Multiple bonding, π-bonding contributions and aromatic character in isoelectronic boron–phosphorus, boron–arsenic, aluminium-nitrogen and zinc-sulfur compounds

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Abstract - Variable temperature ^{1}H NMR studies of various boron-phosphorus (B-P) and boron-arsenic (B-As) compounds have afforded data on the strength of B-P and B-As π-bonds. For [RPBMes$_2$]$^-$ and [RAsBMes$_2$]$^-$ ions the energy of the π-bond can be as high as 24 kcal mol^{-1} and 21 kcal mol^{-1}, respectively. Inversion barriers near 10 kcal mol^{-1} were determined for the pnictide center in simple monomeric phosphino or arsino boranes. The effects of substituent size and type on the B-P or B-As multiple bonds were also investigated. Compounds with extended linear arrays of up to five boron or phosphorus atoms were also synthesized and characterized both structurally and spectroscopically. In addition, the aromaticity of six-membered rings comprised of (B-P)$_3$ arrays was investigated. Structural spectroscopic and theoretical data support the view that the unsaturated B$_3$P$_3$ ring system has greater aromatic character than borazine. The range of quasi aromatic rings was also extended to include the isoelectronic and isolobal rings comprised of the arrays (Al-N)$_3$ (alumazene) (:GeN)$_3$, and (ZnS)$_3$. The bonding and the relative aromatic character of these rings is also discussed.

INTRODUCTION

The isoelectronic and isolobal concepts have proved to be extremely useful in correlating many structural relationships for a great variety of inorganic, organic and organometallic compounds (Ref. 1). The idea that isoelectronic molecules tended to have similar structures has been recognized for a long time. A classic example of such a comparison are the molecules benzene and borazine which possess a close structural (if not chemical) relationship. The analogy also holds for other boron-nitrogen compounds, for example, the aminoboranes, R$_2$BNR$_2$', and iminoboranes, RBNR', which are structurally analogous to alkenes and alkynes (Ref. 2). In a broader context it is often possible to interchange isoelectronic and isolobal fragments of molecules comprised of the first row elements and obtain molecules which have very similar structures. There is, however, a mounting body of evidence, involving recently synthesized derivatives of the heavier main group homologues, that shows that the established structural relationships may not generally hold for these species. An example of this involves the Si, Ge and Sn analogues of the ethenes in which greater pyramidicity at the main group 4 element is observed with increasing atomic number (Ref. 3). Recent work in this laboratory and elsewhere has been focussed on examination of the heavier analogues of the B-N system and some of this work regarding the B-P homologues has been summarized in a recent review, wherein the significant differences between the B-N and B-P systems were discussed (Ref. 4). In this paper the latest developments in the boron-phosphorus area are summarized. In addition, extension of this work to boron-arsenic, aluminum nitrogen compounds, and other isoelectronic and isolobal species is described.

BORON–PHOSPHORUS AND BORON–ARSENIC MULTIPLE BONDING

Unlike aminoboranes, the phosphino- and arsenoboranes are normally associated in a head-to-tail manner to give oligomers that have six- or eight-membered ring structures with 4-coordinate B and P or As centers (Ref. 5). Such compounds are normally very stable and unreactive . In addition, the bonding between the boron and the phosphorus or arsenic centers is of a purely σ-type. Their structures feature an approximately tetrahedral geometry at B and P, and B-P distances that usually fall in the range 1.94 - 2.0A (Refs. 4 and 5). Oddly, no structures of the corresponding arsenic derivatives have been published. Presumably, they resemble the structures of the phosphorus species closely. Multiple bonding becomes significant only when the coordination number of the B and P or As centers can be lowered. The simplest example of multiple bonding may occur in a monomeric phosphinoborane or arsenoborane such as R$_2$BPR$_2$' or R$_2$BAsR$_2$' (R and R' = alkyl or aryl group). Until recently, monomers of this type were unknown (Ref. 4). However, monomers can be obtained if bulky groups are introduced at boron as illustrated by the examples in Figs. 1 and 2 (Ref. 6, 7).
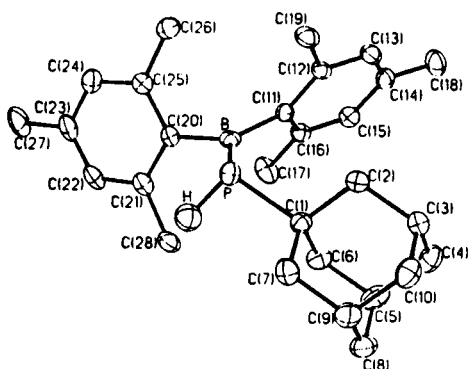
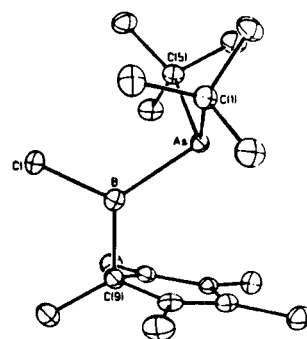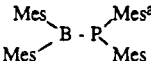Fig. 1 (Ref. 6) Drawing of Mes$_2$BP(H)(1-Ad).
Structural details are in Table 1.
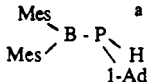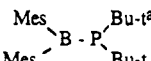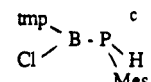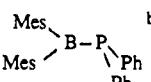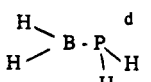
Fig. 2 (Ref. 7) Drawing of Cp*(Cl)BAs(t-Bu)$_2$
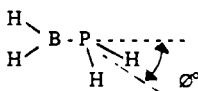B-As = 2.085(4) Å, $\Sigma°$ As = 311.7°, ϕ (Table 1) = 69°.

The structures of the monomers differ from their nitrogen counterparts in that the phosphorus or arsenic center is usually found to have pyramidal geometry. Planarity may be induced at P or As in three ways: (a) by the use of bulky substituents at P or As, (b) by the use of electropositive substituents at P or As or (c) by the use of electron withdrawing substituents on boron. The major reason for the differences in structure between aminoborane compounds and their heavier analogues is the much larger inversion barrier at the heavier element center. For example, the inversion barrier in NH$_3$ is ca. 5-6 kcal mol^{-1} whereas in PH$_3$ it is ~37 kcal mol^{-1} (Ref. 8) and in AsH$_3$ (Ref. 9) it is ~44 kcal mol^{-1}. Calculations on the hypothetical molecule H$_2$BPH$_2$ indicate that,in the ground state,the phosphorus center is indeed pyramidal although the barrier to inversion is greatly reduced to 8.14 kcal mol^{-1} (Ref. 10). The reasons for this reduction involve the significant conjugation of the boron p-orbital and the phosphorus lone pair and also the substitution of the relatively electropositive boryl substituent on phosphorus. Variable temperature ^{1}H NMR experiments on Mes$_2$BPPh$_2$ (Ref. 11) and Mes$_2$BP(H)(1-Ad) indicate the presence of inversion barriers of 10 and 11.4 kcal mol^{-1} (Ref. 6), which are in reasonably good agreement with the theoretical predictions. The B-P bond lengths in these compounds are 1.859(3) and 1.897(3) Å and there is a close correlation between the B-P bond length and the degree of pyramidity at phosphorus. No inversion barriers were observed for Mes$_2$BP(t-Bu)$_2$ or Mes$_2$BPMes$_2$ (Ref. 6),which is in harmony with the planar or near planar phosphorus geometry observed for their crystal structures. The short B-P bond lengths 1.844(6) and 1.839(8) Å are also in accord with the planarity at P. Details of the structures of these and related compounds are provided in Table 1.

As previously mentioned, planarity may also be induced by the introduction of electropositive groups at phosphorus or arsenic. Example of this are the lithium salts illustrated in Figs. 3 and 4 (Ref. 6, 13).

TABLE 1. Important structural parameters of phosphinoboranes.

	B - P, Å	$\Sigma°$P	$\varnothing°$		B - P, Å	$\Sigma°$P	$\varnothing°$
Mes$_2$B-PMes$_2$ [a]	1.839(8)	~360	~0	Mes$_2$B-P(H)(1-Ad) [a]	1.897(3)	315	61
Mes$_2$B-P(Bu-t)$_2$ [a]	1.844(6)	356	3	(tmp)(Cl)B-P(H)(Mes) [c]	1.948(3)	307.1	71
Mes$_2$B-P(Ph)$_2$ [b]	1.859(3)	339.4	40	H$_2$B-P(H)$_2$ [d]	1.91	306.7	70

$\varnothing$ = out of plane angle

[a]Ref. 6, [b]Ref. 11, [c]Ref.12, [d]Ref. 10
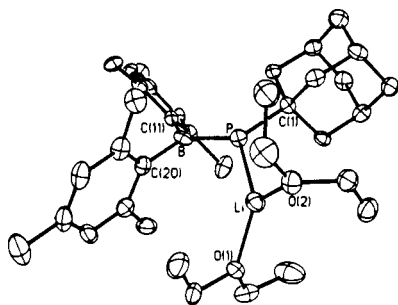
Fig. 3 (Ref. 6) Diagram of [Li(Et₂O)₂P(1-Ad)BMes₂]
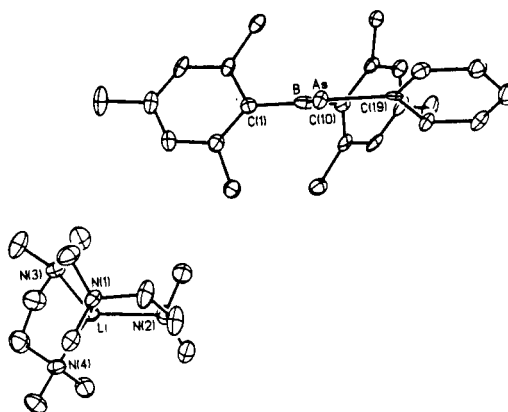The B-P distance is 1.823 Å, the angle between the B
P planes is 15.9°.

Fig. 4 (Ref. 13) Diagram of the ion pair
[Li(TMEDA)]₂[AsPhBMes₂]. The B-As and
distance is 1.936(11) Å. The angle between
the B and As planes is 1.1°.

In these compounds the boron and phosphorus or arsenic centers are planar. In addition, there is only a small (<10°) twist angle between the boron and pnictide planes. The B-P and B-As distances are quite short and vary in the range 1.8°-1.83 Å for B-P (Ref. 4) and 1.92-1.93 Å for B-As bonds. Variable temperature ¹H NMR data show that the barrier to rotation around the B-P bond is at least 24 kcal mol⁻¹ (Ref. 6) and for the B-As compound it is 21 kcal mol⁻¹ (Ref. 13). These values are comparable to rotational barriers around the B-N bond in aminoboranes (Ref. 14) and are indicative of substantial multiple bonding owing to the presence of a fairly strong B-P or B-As π-interaction. The presence of two boryl groups on the phosphorus atom also effects planarity (Fig. 5, Ref. 15). The use of a strongly electron withdrawing substituent on boron as illustrated in Fig. 6 (Ref. 16) also induces the geometry at the phosphorus centers to become much flatter.
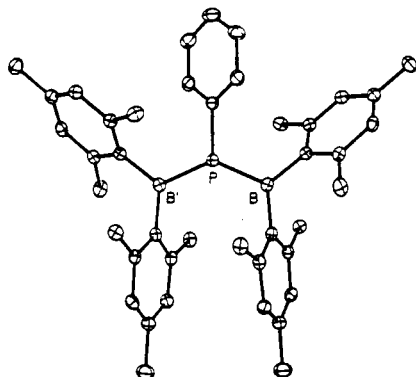

Fig. 5 (Ref. 15) Structure of the allyl cation
analogue PhP(BMes₂)₂ the B₂PC(ipso)₅ array is
planar, the B-P bond is 1.871(2) Å long and the BPB
angle is 131.0(2)°.
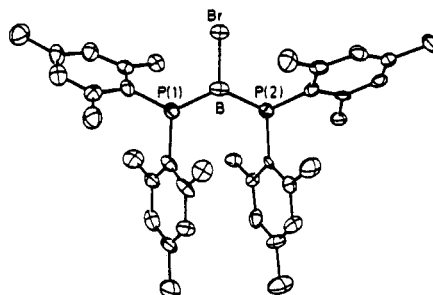
Fig. 6 (Ref. 16) Structure of the allyl anion
analogue BrB(PMes₂)₂, B-P = 1.83 Å,
Σ°P ≈345°.

Other compounds involving arrays of boron and phosphorus atoms are also possible. One such species is the 1,2 diborylphosphane (Ref. 17) as shown in Fig. 7. This compound was synthesized by the reduction of LiP(1-Ad)BMes₂ with CrCl₃.
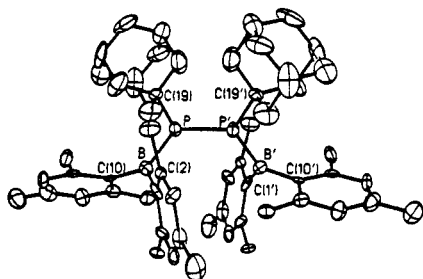

Fig. 7 (Ref. 17) Thermal ellipsoidal plot of the
butadiene analogue [P(1-Ad)BMes₂]₂. The phosphorus
centers are planar. The PP single bond is only
2.109(4) Å long.
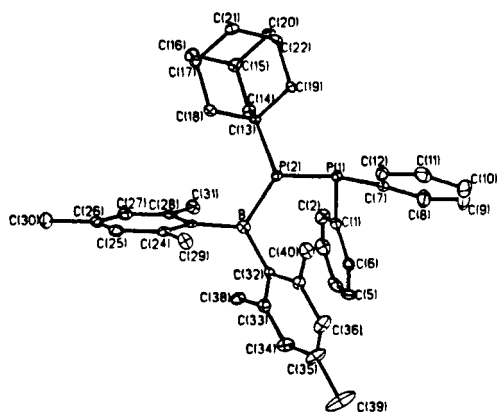
Fig. 8 (Ref. 18) Structure of $Mes_2B(1-Ad)PPPh_2$ which has a bond between pyramidal and planar P centers. The P-P distance is 2.173(2) Å.

Its structure shows that it has an exceedingly short P-P single bond distance of ~2.11 Å and planar phosphorus centers (Ref. 17, 18).   The shortness of this bond length, which is halfway between a normal P-P single and double bond, has been explained on the basis of a strong rehybridization effect upon the PP bond length.   An intermediate case,wherein there is a bond between a planar and a pyramidal phosphorus (Fig. 8), also affords a shortened P-P bond (Ref. 18).   Other interesting variations in the phosphorus or arsenic boron array of compounds involve the 1,2 diphosphino diboron or diarseno derivatives, which may also behave as ligands to transition metal compounds Figs. 9 and 10 (Ref. 21).
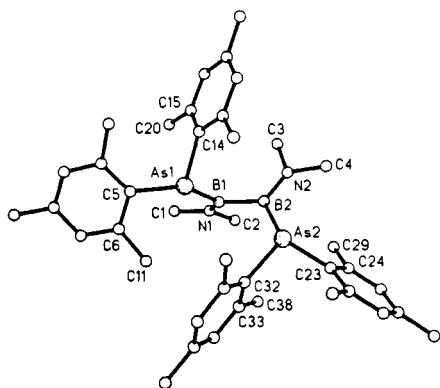

Fig. 9 (Ref. 21) Diagram of $[B(NMe_2)AsMes_2]_2$. The B-N, B-B and B-As distances are 1.383(11) Å (avg.), 1.725(14) Å , and 2.08(1) Å (avg.), $\Sigma°As = 319.5°$.

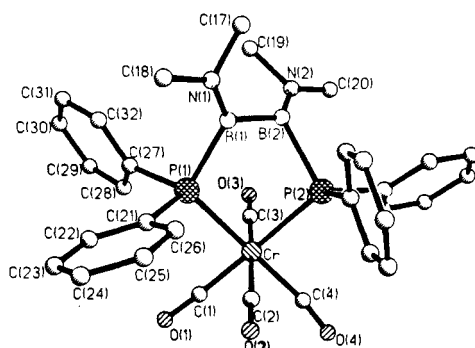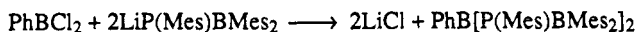Fig. 10 (Ref. 21) Diagram of the complex cis-$[(BNMe_2PPh_2)_2Cr(CO)_4]$. The B-N, B-B B-P and P-Cr distances are 1.36(4) Å, 1.70(4) Å, 1.99(3) Å and 2.426(7) Å.

More extended arrays may be obtained via the reaction (Ref. 6)

$$PhBCl_2 + 2LiP(Mes)BMes_2 \longrightarrow 2LiCl + PhB[P(Mes)BMes_2]_2$$
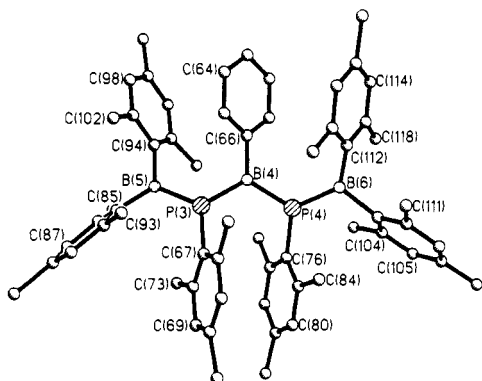
The structure of the product may be illustrated by Fig. 11 (Ref. 6)

Fig. 11. The structure of the pentadienyl cation analogue $PhB[P(Mes)BMes_2]_2$. The B and P centers are planar, the average B-P distance is 1.85 Å and the planes at B and P are twisted relative to each other by an average of 10°.

All the boron and phosphorus centers in this molecule are planar and the B-P distances fall in the range 1.82-1.88 Å. All the planes are twisted ~10° relative to each other. Clearly, there is extensive delocalization in this B-P array and it is isoelectronic to the pentadienyl cation.

In summary, the above experimental data have demonstrated that the phosphino- and arsinoboranes possess significant differences from their nitrogen counterparts. The pyramidity at the main group 5 center can be changed readily by adjusting the size, number and type of the substituents. The B-P or B-As bond order may, in effect, be varied between virtually single and double bonding. When the electronic conditions at the phosphorus or arsenic centers are suitable quite strong multiple bonding may be observed.

BORON–PHOSPHORUS RINGS

The planar structure and the allylic nature of the $>$BPB$<$ and $>$PBP$<$ arrays suggested that it should be possible to obtain delocalized ring systems involving B-P or B-As arrays since such rings would include either one or both moieties. The synthesis of such rings is, in fact, extremely simple and involves the reaction of a primary boron dihalide with two equivalents of a lithium salt of a primary phosphine as in

$$RBBr_2 + 2LiPHR' \longrightarrow 1/n\ (RBPR')_n + H_2PR' + 2LiBr$$
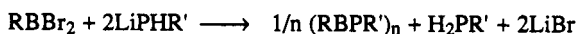
$$n = 2;\ R/R' = Mes/1\text{-}Ad,\ Thexyl/Mes,\ Mes/t\text{-}Bu$$

$$n = 3;\ R/R' = Mes/C_6H_{11},\ Mes/Ph,\ Mes/Mes$$

$$Mes/t\text{-}Bu$$

The six-membered (B-P)$_3$ rings, are boron-phosphorus analogues of borazine or benzene. The four-membered rings (B-P)$_2$ are analogues of the corresponding B-N compounds or cyclobutadiene. Their structures may be illustrated by Figs. 12 and 13 (Ref. 19, 20).
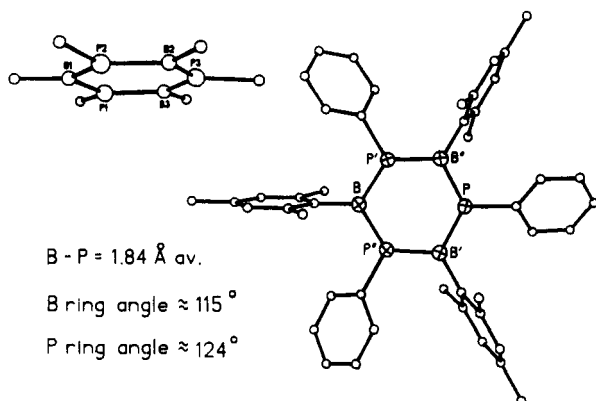

B - P = 1.84 Å av.

B ring angle ≈ 115°

P ring angle ≈ 124°

Fig. 12 (Ref. 19) Schematic drawings of (PhPBMes)$_3$.
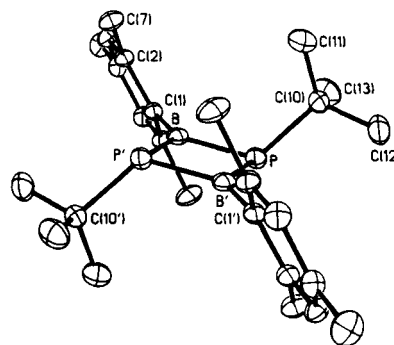

Fig. 13 (Ref. 7) Drawing of (t-BuPBMes)$_2$. The B-P distances average 1.897(2) Å, $\Sigma°P = 328.8°$.

The planar B$_3$P$_3$(C ipso)$_6$ array, the shortness (1.84 Å) and the equivalence of the B-P bonds are suggestive of extensive delocalization. In harmony with this view the B-P bonds in the antiaromatic four-membered rings are longer, 1.9 Å. Moreover, the phosphorus centers are pyramidal indicating that delocalization is much less in these compounds than in the six-membered ring species. In effect, the lone pairs remain much more localized on phosphorus in the four-membered ring which can affect the ^{31}P chemical shift by as much as 100 ppm. A notable feature of all boron phosphorus compounds is that in a competitive bonding circumstance where nitrogen and phosphorus lone pairs compete for an empty boron p-orbital the B-N multiple bonding is dominant as seen in the 1,2-diphosphino(arseno)diboron compounds mentioned earlier. The same situation is observed in the six-membered ring compounds PhP[B(NMe$_2$)B(NMe$_2$)]$_2$PPh featuring two phosphorus and four boron atoms as illustrated Fig. 14 (Ref. 21).
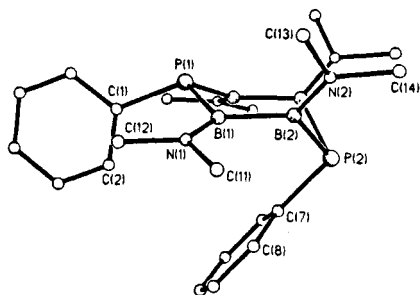
Fig. 14. Drawing of the ring PhP[B(NMe$_2$)B(NMe$_2$)]$_2$PPh.

B-P = 1.945(3) Å (avg.)

B-B = 1.713(5) Å,

B-N = 1.398(4) Å (avg.),

$\Sigma°P(1)$ 329.1°, $\Sigma°P(2) = 284.5°$.

OTHER QUASI AROMATIC RINGS

The facility with which the six-membered rings could be synthesized led, almost immediately, to the search for similar systems involving other array main group elements. An obvious analogy to the B-P system is the corresponding Al-N species. The reaction

$$AlMe_3 + H_2NDipp \longrightarrow 1/3(MeAlNDipp)_3 + 2CH_4$$

$$Dipp = 2,6,-i-Pr_2C_6H_3$$
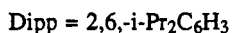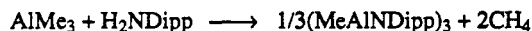
affords a good yield of the 'alumazene' ring, which is an aluminum analogue of borazine and isoelectronic to the $(B-P)_3$ systems (Ref. 22). The $Al_3N_3C_6$ array is p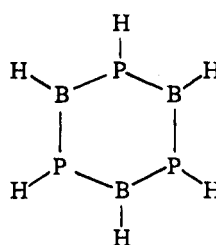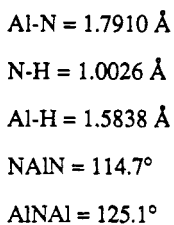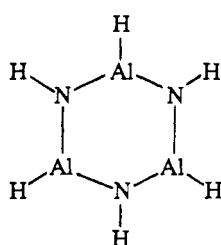lanar and the plane of the Dipp rings are at an angle of 75.2° to the Al_3N_3 plane as illustrated in Fig. 13. The Al-N distance, 1.78 Å, is quite short and is the same length as the Al-N bond in $Al[N(SiMe_3)_2]_3$ the only other structurally characterized compound that features bonding between three coordinate aluminum and nitrogen (Ref. 23). Unlike the six-membered B-P rings the alumazene molecule is very air sensitive and displays no evidence of delocalization. These indications are borne out by the theoretical data on the isoelectronic molecules $Al_3N_3H_6$ and $B_3P_3H_6$. The calculated (Ref. 24) structural parameters, which may be illustrated by the schematic diagrams,

Al-N = 1.7910 Å

N-H = 1.0026 Å

Al-H = 1.5838 Å

NAlN = 114.7°

AlNAl = 125.1°

B-P = 1.8576 Å

B-H = 1.1779 Å

P-H = 1.3944 Å

BPB = 123.0°

PBP = 177.0°
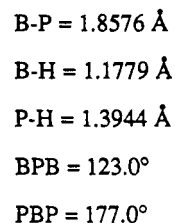
are in good agreement with the experimental data. The degree of aromaticity in the rings has been estimated from the homodesmotic (Ref. 25) reactions as illustrated in Table 2. In these reactions, wherein the number and types of bond remain the same on both sides of the equation, the difference in energy is taken to be an estimate of the stabilization induced by delocalization of the π-electrons. In the case of carbon there is very good agreement with the calculated data and this gives grounds for confidence in the approach.
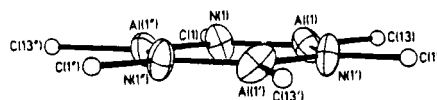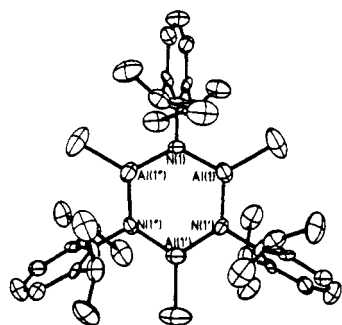

Fig. 15 (Ref. 23) Drawings of (MeAlNDipp)₃.
The AlN distance is 1.782(4) Å.

TABLE 2. Energies of Reaction for Homodesmotic Reactions of $B_3P_3H_6$, $Al_3N_3H_6$, $B_3P_3H_6$ and C_6H_6

	ΔE_{rxn} (kcal)		
Reaction	3-21G*	6-31G*	MP4SDQ 6-31G*
$C_6H_6 + 3C_2H_4 \rightarrow 3C_4H_6$	27.7	24.7	22.1
$B_3N_3H_6 + 3H_2BNH_2 \rightarrow 3B_2N_2H_6$	7.7	8.4	11.1
$B_3P_3H_6 + 3H_2BPH_2 \rightarrow 3B_2P_2H_6$	8.1	7.4	12.7
$Al_3N_3H_6 + 3H_2AlNH_2 \rightarrow 3Al_2N_2H_6$	1.8	0.8	1.9

W.H. Fink, J. Richards, unpublished results 1990.

Transoid optimized geometries were used for all butadiene analogues.

It can be clearly seen that the stabilization for borazine is about half of that for benzene. The stabilization calculated for the $B_3P_3H_6$ molecule is slightly greater than that of borazine whereas the energy for alumazene $Al_3N_3H_6$ is calculated to be only 1.9 kcal. Clearly, the delocalization in the Al-N system is much less than that in $B_3P_3H_6$. This may be rationalized on the basis of the much greater polarity of the Al-N bond in comparison to B-P bonds.

Other ring systems similar to the Al-N and B-P rings may also be envisaged. For example, the reaction

$$Ge[N(SiMe_3)_2]_2 + H_2NDipp \longrightarrow 1/3[GeNDipp]_3 + 2HN(SiMe_3)_2$$
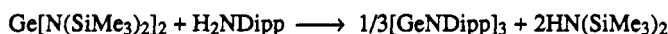
affords (Ref. 27) the planar $Ge_3N_3C(ipso)_3$ array as illustrated by Fig. 16.

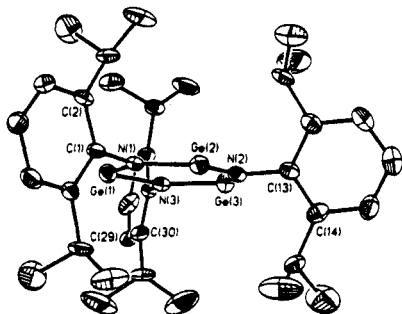
Fig. 16. Drawing of (GeNDipp)₃. The Ge-N distance averages 1.859 Å. The average NGeN and GeNGe angles are 101.8(1)° and 138.0(2)°.

The Ge-N distances are equivalent and average 1.859(2) Å in length. These bonds, although short, are comparable to the values seen in other Ge(II)-N compounds. Since the disparity in electronegativity between Ge and N is comparable to that between Al-N little delocalization can be expected. The marginally short length of the Ge-N bonds is probably due primarily to a large polar contribution to the bond strength.

It is also possible to conceive of other potentially delocalized rings involving constituents with group numbers that are even more disparate than the Al-N, B-P or Ge-N systems. Such a case involves a ring comprised of chalcogenides and bivalent metals from the Be or Zn groups. In order to minimize the electronegativity differences and maximize the potential for delocalization a Zn-S ring system was chosen.

The reaction between ZnR_2 (R = CH_2SiMe_3) and HSAr (Ar = $2,4,6-R_3'C_6H_2-$, R' = i-Pr or t-Bu) afforded the species $(RZnSAr)_3$ as illustrated in Fig. 17. With a more bulky thiol, $HSCPh_3$, a dimeric species $(RZnSCPh_3)_2$ was obtained, Fig. 18.
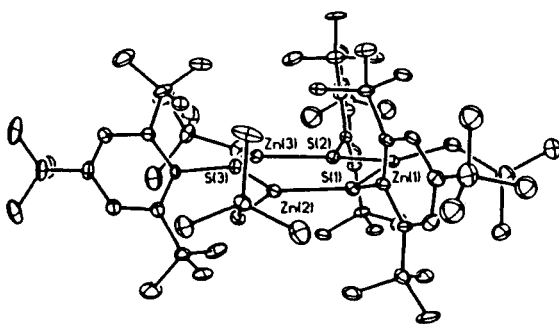

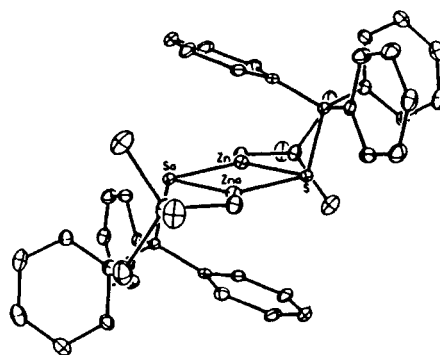Fig. 17. Drawing of (RZnSAr)₃. The average Zn-S distance = 2.308 Å, the average Σ°S = 343.7°.

Fig. 18. (Ref. 28) Drawing of (RZnSCPh₃)₂. The average Zn-S distance is 2.4 Å, the average Σ°S = 285.6°.

The most interesting feature of these rings is the planarity, or near planarity of the $Zn_3S_3C_6$ system in Fig. 17. The planar nature of the sulfur in this molecule is surprising since it is normally pyramidal in a thiolate ligand that bridges two metals.

In the four-membered Zn_2S_2 ring compound (Fig. 18) the sulfur remains pyramidal and the Zn-S distances are longer. This behavior may be interpreted on the basis of some delocalization in the six-membered ring and the lack of this phenomenon in the four membered ring. The Zn-S pair is not quite as polar as B-N so that significant delocalization may be expected. No calculations have been carried out but the unusual structure and low polarity suggests that delocalization energy might approach that of borazine.

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