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The synthesis, characterization and some properties of new quasi-aromatic main group ring systems

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Abstract

The synthesis and characterization of several previously unknown ring systems that involve heavier main group elements are described. Four new types of potentially delocalized six-membered ring compounds that comprise the cyclic arrays (RBPR')₃, (RAINR')₃, (RZnSR')₃ and (GeNR)₃, are considered. The synthetic routes to these rings are straightforward and require only one or two steps to give the respective products in good yield. All the rings have been structurally characterized. The structures, in conjunction with spectroscopic data, indicate considerable variation in delocalization with ring type. Quasi-aromaticity in the case of the (RBPR')₃ ring is well supported by the experimental data and, indirectly, by the non-planar structure that was observed for the 'anti-aromatic' four-membered (RBPR')₂ rings. Further support comes from recent calculations at the SCF level using the basis set 6-31G* which indicate that the (HBPH)₃ system has a similar stabilization to that seen in borazine, whereas the (HAlNH)₃ ring exhibits only a minor degree of delocalization of the π electrons.

Introduction

"The most important ring system of organic chemistry is the benzene ring, either as a separate entity or in polynuclear hydrocarbons such as naphthalene, anthracene and phenanthrene. Inorganic chemistry has two (at least) analogues of benzene: borazine, B₃N₃H₆, and the trimeric phosphonitrilic compounds, P₃N₃X₃."

So begins the section of a modern inorganic text that deals with inorganic rings [1]. Indeed, until recently only a few other cyclic species could have been added to this list. The trithiazyl rings (NSX)₃ [2–4] (isoelectronic with (PNCl₂)₃ [2,4–6] were, perhaps, one possibility. A case could also be made for the inclusion of the (XBO)₃ [7] or (XBS)₃ [8] rings, although the ionic nature of the former and the putative weakness of the B–S bonds in the latter has suggested that the extent of delocalization in these compounds is probably quite limited.

There has, of course, been extensive work elsewhere on quasi-aromatic species that involves different ring sizes and/or different numbers of π -electrons. Classic examples of these rings include the rapidly expanding array of sulfur-nitrogen heterocycles such as S₃N₂²⁺ (6 π -electrons), S₃N₃⁻, (10 π -electrons) or S₄N₄²⁺ (10 π -electrons) [2–4]. The multiple bonding in some homocyclic cations such as S₄²⁺

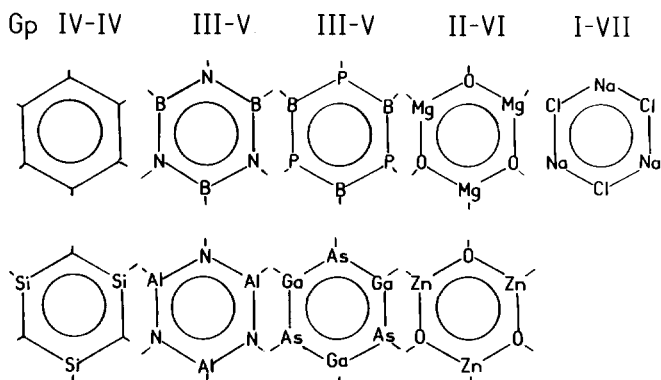


Fig. 1. Schematic representations of some six-membered rings with exactly the same number of valence electrons as benzene or borazine.

[9–11], or anions, such as P_5^- [12], may also be interpreted on the basis of the Hückel rules. Nonetheless, recent work (mostly within the past 5 years) has shown that the number of six-membered, 6 π -electron rings that can be synthesized is much greater than was once realized. For example, there now exist several cyclometallaphosphazene species in which one or more of the phosphorus moieties are replaced by transition metal fragments [13]. Furthermore, it has been shown that it is possible to dispense with phosphorus completely and obtain cyclometallazenes which can, in some instances, be useful precursors for transition metal nitrides [13,14].

This brief review is primarily concerned with novel types of inorganic rings that are more closely related to the borazines. Some examples of these rings are illustrated in Fig. 1, which includes diagrammatic representations of several cyclic species that have exactly the same number of valence electrons as benzene or borazine. Upon proceeding from left to right across this series of rings, the disparity in the electronegativity and the group numbers of the ring components becomes greater, and the bonding becomes more ionic, until the extreme example of trimeric $(NaCl)_3$ is obtained. The suggestion that this species might possess even a tenuous relationship to benzene, either in its electronic properties or chemical behavior is, of course, absurd. For the remaining cyclic species, however, the distinction is not quite as clear because, as will be shown, substantial differences in the electronegativities, the sizes of the ring constituents, and the substituent groups are possible, which makes for considerable variation in the delocalization expected. For the present, the most that may be said about the species in Fig. 1 is that the sum of the valence electrons from adjacent pairs of atoms within these rings is always 8 and these 'even' adjacent pairs each supply two electrons to the π -system.

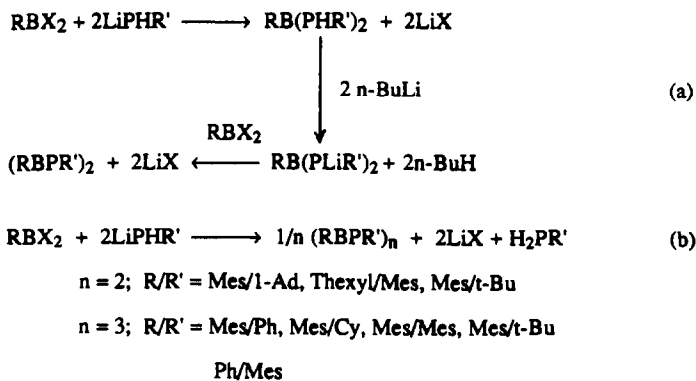
In the simplest case, it is possible to envisage the replacement of some or all of the carbons in benzene by the heavier Main Group 4 congeners Si–Pb to obtain novel delocalized rings. To date, none of these species have been isolated as stable compounds although there have been a number of attempts to synthesize them. The most notable recent example has resulted in the isolation and structural characterization of the interesting trigonal prismatic species $[GeCH(SiMe_3)_2]_6$ [15]. Calculations for the heavier elements have also indicated that species involving framework

σ -bonds are more thermodynamically stable than the more open, π -bonded unsaturated rings [16]. Presumably, this is a consequence of the relatively weak p - p π bonding in the heavier elements. Related species such as SiC_5H_6 have been studied at low (10 K) temperature and its aromatic character was strongly supported by PE spectroscopy and UV-vis data [17]. Greater stability in these rings was introduced by using bulkier substituents but no structures have been reported so far [18]. No doubt a viable synthetic route, involving substituents for either germanium or another of the heavier Main Group 4 congeners, that are appropriate for the kinetic stabilization of a 6π -electron aromatic ring system, will eventually be found.

If the ring atoms in benzene are replaced, alternately, by atoms with one electron more and one electron less than carbon, a ring system comprised of atoms from the Main Group 3 and 5 elements, such as borazine, is obtained. Borazine itself is the foremost example of an inorganic compound that can be closely compared to an organic species. It formally possesses a total of six π -electrons (supplied by the 3 nitrogens) in a manner that is analogous to benzene. It was first reported by Stock in 1926 [19]. Along with the cyclotriphosphazenes (i.e. trimeric phosphonitrilic compounds which were discovered some years earlier) it represented, for many years, the closest approach to aromaticity among purely inorganic compounds. Borazine does indeed possess physical properties that closely resemble those of benzene. There is, however, little evidence for aromaticity in its chemical behavior. This is widely held to be due to less efficient delocalization in the borazine π -electrons owing to differences in electronegativity and size between boron and nitrogen. The polar nature of the BN pairs, in which nitrogen retains some of its basicity and boron its acidity, results in facile addition reactions with HX or X_2 which are not readily observed in conventional aromatic molecules. The electronic structure of borazine has been the subject of considerable experimental and theoretical interest [20]. Photoelectronic spectra of borazine and some of its derivatives show that the highest occupied orbital is of π -type [21]. Calculations of varying degrees of sophistication have indicated, inter alia, that the planar D_{3h} model is energetically preferred to the twisted boat C_2 model. Furthermore, electron population analysis reveals that nitrogen and boron in borazine possess a negative and positive charge, respectively. This distribution arises from the large σ -electron transfer from boron to nitrogen. This is partially compensated by a π -electron donation from nitrogen to boron. The structures of several borazines have also been determined. They reveal that the B-N ring bonds are equivalent within a particular molecule but can vary from 1.39 to 1.436 Å depending on the substituents on nitrogen or boron. The average borazine B-N distances are therefore short and only marginally longer than the values seen in the aminoboranes (1.35 Å) [23], which are the B-N counterparts of ethylene. For comparison a B-N single bond can be estimated (from the sum of the atomic radii [22]) to be about 1.56 Å long and the C-C bond in benzene is 1.40 Å long.

Boron-phosphorus ring systems

In spite of the considerable attention that borazine and its derivatives have received from theorists virtually no computational work had been carried out on rings in which either boron or nitrogen is replaced by their heavier congeners. An isolated instance of an earlier calculation indicated that it might be possible to



Scheme 1. The proposed (a) and actual (b) route to the unsaturated boron–phosphorus rings (RBPR')_n (n = 2 or 3) [26–28].

obtain an unsaturated, stable cyclic B₃P₃ species analogous to borazine [24]. Nonetheless, no well-characterized [25], stable rings of this type appeared until 1987 [26]. Ironically, the synthesis of these rings is, in fact, comparable in simplicity to that of borazine. They were first isolated during the attempted synthesis of the related unsaturated four-membered B₂P₂ rings as indicated by Scheme 1.

A key feature of their synthesis is the use of appropriately sized substituents on boron and phosphorus. Individually the substituents are, by no means, the bulkiest possible. Collectively, however, the six organic groups afford the ring considerable steric protection. Several of the rings have now been isolated and structurally characterized [26,27]. Common structural features of these rings are a planar B₃P₃C(ipso)₆ array and, in addition, equivalent and relatively short B–P bonds that are about 1.84 Å long (cf. B–P single bond ≈ 1.94 Å) (Fig. 2). In contrast, the related four-membered rings (RBPR')₂ feature pyramidal phosphorus centers and

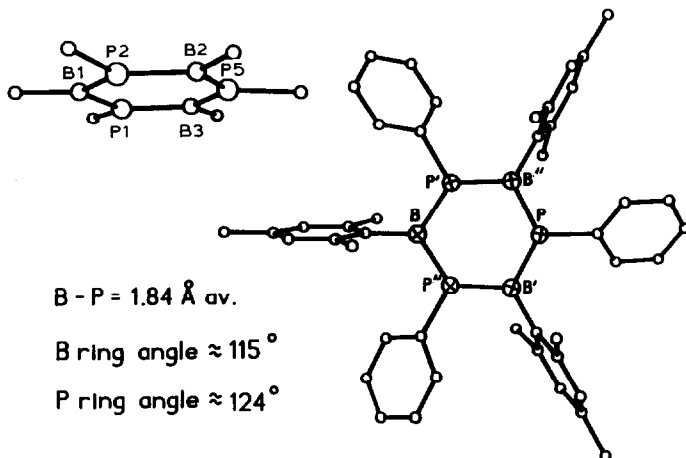


Fig. 2. Computer-generated drawing of the compound (MesBPPPh)₃ [27]. Important structural data are also included.

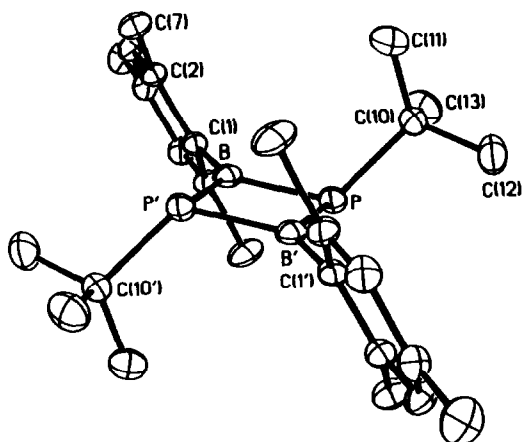


Fig. 3. Computer-generated drawing of the compound (MesBP-*t*-Bu)₂. Important bond distances (Å) and angles (°). B–P = 1.896(2), B'–P = 1.897(2), B–P–C(10) = 120.1(1), B'–P–C(10) = 119.8(1), B–P–B' = 88.9(1).

significantly longer (1.9 Å) B–P bonds (Fig. 3) [27,28]. The four-membered rings were synthesized by the use of larger substituents on boron and phosphorus [27–29]. With some substituent combinations (e.g. *t*-Bu on P and Mes on B) a mixture of both four- and six-membered rings is formed [27,29]. Other examples of these diphosphadiboretanes, that include –NR₂ substituents on boron (e.g. (tmpBPMes)₂ [29(a)] or (tmpBPCEt₃)₂ [29(b)]), have been synthesized by different routes. The result of the nitrogen–boron interaction is seen in the lengthening of the BP bonds. The complicating effect of the amide substituent on the possible multiple bonding ring is avoided by restricting the B and P substituents to alkyl or aryl groups. For further discussion see ref. 30. With smaller substituent groups no pure compounds have been isolated so far. Presumably, these could possess either a polymeric chain structure or, perhaps, cage structures analogous to those observed for the polyiminooalanes [31].

For the six-membered rings, the delocalization suggested by the planar structure is supported by some spectroscopic data. The ³¹P chemical shifts observed appear approximately 70 ppm further downfield than the shifts for the four-membered rings [27,28]. This suggests a considerable deshielding of the phosphorus nucleus by the delocalization of electron density onto boron. In addition, the ¹¹B shifts of the six-membered rings appear further upfield (40–50 ppm) than those of the four-membered rings, which points to a greater shielding of the boron nuclei as a result of the delocalization. The spectroscopic and structural data above are in harmony with the degree of π-bonding predicted for the four and six-membered ring systems on the basis of orbital symmetry. In the six-membered ring three bonding π-orbitals are predicted whereas for the four-membered ring only one strongly bonding π-molecular orbital is possible. For the latter, the next highest energy molecular orbitals available are either weakly bonding or antibonding or non-bonding. In effect, there is, apparently, a considerable energy gain by the delocalization of the π-electrons in the case of the six-membered ring. In the four-membered ring, however, the delocalized structure is not favored because of the higher energy of the highest occupied π-orbitals. The observed structure, in which the lone pairs are

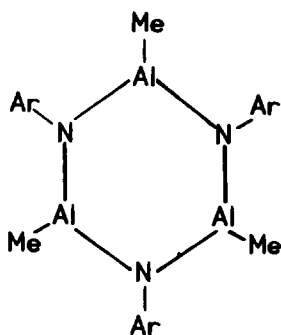
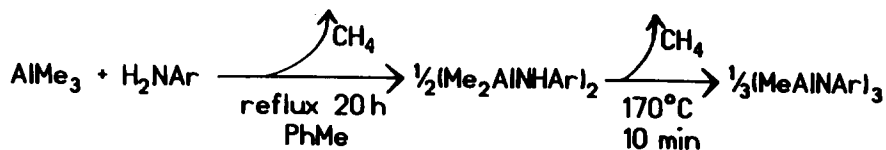
located mainly in relatively stable phosphorus orbitals, is thus consistent with the above bonding model. Further support for delocalization and quasi-aromaticity of the $(\text{RBPR}')_3$ rings comes from ^1H NMR data of species in which either boron or phosphorus or both are substituted by mesityl groups. The chemical shift differences displayed by the *ortho*- and *para*-methyl groups are on average greater than those in open-chain B–P compounds. One possible explanation of this phenomenon involves a ring current in the $(\text{BP})_3$ ring which would affect the *ortho*-methyls much more strongly than the *para*-methyls [27,28].

The chemical properties of the $(\text{RBPR}')_3$ rings are also suggestive of enhanced stability. They are only mildly air sensitive in comparison to the four-membered rings. They react slowly with water to give primary phosphines and boron oxygen compounds. They also react with HCl and Br_2 to give $[\text{RB}(\text{Cl})\text{P}(\text{H})\text{R}']_n$ or RBBR_2 or $\text{R}'\text{PBR}_2$ [32]. This pattern of reactivity resembles that of borazine in some respects. The presence of some polarity in the BP bonds, combined with the strength of the BX and the PH or PX (X = halogen) bonds, provides a favorable pathway and a substantial energy incentive for the above reactions. In spite of a number of attempts, no metal π -complexes featuring the $(\text{BP})_3$ rings have yet been obtained. This is probably due to the collectively high steric requirements of the substituents of the rings isolated so far. Also, it should be feasible to prepare heavier congeners where the phosphorus atoms are replaced by As, Sb, or Bi. These and other interesting derivatives have yet to be isolated.

Aluminum–nitrogen rings

Replacement of the borons, rather than the nitrogens, by heavier congeners is an alternative approach to the synthesis of other cyclic systems. For example, if all the borons are replaced by aluminum it should, at least in principle, be possible to stabilize an Al_3N_3 array to give an 'alumazene' ring. These rings are, in effect, trimers of the iminoalane RAINR' . Higher oligomers of iminoalanes, corresponding to the formula $(\text{RAINR}')_n$, $n = 4-16$, have been known for some time and their structures form a fascinating series of cage complexes with no current parallel in boron chemistry [31,33]. A number of cage structures are also known for gallium [34]. Although several synthetic routes to iminoalanes are known, the most convenient involves a double alkane elimination reaction between a primary amine and an aluminum alkyl. This is because of the ready availability of a significant number of organo-aluminum compounds. In the case of the synthesis of alumazene, methane elimination proceeded smoothly under the conditions described in Scheme 2 to afford the product in high yield [35].

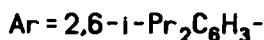
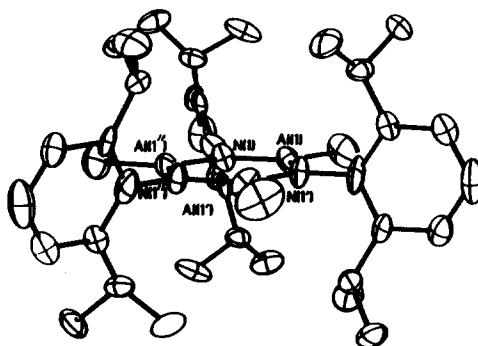
The structure of $[\text{MeAlN}(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)]_3$ consists of a planar $\text{Al}_3\text{N}_3\text{C}_6$ array (Scheme 2). The Al–N bonds are $\sim 1.78 \text{ \AA}$ long and there are slight deviations from idealized 120° angles at N and Al which display internal ring angles of $124.7(5)^\circ$ and $115.3(5)^\circ$, respectively. Obviously, the planar configuration of the ring ensures that the *p*-orbitals on N and Al are correctly aligned for the most efficient overlap. The significance of the amount of shortening in the Al–N bonds is, however, difficult to gauge accurately—much more so than it was in the case of the $(\text{RBPR}')_3$ ring. There are two major reasons for this difficulty. First, the effective radius of aluminum in its compounds appears to vary considerably with substituent type. For example, in the compound R_2AlAlR_2 (R = $\text{CH}(\text{SiMe}_3)_2$) the Al–Al distance is 2.66



$$\text{Al-N} = 1.78 \text{ \AA}$$

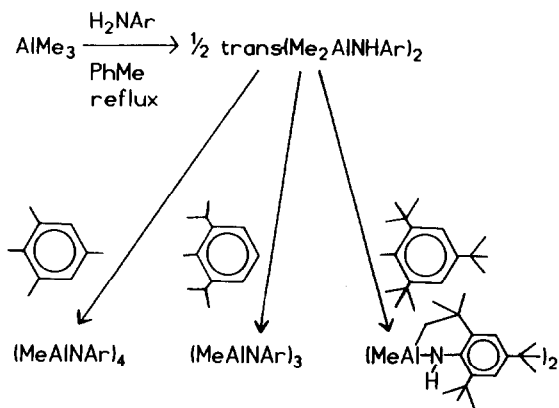
$$\text{N-Al-N} = 115^\circ$$

$$\text{Al-N-Al} = 125^\circ$$



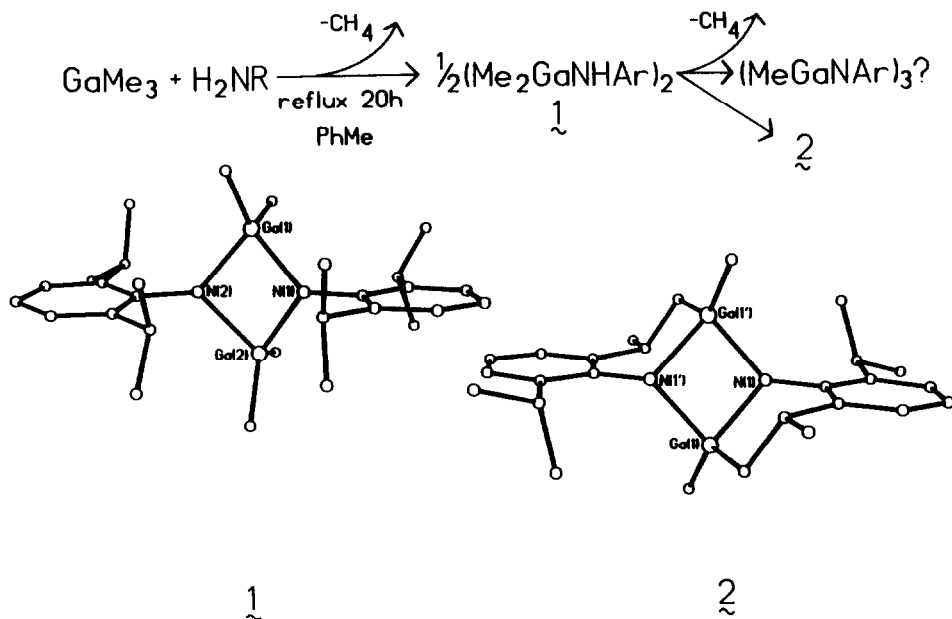
Scheme 2. The simple two-step alkane (CH_4) elimination route to alumazene. Diagrammatic representation and important bond distances and angles are also provided [35].

\AA , implying a radius of 1.33 \AA for Al [36]. In the case of most organoaluminum compounds, however, the Al-C distances fall in the approximate range $1.92\text{--}1.98 \text{ \AA}$ [37]. This implies an effective Al radius of $1.15\text{--}1.21 \text{ \AA}$, if a radius of 0.77 \AA for carbon is assumed. These values, when combined with 0.73 \AA for the radius of N, afford Al-N bond lengths of $1.88\text{--}1.94 \text{ \AA}$, which are considerably longer than the 1.78 \AA bond length in alumazene. The second difficulty arises from the lack of structural information concerning Al-N double bonds. There are, for example, no structurally characterized monomers of formula $\text{R}_2\text{AlNR}'_2$ where R and R' are alkyl or aryl groups [23]. Monomeric iminoalanes RAINR' are also unknown. The Al-N distance in these monomeric compounds or related species such as $\text{RAl}(\text{NR}'_2)_2$ or $\text{R}'\text{N}(\text{AlR}_2)_2$ would have given some indication of the significance of the bond distance observed for the alumazene. Currently, there appears to be only one other structurally characterized compound that features bonds between three coordinate aluminum and nitrogen centers. This is the species $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ which has a trigonal planar AlN_3 framework [38]. The Al-N bonds are 1.78 \AA long and are exactly the same length as those in alumazene. In $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ three nitrogen lone pairs compete for overlap with the Al p -orbital which leads to the expectation of a longer Al-N bond than that predicted for $\text{R}_2\text{AlNR}'_2$. Bonding arguments are further complicated by the presence of SiMe_3 groups on N which may interact with the nitrogen lone pair. In effect, it is very difficult to draw accurate conclusions on the significance of the AlN bond length in $[\text{MeAlN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_3$ from a comparison of the two aluminum compounds.

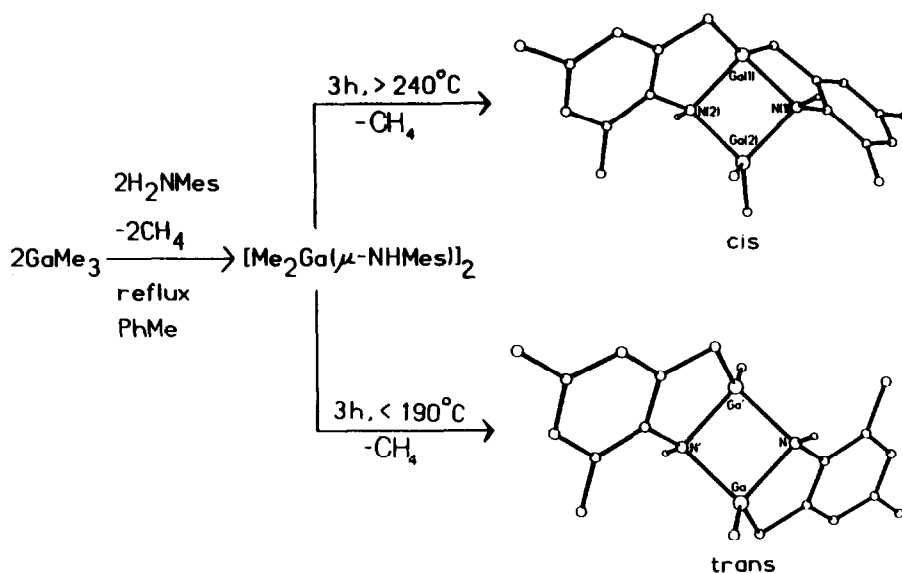


Scheme 3. The reaction of AlMe_3 with H_2NMe [40], $\text{H}_2\text{N}(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)$ [35] and $\text{H}_2\text{N}(2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2)$ [41].

In spite of the isoelectronic nature of their rings the $[\text{MeAlN}(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)]_3$ and $(\text{RBPR}')_3$ species are chemically very dissimilar. The high thermal stability and low air and moisture sensitivity of the $(\text{RBPR}')_3$ rings has already been noted. The alumazene molecule, although it displays considerable thermal stability, decomposes rapidly in the presence of air and moisture. The reaction with water affords the amine and an amorphous white solid containing both aluminum and oxygen. Attempts to form complexes with metals, which are known in the case of the borazines [39], have not been successful. The complex $[\text{MeAlN}(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)]_3$ has remained unique so far. Attempts to form other examples of complexes with a



Scheme 4. The reaction between GaMe_3 and $\text{H}_2\text{N}(2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)$ [40].



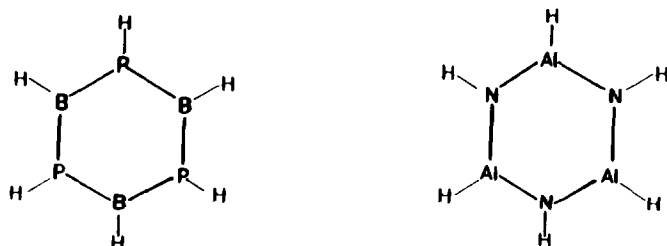
Scheme 5. The reaction between GaMe_3 and H_2NMes [40].

six-membered Al_3N_3 ring have not given the expected product. The reaction between $(\text{AlMe}_3)_2$ and a variety of bulky amines featured in Scheme 3 gave either more highly aggregated products [40], or species in which Al–C bond is formed by activation of a C–H group [41]. Similar experiments using the starting material $[\text{Al}(\text{NMe}_2)_3]_2$ instead of $(\text{AlMe}_3)_2$ have not yet afforded oligomeric iminoalane products [40,42].

The close similarity in size between aluminum and gallium suggests that it should be possible to isolate an example of a ‘gallazene’ via the same route as that employed in Scheme 2. Unfortunately, activation of an isopropyl C–H bond took place under similar reaction conditions (Scheme 4) [40]. In these systems gallium appears to display a greater tendency than aluminum to activate C–H bonds. For example, whereas the reaction between $(\text{AlMe}_3)_2$ and H_2NMes gave the cubane species $(\text{MeAlNMe}_3)_4$, GaMe_3 formed two different products in which the *ortho*-methyl group on mesityl becomes bound to gallium (Scheme 5) [40]. The type of product obtained can be controlled by reaction conditions.

Theoretical data

Although extensive calculations [20] have been carried out on both benzene and borazine, data on the $(\text{HBPH})_3$ and $(\text{HAlNH})_3$ ring species have become available only very recently. Figure 4 gives, in diagrammatic form, details of the calculated structural parameters for the hypothetical molecules $\text{B}_3\text{P}_3\text{H}_6$ and $\text{Al}_3\text{N}_3\text{H}_6$ [43]. The values, derived from calculations at the SCF level using the basis set 6-31G*, are close to those found experimentally for the organic derivatives. The Al–N and B–P bond distances of 1.791 Å and 1.857 Å are only marginally longer than the average values 1.78 and 1.84 Å, measured by X-ray crystallography [27,28,35]. The calculated deviations in the internal angles from 120° also follow the same trends that



$$\text{B-P} = 1.8576 \text{ \AA}$$

$$\text{B-H} = 1.1779 \text{ \AA}$$

$$\text{P-H} = 1.3944 \text{ \AA}$$

$$\text{BPB} = 123.0^\circ$$

$$\text{PBP} = 117.0^\circ$$

$$\text{Al-N} = 1.7910 \text{ \AA}$$

$$\text{N-H} = 1.0026 \text{ \AA}$$

$$\text{Al-H} = 1.5838 \text{ \AA}$$

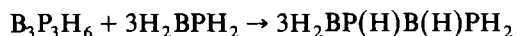
$$\text{NAlN} = 114.7^\circ$$

$$\text{AlNA1} = 125.1^\circ$$

Fig. 4. Schematic drawing illustrating the calculated structural parameters for the hypothetical molecules ($\text{B}_3\text{P}_3\text{H}_6$) and ($\text{Al}_3\text{N}_3\text{H}_6$) [43].

were measured structurally with very good agreement being obtained in the case of the aluminum compound. The angles in the BP system differ by only about 2° from those observed experimentally. An interesting feature of the calculations on the BP system concerns the overall charge distribution between the boron and phosphorus centers. It was found that the boron has a partial negative and the phosphorus a partial positive charge. This charge distribution is opposite to that found in borazine. This result is in agreement with the very small electronegativity difference between phosphorus and boron [44]. The slightly higher electronegativity of phosphorus requires only a small partial negative charge on phosphorus whereas the π -delocalization of the phosphorus lone-pairs onto the borons apparently results in a larger shift in electron density toward boron. This view of the bonding is, of course, supported by the ^{31}P and ^{11}B spectroscopic data mentioned earlier.

An important objective of the calculations on the Al-N and B-P ring systems is the estimation of the aromatic character and the extent of delocalization in the ring. In the case of thermochemical data, one way of developing an index of the aromaticity involves ab initio electronic structure calculations of homodesmotic reaction sequences involving the hypothetical compounds $\text{B}_3\text{P}_3\text{H}_6$ and $\text{Al}_3\text{N}_3\text{H}_6$ which may be represented by the equation:



In this type of reaction the hybridization of B and P and the number and type of bond on each side of the equation remains essentially unchanged. The difference in energy is then taken to be representative of the additional stabilization of the ring compound as a result of the delocalization process. Using heats of formation data for ethylene, butadiene and benzene it is possible to estimate that the energy difference for the homodesmotic reaction is $22.9 \text{ kcal mol}^{-1}$ [45]. It is, unfortunately, not possible to make similar calculations for borazine or the Al_3N_3 or B_3P_3 ring compounds since the parent hydrogen substituted compounds or their ethylene

Table 1 ^{a,b}Energy of reaction results for homodesmotic reactions of B₃P₃H₆, Al₃N₃H₆, B₃N₃H₆ and C₆H₆

Reaction	ΔE_{rxn} (kcal)		
	RHF 3-21G*// RHF 3-21G*	RHF 6-31G*// RHF 6-31G*	MP4SDQ 6-31G*// RHF 6-31G*
B ₃ P ₃ H ₆ + 3H ₂ BPH ₂ → 3B ₂ P ₂ H ₆	8.1	7.4	12.7
Al ₃ N ₃ H ₆ + 3H ₂ AlNH ₂ → 3Al ₂ N ₂ H ₆	1.8	0.8	1.9
B ₃ N ₃ H ₆ + 3H ₂ BNH ₂ → 3B ₂ N ₂ H ₆	7.7	8.4	11.1
C ₆ H ₆ + 3C ₂ H ₄ → 3C ₄ H ₆	27.7	24.7	22.1

^a W.H. Fink and J. Richards, unpublished results 1990. ^b Transoid optimized geometries were used for all butadiene analogues and chair conformers for all cyclohexane analogues.

and 1,3-butadiene analogues do not exist as stable entities. Nonetheless, the good agreement between the calculated and experimental estimation in the case of benzene gives grounds for some confidence with the other three hypothetical molecules. Some of the values for the four ring systems are given in Table 1. Clearly, the energy difference for benzene is the largest, which is in keeping with the ideal aromatic character of this compound. The calculations also indicate that the borazine and (HBPH)₃ rings have about equal energy values for the homodesmotic reactions. The alumazene species indicates very little energy difference so that little aromatic character is predicted. These results are in harmony with the spectroscopic and chemical and physical properties of these compounds. Thus, for alumazene it was mentioned that this compound has, in spite of bulky substituents, the high air and moisture sensitivity that is characteristic of most iminoalanes. Its reactivity is consistent with ionic Al–N bonds owing to the large difference in electronegativity between aluminum and nitrogen. The (RBPR')₃ rings are much less reactive toward air and moisture in agreement with the more covalent delocalized character of the B–P bonds in the rings. In short, the calculations indicate that the delocalization in borazine and B₃P₃H₆ is worth about half as much, in terms of energy, as that in benzene whereas the delocalization in alumazene apparently contributes very little to the stabilization of this molecule.

Zinc–sulfur rings

Upon proceeding further to the right in Fig. 1, the next class of rings that are obtained are species comprised of elements from Main Groups 2 and 6. It is also possible to envisage cyclic arrays where the Main Group 2 metals are replaced by metals from the zinc family. Clearly, in the case of the latter rings, the disparity in the electronegativity is considerably less owing to the reduced electropositive character of the zinc group. For rings comprised of the pairs of elements (Be–O)₃, (Mg–O)₃ or (Ca–O)₃ strong ionic characteristics are expected with no significant delocalization of the oxygen electron pairs. In this context, it is notable that, to date, no six-membered rings of the general formula (RMOR')₃, where M = Be, Mg, Ca, etc.), have been well characterized. Neither have compounds that involve the cyclic array (RMSR')₃ received much attention. The rare occurrence of the trimers among these compounds is somewhat surprising in view of the wider range of related compounds that involve both lower and (especially) higher degrees of association.

For example, a fairly extensive range of organoberyllium alkoxides $(RBeOR')_n$ have been reported; yet, with two notable exceptions ($R/R' = Et/CEt_3$ or $i-Bu/CH_2-t-Bu$) their structures have been reported to be either dimeric or tetrameric in solution [46]. Oddly, none of the trimers have been structurally characterized. In this respect, it is possible that the solution 'trimers' could be equilibrium mixtures of dimers and tetramers. In addition, most organoberyllium thiolate compounds are either tetrameric or polymeric. There is also a range of organomagnesium alkoxides known which can have variable association numbers (2–6) in donor solvents. Higher degrees of association are observed in solvents such as benzene [47]. Information on the sulfur analogues, however, is much more scarce. No structures of either class of compound have been reported to date. The situation is a little more clear in the case of organozinc alkoxides or thiolates. Most of the $(RZnOR')_n$ compounds are tetramers or dimers although threefold association has been reported for solutions of $[t-BuZnO(t-Bu)]_3$ [46(b)] or $(MeZnOCH_2CH_2NMe_2)_3$ [46(a)]. A trimeric structure has recently been determined for the compound $[\{\eta^2-H_2B(3-t-BuPz)_3\}_2ZnOH]_3$ but in this case the zinc is four-coordinated [48]. Only a few structures of organozinc thiolates have appeared. These concern the pentamer $[MeZnS(t-Bu)]_5$ [47] and the octamer $[MeZnS(i-Pr)]_8$ [50]. There has been considerable recent interest in the structures of zinc thiolates in connection with the modeling of zinc sites in biological systems.

For the synthesis of the trimeric alkylmetalalkoxides or aryloxides, the first experiments were performed using zinc rather than the more electropositive metals beryllium or magnesium. Simple alcoholysis of the zinc dialkyl is the most conveni-

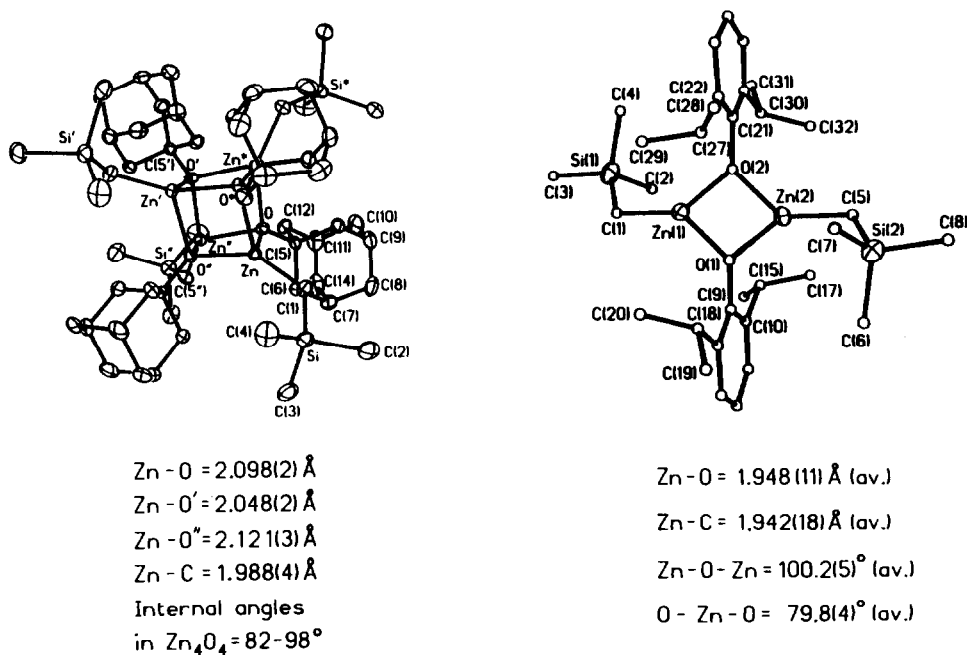
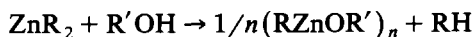


Fig. 5. Computer-generated diagram of the dimer $[RZnO(2,6-i-Pr_2C_6H_3)]_2$ and the tetramer $[RZnO(1-Ad)]_4$, $R = -CH_2SiMe_3$ [52].

ent route to such compounds. Current experiments in this laboratory have been limited to the zinc dialkyl $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$ [51]. When treated with one equivalent of an alcohol this compound reacts smoothly in a hydrocarbon solvent to give the organozinc alkoxide or aryloxide product in good yield as illustrated by the equation



The range of alcohols employed include *t*-BuOH, 1-AdOH, 2,6-*i*-Pr₂C₆H₃OH, 2,4,6-*t*-Bu₃C₆H₂OH. All the resulting $(\text{RZnOR}')_n$ products have been characterized by X-ray crystallography [52]. Only dimeric or tetrameric molecules have been observed so far. Their structures are exemplified by the examples illustrated in Fig. 5. The tetramer, which has average Zn–O and Zn–C bond lengths of 2.1 and 1.99 Å, respectively, shows some deviations from a regular cubane structure (internal angles vary from 82 to 98°). It is thus very similar to the tetrameric structures already reported [53]. The dimeric structure, of which the species in Fig. 5 displays a planar Zn₂O₂ core and planar Zn and O coordination with Zn–O and Zn–C distances of ca. 1.95 and 1.94 Å. The internal angles at Zn and O are 79.8 and 100.2°. The shorter Zn–O and Zn–C bonds are consistent with the lower coordination number at Zn and O. The planarity at O is a normal feature of bridging alkoxide ligands (cf. bridging thiolates). In sum, no delocalization can be inferred from the planar structure and the short distances since these can be explained on the basis of lower coordination number at both Zn and O and a low effective inversion barrier at oxygen.

Sulfur analogues of the alkylzincalkoxides just described may be isolated, by an identical experimental procedure, according to the equation



The first two reactions involving the thiols $\text{HSC}_6\text{H}_2\text{-2,4,6-R}_3$ (R = *i*-Pr or *t*-Bu) afforded excellent yields of colorless crystalline products corresponding to the empirical formula RZnSR' . The X-ray crystal structures of both compounds showed that they were trimers that involved a six-membered (Zn_3S_3) ring framework as their major structural feature. The facile synthesis of these two compounds, in high yield, suggested that the $(\text{ZnS})_3$ rings were more inclined to form and have greater stability than their oxygen counterparts. Both compounds are illustrated in Fig. 6. The $[\text{Me}_3\text{SiCH}_2\text{ZnSC}_6\text{H}_2\text{-2,4,6-*i*-Pr}_3]_3$ molecule possesses an almost planar array of Zn_3S_3 atoms. The zincs have a distorted trigonal planar configuration. The sulfur centers, although flattened, are noticeably pyramidal ($\Sigma^\circ\text{S} \approx 343.7^\circ$) and the Zn–S bonds average 2.308 Å. The bulkier species $[\text{Me}_3\text{SiCH}_2\text{ZnSC}_6\text{H}_2\text{-2,4,6-*t*-Bu}_3]_3$ has a similar structure except that in this case, the sulfurs are much closer to planarity ($\Sigma^\circ\text{S} \approx 356.3^\circ$). In both compounds the internal ring angles at Zn and S display large variations from the idealized 120° values; angles near 140° were observed at sulfur and angles near 100° observed at zinc. Normally, thiolate ligands that bridge two metals are quite pyramidal ($\Sigma^\circ\text{S} \approx 300^\circ$), with significant barriers to sulfur inversion, whereas in both the zinc thiolate compounds the sulfur coordination is clearly much closer to planarity. Two other aspects of the structures of zinc thiolate compounds are of relevance to the discussion of the $(\text{Zn–S})_3$ framework bonding. First, by choosing the appropriate substituent it is possible to isolate a four-membered ring compound involving a Zn_2S_2 array. By the reaction of the thiol HSCPh_3

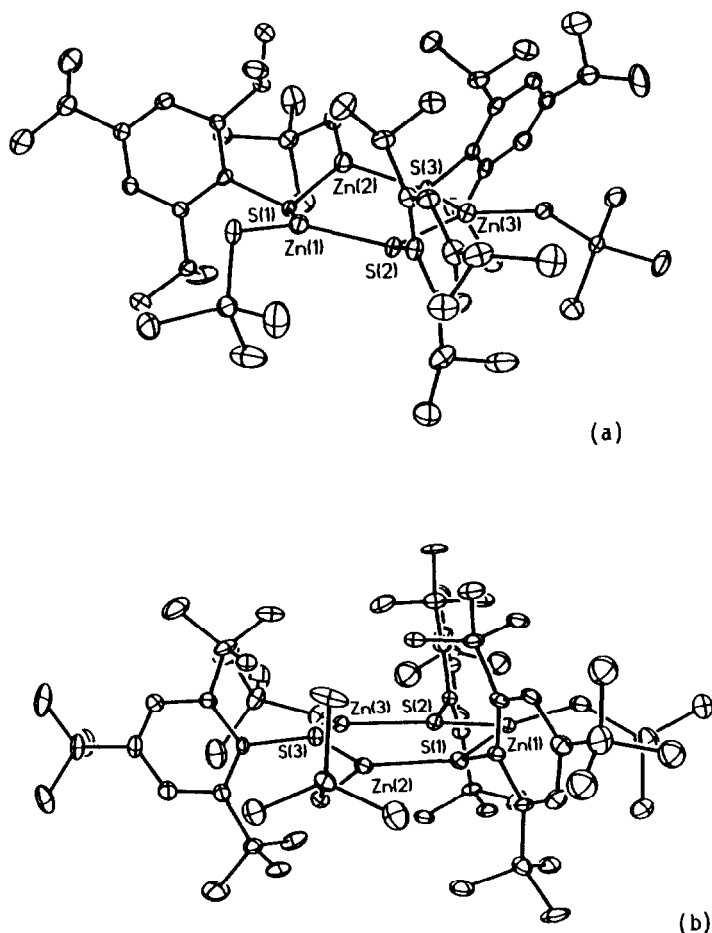


Fig. 6. Thermal ellipsoidal plot of $[\text{Me}_3\text{SiCH}_2\text{ZnS}(\text{2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]$ (a) and $[\text{Me}_3\text{SiCH}_2\text{ZnS}(\text{2,4,6-}t\text{-BuC}_6\text{H}_2)_3]$ (b). In (a) the Zn–S bonds are ~ 2.308 Å long and the average $\Sigma^\circ\text{S}$ is $\sim 343.7^\circ$. In (b) Zn–S is ~ 2.32 Å long and the average $\Sigma^\circ\text{S}$ is $\sim 356.3^\circ$. The Zn centers are planar in both molecules [52].

with $\text{Zn}(\text{CH}_2\text{SiMe}_3)_2$, the compound $[\text{Me}_3\text{SiCH}_2\text{ZnSPh}_3]_2$, which is illustrated in Fig. 7, was obtained in good yield. The X-ray crystal structure shows that the Zn_2S_2 array is planar but the sulfur centers have a very pyramidal coordination with $\Sigma^\circ\text{S} \approx 285.6^\circ$. The zinc–sulfur distances (2.4 Å) are also significantly (0.06–0.07 Å) longer than those observed in the six-membered rings. The second finding of relevance to these structures concerns the recently reported cyclic compounds $(\text{X}_2\text{FeSR})_3^{3-}$ [54] which also possess a planar ring and very large internal ring angles of about 140° at sulfur. In this case it was argued that the stereochemical preference of the S–Fe–S angle and transannular non-bonded repulsions are primarily responsible for the planarity of the (Fe_3S_3) ring.

The most notable difference between the four- and six-membered zinc sulfur rings is the coordination geometry at sulfur. One obvious explanation for this difference involves delocalization arguments that are identical to those employed for the boron–phosphorus four- and six-membered rings discussed earlier. Thus, the

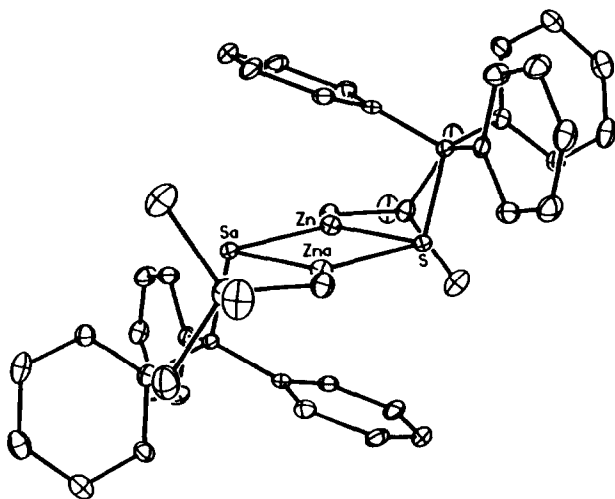


Fig. 7. Thermal ellipsoidal plot of $[\text{Me}_3\text{SiCH}_2\text{ZnSCPh}_3]_2$. The ring is planar, the Zn–S distances average 2.4 Å, and the $\Sigma^\circ\text{S} = 285.6^\circ$ [52].

$(\text{RZnSR}')_3$ ring has the correct arrangement of six p -orbitals to form a π -system in which three of the molecular orbitals are bonding whereas $(\text{RZnSR}')_2$ ring can only form one bonding π -molecular orbital with the remaining orbitals being weakly-bonding or weakly anti-bonding. In the latter, the two lone pairs on sulfur are more stabilized by remaining localized in two orbitals that are primarily of s -character. A possible alternative explanation involves the same arguments as those employed to explain the wide angles at the sulfurs in the $(\text{X}_2\text{FeSR})_3^{3-}$ rings [54]. It is doubtful, however, that the considerations that resulted in the setting of a planar configuration for the $(\text{X}_2\text{FeSR})_3^{3-}$ ring are applicable in the case of the zinc–sulfur rings. This is because the same transannular interactions are not present in the latter owing to the three-coordination at the Zn centers. In addition, the stereochemical preference for the smaller S–Fe–S angle is not present in the case of zinc species. One further explanation might account for the near planar configuration of the zinc thiolate trimers in terms of interligand steric repulsions. Undoubtedly, this factor contributes to the structures observed since the *t*-Bu substituted aryl-thiolate derivative is more planar than the *i*-Pr substituted compound. Nonetheless, it is difficult to see how steric effects could be the whole story since, if they were the most important factor in determining the overall planar structure, a dimer or even a monomer should be formed instead of a trimer so that the steric repulsions could be minimized.

The pyramidal coordination of the sulfurs in the dimer $(\text{Me}_3\text{SiCH}_2\text{ZnSCPh}_3)_2$ indirectly supports the delocalized bonding model in the trimers. Furthermore the Zn–S bond, although polar (electronegativity 1.65 vs. 2.58) [44], is not as polar as Al–N (electronegativity 1.61 vs. 3.04) and it has a marginally lower electronegativity difference than the B–N bond (2.04 vs. 3.04). The (relatively) small electronegativity differences in the Zn–S ring suggest less polar bonding, which should encourage more efficient π -electron delocalization. The size difference between zinc and sulfur is also not as great as that between Al and N. In terms of percentages the difference

is very similar to that between B and N. One other noteworthy difference between the Zn–S trimer and dimer concerns the Zn–S bond lengths, which are 0.06 to 0.07 Å shorter in the trimer. Some of this difference could be attributed to the change in the hybridization at sulfur. Unfortunately, the different hybridization and nature of the carbon centers attached to sulfur do not allow this factor to be accurately assessed.

A further aspect of the bonding in the Zn–S rings that should be borne in mind is that they are associated through dative bonding. In other words, the –SR moieties behave as bridging groups. In this respect the bonding is distinct from the other three ring systems under discussion. In the formal sense three of the six σ -ring bonds are due to the involvement of one of the lone pairs from each sulfur. This suggests weaker overall σ -bonding in the ring. The Zn–S distances of ~ 2.3 Å, although not as short as those (2.23 Å) observed in the recently synthesized ion $\text{Zn}(\text{SR})_3^-$ [55], are indicative of remarkably strong bonding in spite of the bridging nature of the σ -bonds. These data tend to argue for a significant π -interaction between Zn and S.

Synthesis of a ‘germanazene’

It has already been mentioned that one of the more conspicuous aspects of the rings described in Fig. 1 is that they are comprised of three pairs of atoms, each with a total of eight valence electrons. The presence of this feature is, of course, not a requirement for possible delocalization or quasi-aromatic characteristics. It is possible to construct a much greater variety of six-membered inorganic rings comprised of elements from different groups that would also meet the requirement for six π -electrons. One such combination may be given by the schematic drawing in Fig. 8 in which M and E are Main Group 4 and 5 elements, respectively. The six π -electrons are provided by the Main Group 5 ring members whereas the lone pair on M is in a σ -orbital and is not involved in the delocalization. In the theoretical sense any combination of Main Group 4 (C–Pb) 4 and 5 (N–Bi) elements are possible for this ring. The instability of the divalent, monomeric precursors in the case of carbon or silicon suggested that, initially at least, the use of known Ge(II), Sn(II) or Pb(II) compounds could offer a more facile route to the ring shown in Fig. 8. So it has proved, at least in the case of Ge. The treatment of the readily available Ge(II) species, $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$, with an equivalent of H_2NAr ($\text{Ar} = 2,6\text{-i-Pr}_2\text{C}_6\text{H}_3$) under mild conditions gave the product $(\text{GeNAr})_3$ in high yield according to Scheme 6 [56]. The species $(\text{GeNAr})_3$, which is a trimer of the germanium analogue

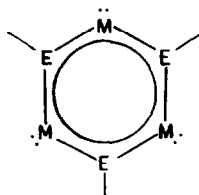
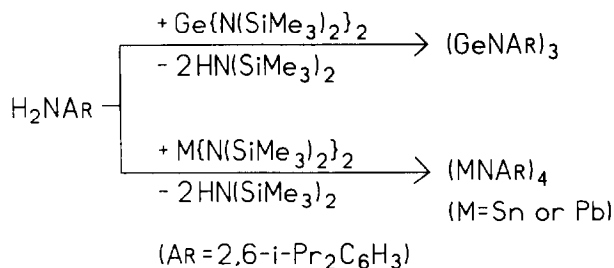


Fig. 8. Schematic representation of the quasi-aromatic ring system $(\text{MER})_3$ (M and E = Main Group 4 and 5 elements, respectively).



Scheme 6. The synthetic route to $(\text{GeNAR})_3$ [56] or $(\text{MNAR})_4$ (M = Sn or Pb, Ar = 2,6-*i*-Pr₂C₆H₂) [62].

of an isonitrile, has the structure shown in Fig. 9. It consists of an almost planar array of $\text{Ge}_3\text{N}_3\text{C}(\text{ipso})_3$ atoms, and the Ge–N bond lengths are equal and average 1.859(2) Å in length. It also represents the first structural characterization of an unsaturated system involving the heavier Main Group 4 elements (Si–Pb) for which a classical, quasi-aromatic bonding model is possible. In some respects, the structure resembles that of alumazene inasmuch as three 2,6-*i*-Pr₂C₆H₃ substituents stabilize its trimeric structure. In addition, the close resemblance in size between Al and Ge ensure that the steric requirements for the stabilization of both species are very similar. There are, however, some important differences between the rings. The most prominent of these involves the internal angles which, in the case of the germanazene, are $\sim 138^\circ$ and $\sim 102^\circ$ at nitrogen and germanium, respectively. In contrast, for the $(\text{RAlNR}')_3$ and $(\text{RBPR}')_3$ rings, that were discussed earlier, the deviations from the idealized 120° angle are scarcely 5° . The large angular distortions in the germanium ring may be due to the increased reluctance of the heavier main group elements to form well-hybridized bonding orbitals. The consequent low internal angle (102°) at germanium has to be matched by the wide (138°) at nitrogen in

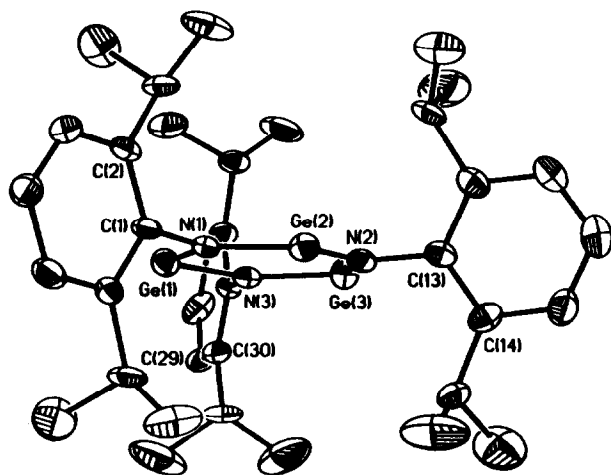


Fig. 9. Perspective drawing of $[\text{GeN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_3$ [56]. Average Ge–N distance = 1.859(2) Å; average N–C = 1.452(5) Å; average values for N–Ge–N and Ge–N–Ge = $101.84(1)^\circ$ and $138.0(2)^\circ$, respectively. The average dihedral angle between the Ge_3N_3 plane and the Ar planes = 86.2° . Average $\text{Ge}\cdots\text{Ge}$ distance = 3.471 Å.

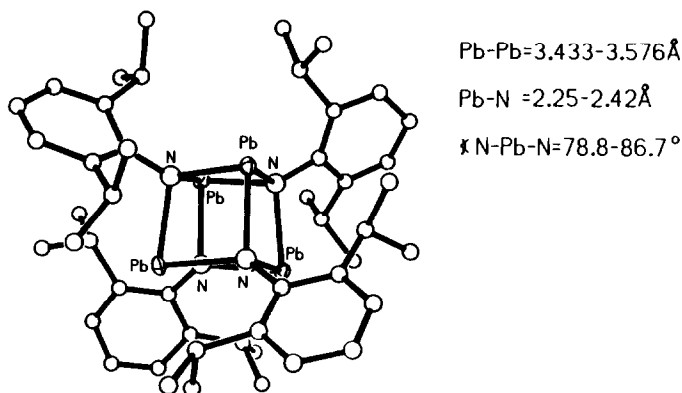


Fig. 10. Computer-generated drawing of $(\text{PbNAr})_4$ ($\text{Ar} = 2,6\text{-i-Pr}_2\text{C}_6\text{H}_3$) including important bond distances and angles [61].

order to preserve the planarity of the ring. Molecular models suggest that, for this ring system, much of the angular strain could be avoided if the ring were to assume an approximately twist conformation. The retention of the planar conformation of the ring is therefore suggestive of the presence of some delocalization since the overlap of the Ge and N *p*-orbitals are maximized in this way. The Ge–N bonds, however, are only marginally shortened with respect to some other Ge(II)–N nitrogen bond lengths. For example, in the compounds $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ [57] and $\text{Ge}[\text{NCeMe}_2(\text{CH}_2)_3\text{CMe}_2]_2$ [58] the Ge–N bond is near 1.89 Å. In the strained ring systems in $[\text{GeN}(2,4,6\text{-t-Bu}_3\text{C}_6\text{H}_2)]_2$ [59] (an ‘antiaromatic’ four-membered Ge_2N_2 ring) and $\text{Ge}(\text{t-BuN})_2\text{Si}(\text{N-t-Bu})_2\text{Ge}$ [60] the Ge–N distances are 1.844 and 1.856(6) Å, respectively, and a Ge–N double bond distance has been reported to 1.688(9) Å [61].

The structural data indicate that the extent of delocalization in the germanazene is probably low. The substantial disparity in the electronegativity of Ge and N (2.0 vs. 3.04) in addition to the greater periodic differences between this pair of elements is also in harmony with this conclusion. One possible explanation for the lack of shortening of the Ge–N bonds might have involved steric interference of the *i*-Pr groups. Although the Ge–N bonds are ~ 0.08 Å longer than the Al–N bonds in the corresponding Al compound, the wide angles imposed on nitrogen cause the nitrogens to approach each other just as closely in the Ge compound. However, this argument is not borne out by decreased dihedral angle between the Ge_3N_3 plane and the Ar plane, which is 86.2° in the case of the Ge compound and 75.3° in the case of alumazene. Attempts to synthesize tin and lead analogues of the germanium–nitrogen ring have not yet been successful. Identical reactions between the amides $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{M} = \text{Sn}$ or Pb) and H_2NAr have given tetrameric products $(\text{MNAr})_4$ [62]. These have a cubane structure featuring an M_4N_4 core, Fig. 10. Presumably, the fairly large difference in size (0.2 Å) between germanium and tin accounts for the higher degree of aggregation observed.

Conclusion

Four new types of six-membered inorganic rings that possess the potential for delocalization have been isolated and structurally characterized. The physical and

chemical characteristics of the 'alumazene' and the 'germanazene' rings suggest that little delocalization takes place. This conclusion is also supported by theoretical calculations in the case of the former compound. In contrast, the boron–phosphorus and, probably, the zinc–sulfur rings possess significantly greater delocalization. This is in keeping with their physical and chemical properties, and the calculations in the case of the boron–phosphorus species. The primary reason for the stability of the structures observed involves the steric bulk of the substituent groups. The structures are, to a large extent, kinetically stabilized and, even when they possess significant delocalization, have no inherent stability. As a result, in the absence of these steric restrictions, the Al–N, Ge–N, B–P compounds and, to a lesser extent the Zn–S species, rapidly convert to higher aggregates that involve four-coordination and sp^3 hybridization at the element centers. These results are in essential agreement with theoretical data [16] on Si_6H_6 (hexasilabenzene), which, according to the calculations, exhibits a delocalization energy that is about 70% of the value for benzene. Yet, in spite of this large 'aromatic' stabilization, the structure is not as stable as hexasilaprismane. This result emphasizes the relatively small role that delocalization energy is likely to play in the determination of the structures of such compounds. The message is clear; elements from the third row onward prefer a multiplicity of single bonds and higher coordination whereas carbon has a preference for sp^2 hybridization (cf., graphite) not seen in the heavier elements [63]. Furthermore, in view of vastly different reactivity patterns of compounds of the elements such as phosphorus, silicon or aluminum, it is unlikely that any six-membered ring species involving these elements would display aromaticity, in the organic sense of that term, even if its delocalization energy were as great as benzene.

Acknowledgements

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