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Phosphorus, Sulfur, and Silicon and the Related Elements

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COMPARATIVE ELECTRON DENSITY STUDIES OF THE PHOSPHORUS-SULPHUR BONDING AND OF THE EXTENT OF THE AROMATIC SYSTEM IN A 1,3,2-BENZODITHIAPHOSPHENIUM CATION AND THE RELATED 2-PHENYL-1,3,2-BENZODITHIAPHOSPHOLE.

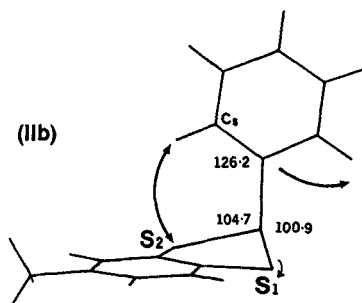
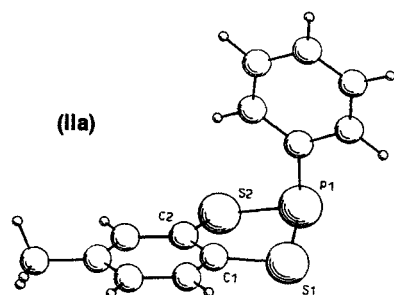
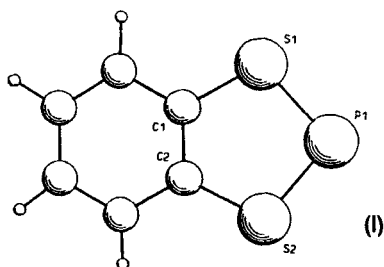
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Abstract The low-temperature X-ray crystal structures of 1,3,2-benzodithia-phosphenium tetrachloroaluminate and the corresponding neutral 2-phenyl-1,3,2-benzodithia-phosphole have been determined at 210 K. A comparison of the X-X_{HO} charge density studies for the two systems confirms that the phosphenium cation possesses a planar 'aromatic' configuration. However, there are strong indications for a substantial contribution to the structure from a quinoid-like structure with about 60% of the charge localised on the phosphorus atom.

INTRODUCTION

It has been suggested¹ that the 1,3,2-benzodithia-phosphenium cation (I) contains an extended 10 electron $p\pi-p\pi$ system. A preliminary examination of the residual electron density from data collected at room temperature indicated² that the situation might not be as simple as this. We report here the low-temperature residual electron density (deformation density³) studies of the cation (I), and, because the electron distribution in the related neutral molecule 2-phenyl-

1,3,2-benzodi-thiaphosphole (II) should be predictably different from that of the cation¹, we also report the low-temperature deformation density study of (II). The extent to which the deformation density studies show all the expected features in the two systems will be used as a reasonable measure of the validity of the conclusions drawn for the bonding in the cation. However, the neutral molecule (II) is unexpectedly sterically strained (IIb) and



the resulting twisted conformation of the molecule should be reflected in a distortion of the sulphur lone-pair electrons from their expected positions. The extent to which the deformation density studies show this distortion provides an additional measure of the validity of the conclusions on the bonding.

STRUCTURE SOLUTION

Crystal data: (I) $C_6H_6AlCl_4PS_2$, $M = 339.98$, monoclinic $P2_1/c$, $a = 6.589(3)\text{\AA}$, $b = 23.351(5)$, $c = 8.657(3)$, $\beta = 100.25(3)^\circ$, $V = 1311(1)\text{\AA}^3$, $Z = 4$, $D_c = 1.723\text{Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha_1) = 0.70926\text{\AA}$, $\mu = 13.62\text{ cm}^{-1}$, $T = 218 \pm 1\text{ K}$, $\sin(\theta_{\max})/\lambda = 1.0$ ($\theta_{\max} = 45^\circ$), 17,128 measured reflections, 10,380 unique reflections, $R = 0.0326$, $R_w = 0.0328$, crystal size .05 x .35 x .4 mm. (II) $C_{13}H_{11}PS_2$, $M = 262.32$, monoclinic $P2_1/n$, $a = 14.696(7)\text{\AA}$, $b = 6.244(7)$, $c = 14.793(6)$, $\beta = 114.64(4)^\circ$, $V = 1233(2)\text{\AA}^3$, $Z = 4$, $D_c = 1.422\text{Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha_1) = 0.70926\text{\AA}$, $\mu = 5.11\text{ cm}^{-1}$, $T = 212 \pm 1\text{ K}$, $\sin(\theta_{\max})/\lambda = 1.0$ ($\theta_{\max} = 45^\circ$), $\sim 17,000$ measured reflections, 13880 unique reflections, $R = 0.0466$, $R_w = 0.0488$, crystal size .15 x .25 x .25 mm. The crystals were mounted in glass capillaries and the data were collected at the lowest temperature compatible with crystal stability. The structures were solved by routine procedures (absorption corrections⁴ were applied) and they were refined with full-matrix least-squares using CRYSTALS⁵ and Dunitz & Seiler weights⁶. Some selected bond lengths for the heterocyclic rings are shown below. Full structural details will be reported later.

Once the refinements had converged, $X-X_{H0}$ calculations³ were performed. Figure 1 shows the resulting difference maps through the plane of the cation and along the buckled surface of the corresponding portion of the neutral molecule. The difference between these is immediately obvious with greater spread of σ and π bonding density in the cation (I) and a greater concentration of the density in the C_6 ring in the neutral molecule (II). Interestingly, there is considerably more bonding density along the C - S bonds in the cation than in the neutral molecule. Apart from this concentration of bonding electron density along the C - S

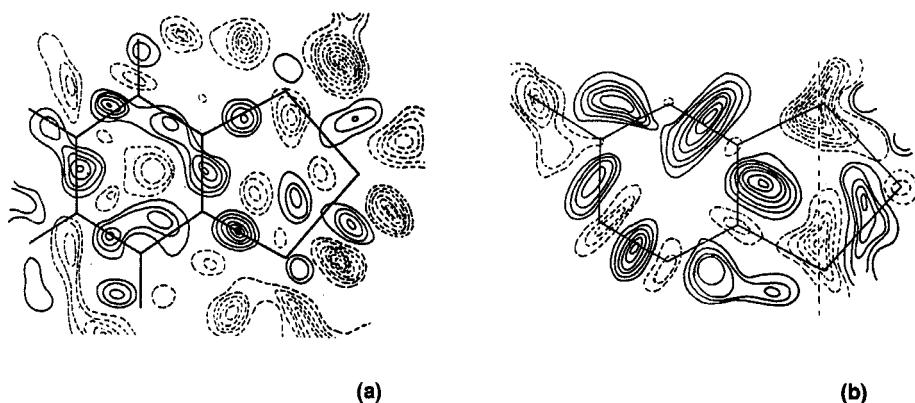
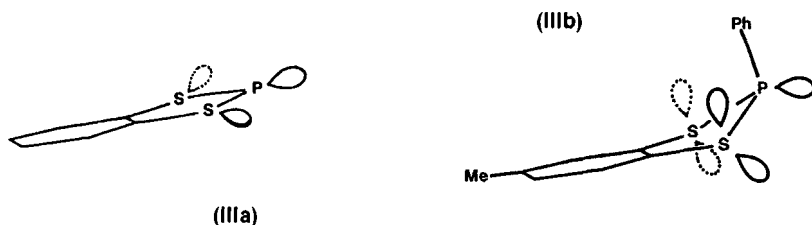


FIGURE 1 Deformation densities in the plane of (a) the cation, (b) the neutral molecule. The broken lines show negative difference density³, contours at $0.1e/\text{\AA}^3$.

bonds, the deformation densities in the cation resemble those of naphthalene⁷. The sulphur and phosphorus atoms of the cation have each one set of lone-pair electrons (**IIIa**) which should be located in the ring plane. In the neutral molecule, the phosphorus atom has one set of lone-pair electrons while the sulphur atoms have two sets each (**IIIb**). A careful examination of the cation shows that it is, in fact, slightly saucer shaped while the neutral



atom is distorted by a steric interaction (**IIIb**). When the $X-X_{HO}$ density is examined in the plane perpendicular to the ring plane which passes along the $S \cdots S$ axis (figure 2), the locations of the sulphur lone-pair electrons are seen to follow the saucer shape for the cation, while they are distorted in exactly the way that could be predicted from the twisting of the neutral molecule.

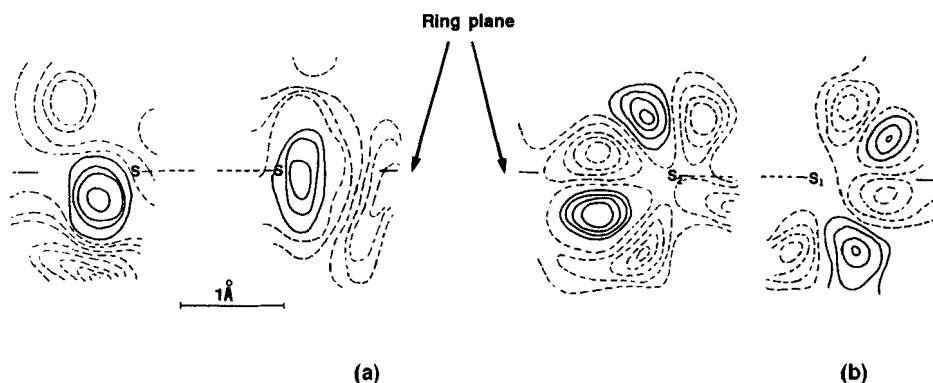


FIGURE 2 Deformation density at sulphur (a) for the cation showing the saucer inverted; (b) the neutral molecule with S_2 above and S_1 below the C_6 plane, contours $0.1e/\text{\AA}^3$.

The lone-pair electrons on the phosphorus atom of the neutral molecule are clearly visible, while those in the cation do not show up in the original $X-X_{HO}$ calculations. However, when the cation phosphorus atom was allowed to assume a positive charge, and the portion of the charge included in the refinement, the calculations converged with a charge of $+0.58$ on this atom and the $X-X_{HO}$ map now showed the faint outline of the lone-pair (figure 3).

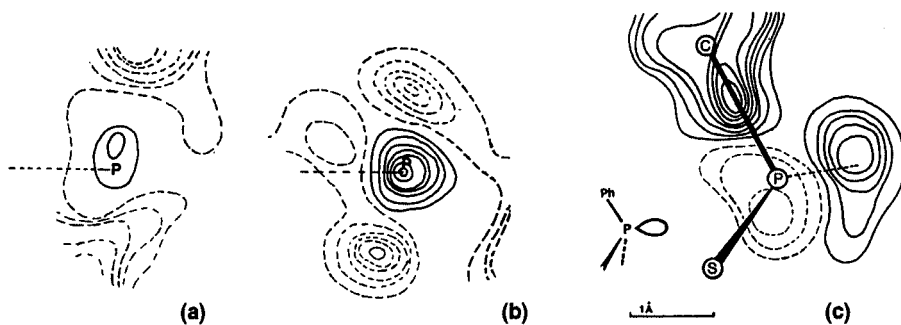
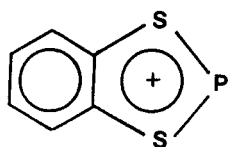
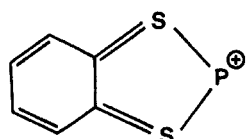


Figure 3 Deformation densities at phosphorus. The cation with phosphorus (a) uncharged, (b) with a charge of +0.58 and (c) the neutral molecule. Contours $0.1\text{e}/\text{\AA}^3$.

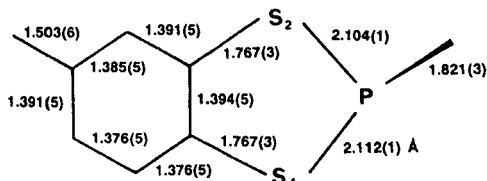
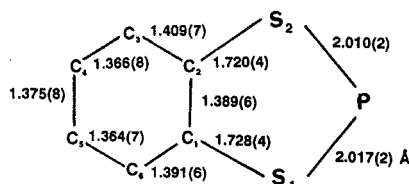
While the deformation densities within the rings of the cation are broadly in agreement with a 10 electron $p\pi$ - $p\pi$ aromatic system (IVa), the apparent concentration of positive charge on the phosphorus atom, the increase in the density along the C - S bond and the pattern of the bond lengths in the two systems all suggest that there is a significant contribution to the structure from the quinoid form (IVb).



(IVa)



(IVb)



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