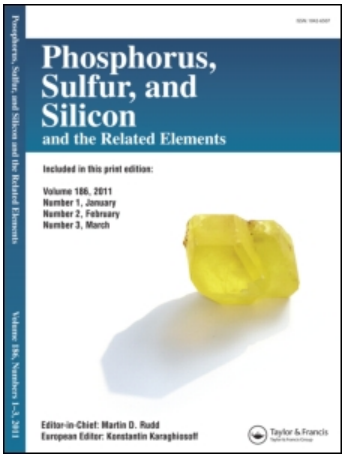

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ELECTRON DENSITY STUDIES OF THE PHOSPHORUS-SULPHUR BONDING IN THE 1,3,2-BENZODITHIAPHOSPHENIUM CATION

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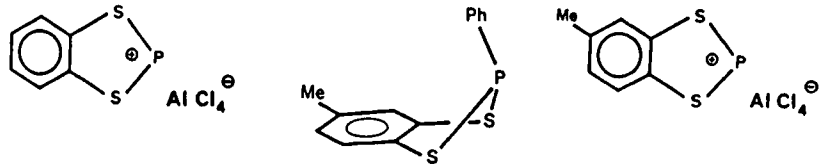
Abstract Detailed electron density studies of 5-methyl-2-phenyl-1,3,2-benzodithiaphosphine have revealed the lone-pair electrons on the phosphorus and sulphur atoms. Corresponding studies of 5-methyl-1,3,2-benzodithiaphosphenium tetrachloroaluminate support the proposal that the planar cation is a 10 electron $p\pi$-$p\pi$ aromatic system analogous to naphthalene, although some quinoid character is evident.

INTRODUCTION

In the recent report[1,2] of the preparation and X-ray structure determination of 1,3,2-benzodithiaphosphenium tetrachloraluminate (1) and the corresponding 5-methyl-2-phenyl-1,3,2-benzodithiaphosphine (2) it was observed that while the atoms of the benzodithiaphosphenium (bdp) cation were all coplanar, the phosphorus atom in 2 was 0.53 Å from the plane of the remaining eight atoms of the benzodithiaphosphine group. The coplanarity of the atoms in the bdp cation (mean deviation from the plane of 0.01 Å) has since been observed[3] in 5-methyl-1,3,2-benzodithiaphosphenium tetrachloroaluminate (3). These observations, in conjunction with nmr studies led the authors to propose that the bdp cation was a ten electron $p\pi$-$p\pi$ aromatic system analogous to naphthalene.

Though the evidence for this proposal is strong, it is circumstantial. With the nmr studies, the bdp cation is a sufficiently novel system that there are few close comparisons, and the studies themselves suggest that the highly reactive bdp



1 2 3

cation may be undergoing further modifications in solution. While the X-ray studies show a high degree of coplanarity among the atoms of the bdp cations (1,3), they also show 8 and 9 significant interactions respectively between the cation and chlorine atoms from several anions within each structure (Figure 1). The possible influence of these interactions cannot be ignored.

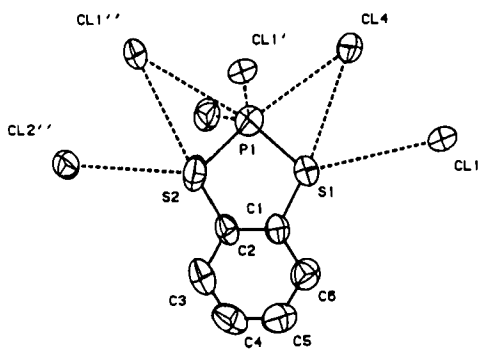


FIGURE 1 Cation - anion interactions for 1.

In an attempt to clarify the situation, it was decided to look more carefully at the structures of the phosphene (2) and the 5-methyl bdp cation (3) to see if it was possible to establish the nature of the bonding within the bdp cation by direct observation of the pattern of electron density.

RESIDUAL ELECTRON DENSITY STUDIES

It has been shown[4] that if great care is taken with the collection of X-ray intensity data from well formed crystals, it is then possible to subtract the contribution of the spherically symmetric

core electrons from the observed X-ray data. When a Fourier synthesis is calculated with the residuals (the Difference Map), a picture emerges of the electron density of the spatially restricted (bonding and lone-pair) electrons. Naphthalene is one of the molecules well studied[5] by this method and so is available for comparison with the bdp cations (1,3).

Unlike naphthalene, however, bdp contains sulphur and phosphorus atoms in the fused rings of the cation. These atoms not only contribute their bonding electrons to the system but also are thought to have non-bonding, spatially-restricted lone-pair electrons which might be an added complication with the study, and it was important to know whether the presence of these non-bonding electrons could be detected. The work of Coppens[6,7] and of Hermansson[8] have shown that, for compounds containing nitrogen and oxygen atoms, residual electron density can be observed in regions where lone-pair electrons are expected. As far as the authors are aware, there have been no reports of observations of lone-pair electron density near either sulphur or phosphorus atoms of molecules containing both sulphur and phosphorus.

Analysis of the Phosphine (2)

The phosphorus and sulphur atoms in the phosphine (2) should have lone-pair electrons in well defined and predictable positions (Figure 2) and, as an initial investigation, a new set of carefully collected X-ray intensity data was prepared. The data were collected at room temperature (291 K ± 0.5) with a long maximum scan time (120 s), with individual centering checks on each reflection, and over a θ range of 2-27° ($\sin(\theta_{max})/\lambda$ = 0.64). The space group for the phosphine is monoclinic but somewhat more than the triclinic set of reflections was collected. When the 6997 individual reflections were merged into a unique set of 2721 reflections the merging agreement index, R_{merg}, was 2.2%. Of the 2721 unique reflections 1199 had $I > 2\sigma(I)$.

The crystal was unusually well formed and gave reflections

that were sharp with a well defined, clean rise from the baseline. At no time in the data collection did the observed reflection maximum deviate by more than 0.01° from the expected position. A detail of the electron density map is shown in Figure 2 where it can be seen that the prominent features of the map include electron density protruding from the sulphur and phosphorus atoms in the positions and directions which would be predicted for lone-pair electrons. The results of the residual electron density calculations in the regions of the sulphur and phosphorus atoms can be seen in Figure 3. It would appear from this study that it

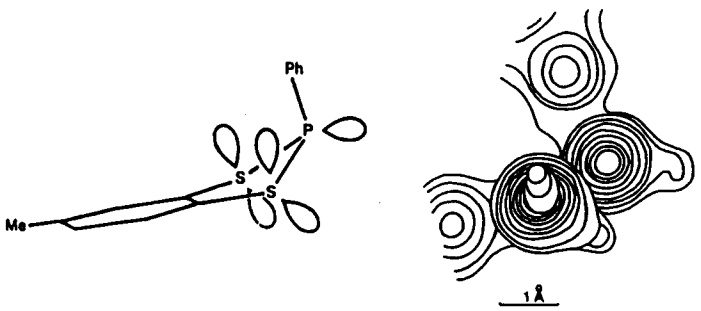


FIGURE 2 Predicted locations of lone-pairs on 2 and the electron-density map of 2 projected down the S(1)-S(2) axis.

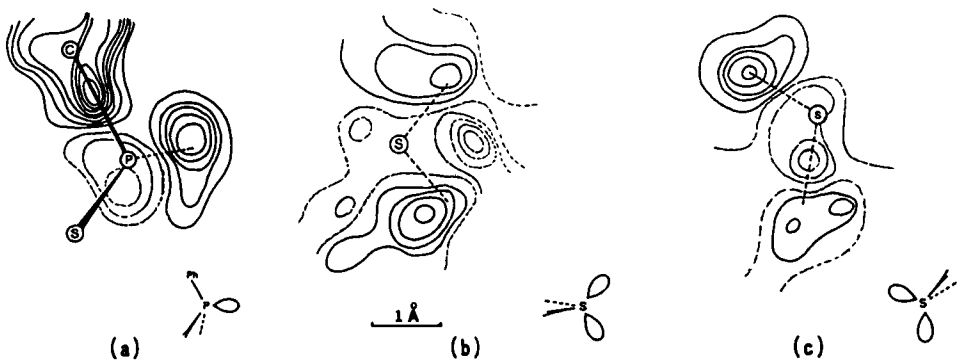


FIGURE 3 Residual electron-density for 2: (a) about P; (b) about S(1); (c) about S(2). Broken lines indicate regions of negative density.

may be possible to detect the electron density associated with the lone-pairs on phosphorus and sulphur atoms.

Analysis of the Bdp Cations (1,3)

The crystals of 1, although perfectly adequate for the routine X-ray structure determination have not yet been grown to a quality suitable for residual electron density work. However the crystals of the corresponding 5-methyl bdp cation (3) have many of the qualities of those of the phosphine (2). Accordingly a carefully collected set of data was prepared* for 3 and the residual electron density Fourier map was calculated. Figure 4 shows the residual electron density in the plane of the cation with the corresponding dimensions of the cation, while, for comparison, Figure 5 shows the residual electron density for naphthalene together with the latest dimensions of naphthalene.

There are striking similarities and differences between the two Figures. The bonding electron density in naphthalene is clearly visible between the carbon atoms, but not so clearly as in other work by Coppens[6]. The residual electron density of the 5-methyl bdp cation (3), though less regularly symmetric than that observed for naphthalene, still retains considerable symmetry. The density along the C - H bonds is clear but not so well defined as in the Dunitz work[5] and only some of the ring bond density appears. However, since it is not clear where the positive charge is located on the cation, neutral atoms were used in the model that calculated the contribution from the non-bonding electrons. Consequently the contribution from the non-bonded electrons has been exaggerated by one extra electron. It is interesting in this

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*Crystal data for 3: $C_7H_6PS_2AlCl_4$, M = 354.01, monoclinic, space group $P2_1/c$, a = 8.030(1), b = 9.346(3), c = 18.758(3) Å, β = 96.47(1)°, V = 1398.9 Å^3, Z = 4, D_c = 1.681 g cm^{-3}, μ = 12.67 cm^{-1}, Mo K_α radiation (λ = 0.70926 Å), final R = 0.0427. Reflections: 3231 measured, 2458 unique, 1204 observed ($I > \sigma(I)$).

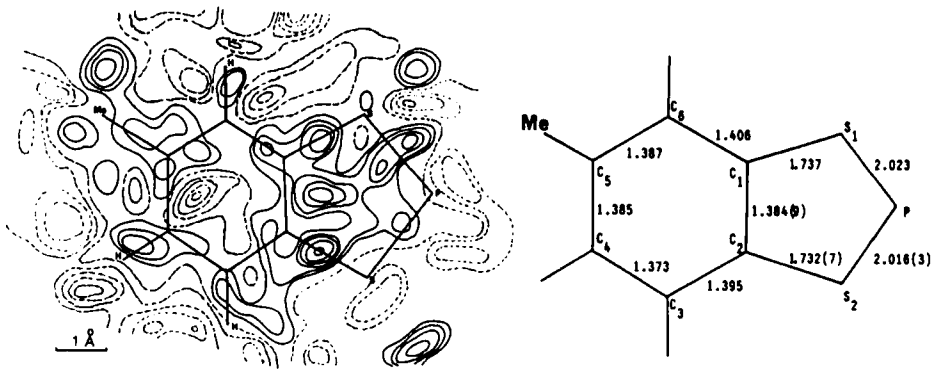


FIGURE 4 The bdp cation of 3: residual electron-density map at 291 K and bond distances.

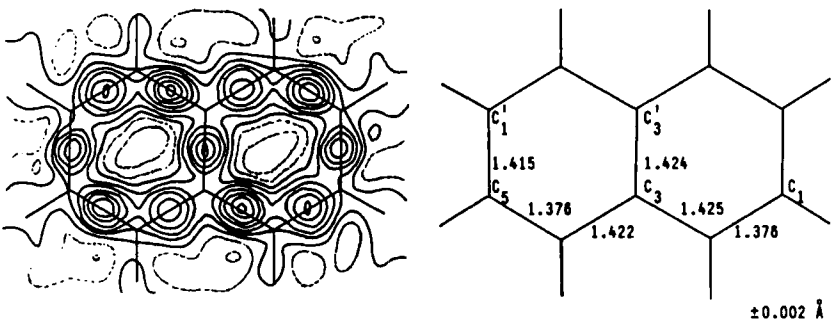
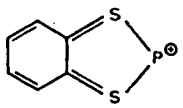


FIGURE 5 Naphthalene: residual electron-density map at 92 K (with permission from J.D. Dunitz) and bond distances.

respect to note that in Figure 4, the phosphorus atom occurs in a negative region of the map, indicating that proportionally rather more electron density has been removed from the vicinity of the phosphorus atom than should have been removed. This would imply that, of all the atoms, phosphorus is the most positively charged. There also appears to be considerable additional electron density along the C-S bonds and along C(4)-C(3) and C(5)-C(6) which would suggest a contribution from a quinoid structure (4).



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There is sufficient similarity between Figures 4 and 5 to support the conclusion that the bdp cations (1,3) may be 10 π-electron aromatic systems, albeit with some quinoid character, but curiously, there is no clear indication in the residual electron density map of 3 of any lone-pair electrons at the phosphorus or sulphur atoms.

In conclusion it should be noted that the work reported here should not be regarded as in any way definitive but more as an indication that the investigation is showing some promise. Before any firm conclusions can be made it will be necessary to examine the residual electron density maps from data collected at a number of temperatures and in particular at the lowest temperature obtainable at which the crystals remain intact. Only if the features seen at room temperature are retained, more sharply defined, at lower temperatures can the observations reported here be confirmed. This work will be undertaken in winter when suitably dry atmospheric conditions can be obtained in our laboratory.

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REFERENCES

1. N. Burford, B.W. Royan, A. Linden and T.S. Cameron, J. Chem. Soc., Chem. Commun., 842 (1988).
2. N. Burford, B.W. Royan, A. Linden and T.S. Cameron, to be published in Inorg. Chem.
3. T.S. Cameron and A. Linden, unpublished work.
4. J.D. Dunitz, Bull. Chem. Soc. Japan, 61, 1 (1988).
5. C.P. Brock and J.D. Dunitz, Acta Crystallogr., B38, 2218 (1982).
6. P. Coppens, R. Boehme, P.F. Price and E.D. Stevens, Acta Crystallogr., A37, 857 (1981).
7. F. Baert, P. Coppens and E.D. Stevens, Acta Crystallogr., A38, 143 (1982).
8. K. Hermansson, J.O. Thomas and I. Olovsson, Acta Crystallogr., C40, 335 (1984).