon chemistry is the energetic balance between σ -bonding and π -bonding, observed for bonding with carbon, nitrogen and oxygen. In contrast, the inorganic chemistry of nitrogen and oxygen is dominated by strong π -bonding, while the heavier non-metals exhibit a dramatic thermodynamic preference for σ -bonding.¹ None of the heavier p-block elements are observed to employ GENERAL stable, genuine $p\pi$ -bonding, and very strong $p\pi$ -bonds are anomalous to the second row ($n = 2$) non-metals.² $p\pi$ -Bonds between the heavier elements of groups 14 and 15 can be

kinetically stabilised by the steric constraints of bulky substituent groups.³ Such arrangements are not possible for elements of groups 16 and 17, which rely on the presence of a molecular positive charge to induce $p\pi$ -bonding.⁴ Despite the recent prediction that "Eventually compounds representing all possible double bonds between atoms of groups 14-16 will be isolated and characterised",⁵ there is no experimental evidence for $p\pi$ - $p\pi$ bonding between the heavier elements ($n > 2$) from opposite sides of the p-Block. In this context, we have prepared and fully characterised the first dithiaphosphenium cation 1a, which contains a unique example of thermodynamically stable $3p\pi$ - $3p\pi$ bonding between phosphorus and sulfur.⁶ Initial results indicate that the series can be extended to the arsenic and antimony analogs 1b,c.⁷



| | | |
|----------|--------|--------|
| <u>a</u> | E = P | X = Cl |
| <u>b</u> | E = As | X = Cl |
| <u>c</u> | E = Sb | X = Cl |
| <u>d</u> | E = P | X = Ph |



RESULTS AND DISCUSSION

The versatile chloride ion abstraction reaction⁸ has been employed to obtain the first example of a dicoordinate phosphorus cation possessing heavy ($n > 2$) elements as substituents. AlCl_3 , AlBr_3 and MoCl_5 all rapidly remove Cl^- from 2-chloro-5-methyl-1,3,2-benzodithiaphosphine 2a to give the corresponding salt of cation 1a.⁶ A similar approach has been attempted with the arsenic 2b and antimony 2c analogs using AlCl_3 .⁷ Benzo and tolyl derivatives of 1a have been studied by IR, N.M.R. and mass spectroscopy and by elemental analysis and the AlCl_4^- salt of the benzo derivative has been structurally characterised by X-ray techniques.⁶ Significant deshielding is observed in the ^1H and ^{13}C N.M.R. spectra for the carbocyclic frameworks of 1a, with respect to the corresponding chlorophosphines 2a and dithiols.^{6b} This infers a significant delocalisation of the molecular charge into the benzo unit, possibly via the π -system. Indeed, the ^1H and ^{13}C chemical shifts are very similar to those of the benzodithiolium 3 systems, which are regarded as aromatic.⁹ In this respect, the heteroatoms of 1a can be viewed as an integral part of a bicyclic 10π -electron (Hückel) system, isovalent with naphthalene. Such an arrangement requires the use of $3p\pi$ - $3p\pi$ bonding between the phosphorus and sulfur centers.

The cation 1a (tolyl) exhibits a broad ^{31}P N.M.R. signal at 408 ppm (414 ppm for the benzo) which is dependent on the temperature and the nature of the anion. The chemical shift values for most aminophosphenium ions are approximately 100 ppm deshielded from the corresponding precursor chlorophosphine.⁸ By comparison, the ^{31}P chemical shift observed for 1a is more than 200 ppm deshielded, perhaps demonstrating the less effective π -donating capabilities of sulfur. The signal sharpens on cooling to -80°C with no significant change in chemical shift. We assign this behavior to the presence of an equilibrium process involving

the reabstraction of Cl^- by the cation. The chlorophosphine 2a ($^{31}\text{P} = 160\text{ppm}$) is not observed at -80°C perhaps indicating a very small equilibrium constant. However, the formation of an adduct 4 is expected to be facile, as 1a is observed by ^{31}P N.M.R to form a solution stable 1:1 adduct with Ph_3P .¹⁰ An N.M.R. study of the reaction between 1a and 2a reveals labile adduct formation at room temperature as a broad signal between 400 and 160 ppm, the position of which is dependent on the relative molar ratios.^{6b} At -50°C the system achieves coalescence, and at -80°C two broad signals are discernible corresponding to 1a and 2a. A reabstraction process for salts of 1a in solution is further supported by the ^{27}Al N.M.R spectrum of the AlCl_4^- salt, which shows a strong signal at 103 ppm corresponding to the anion and a small peak at 90 which may be assigned to AlCl_3 or an adduct of AlCl_3 . The mass spectra of 1a are consistent giving a parent ion corresponding to 2a, the result of a reabstraction in the spectrometer. These observations are an indication of the borderline thermodynamic stability of the free cation with respect to an alternative covalent chlorophosphine- AlCl_3 adduct. It seems that the crystal lattice energy of the salt plays an important role in the stabilisation of the cation.⁴

The preparation of 1a can provide yields in excess of 90% under conditions in which 2a is in high dilution, however, a dramatic concentration effect is observed. Compounds 1a and 2a are resilient to electrophilic substitution by the solvent in the presence of powerful Friedel-Crafts reagents such as AlCl_3 . However, it seems that charge dilute species such as 4 are susceptible and undergo a reaction at the benzo moiety which is competitive with or more favorable than the chloride ion abstraction process. Therefore, in order to maximise yields, it is essential to avoid the formation of multimolecular systems 4 in the reaction mixture by means of high dilution.

The S-E-S (E = P, As, Sb) unit of cations 1 can be regarded

as isolobal¹¹ to any three atom segment of the square planar Ch_4^{2+} cations ($\text{Ch} = \text{S}, \text{Se}, \text{Te}$), and the five membered ring of the cation is isovalent with Ch_4^{2+} . Consistently, the structure of la displays contacts to the AlCl_4^- anions which are similar to those observed in Ch_4^{2+} salts.¹² Cation la is planar and does not display the stereochemical (pyramidal) presence of the lone pair, which is evident in the structure of the closely related fully σ -bonded neutral phenyl substituted compound 2d.⁶ Moreover, la contains the shortest P(III)-S bond (2.01 Å) yet reported, intermediate between the "standard" P-S single (Experimental - 2.1 Å,¹ calculated in H_2PSH 2.119 Å⁵), and double P=S bonds, both genuine (calculated for $\text{HP}=\text{S}$ - 1.903 Å)⁵ and non-genuine ($3d\pi$ - $3p\pi$ bonding) in phosphorus (V) sulfides (1.91 Å).¹ The carbon-sulfur bonds (1.74 Å) of la are also substantially shorter than a single C-S bond (1.80 Å),¹ indicating a significant π -interaction between the sulfur centers and the benzo moiety.

Compound la is an important addition to the series of dicoordinate phosphonium cations, which primarily rely on the π -donation of lone pair electrons from amino nitrogen centers into the p orbital of the planar phosphorus center.¹³ In this respect, the stability of la and related aminophosphenium cations⁸ represents an example of the isolobal relationship between an amino group and a dicoordinate sulfur center. The discovery of a thermodynamically stable $3p\pi$ - $3p\pi$ bonding in the first phosphorus(III)-sulfur cation is the foundation of a potentially comprehensive π -chemistry for the heavier non-metals. Preliminary spectroscopic data obtained for lb and lc are in agreement with 10π -electron bicyclic systems, containing $np\pi$ - $3p\pi$ bonding ($n = 4$ and 5 respectively). Complete characterisation of these compounds is in progress.

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