

Molecular and electronic structures of planar inorganic rings

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Abstract - Over the last 30 years, many inorganic compounds have been prepared which have molecular and electronic structures that are related to those of well-known aromatic hydrocarbons. These planar inorganic rings are composed of the main-group elements B, N, O, S, and others, but no carbon at all. In this paper, the structures of inorganic aromatic rings will be reviewed and their properties will be compared to those of aromatic hydrocarbons. Relative stabilities and structures will be rationalized and the possible complexes these rings might form with transition metals will be discussed.

INTRODUCTION

Ten years ago, at an aromaticity symposium in Dubrovnik, I gave a talk on inorganic aromatic rings (ref. 1). Over the intervening years, I have given some thought to inorganic aromatic rings and even published a few papers on their molecular and electronic structures (refs. 2-5). I welcome this opportunity to reevaluate my thinking and, in a few cases, to get my story straight.

Fig. 1 displays only a few examples from the large collection of known planar inorganic rings. Haiduc and Sowerby have proposed that an inorganic ring must contain no carbon atoms at all (ref. 6). To admit even a single carbon atom into a ring would increase enormously the number of known examples in this class. Although such a rule would seem to be logical and practical for inorganic chemists, it does obscure the beautiful interrelation between organic and inorganic structures. The inorganic rings shown in Fig. 1 are composed of the main-group elements B, N, O, and S but others contain P, Al, and elements from lower rows of the periodic table.

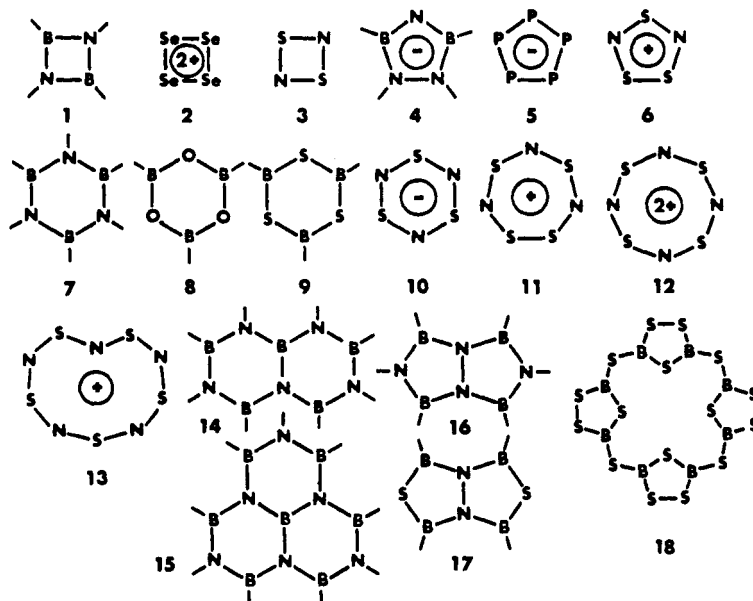


Fig. 1. Some representative planar inorganic rings.

I have chosen planar inorganic rings because the plane of the ring establishes a set of molecular orbitals (MO's) composed exclusively of p atomic orbitals (AO's) that are perpendicular to the ring plane. These MO's are antisymmetric with respect to reflection in the plane of the ring and we refer to them as the pi MO's. The remaining MO's are symmetric with respect to the ring plane

and it is appropriate to call them the sigma MO's. A glance at Fig. 1 reveals a varied level of *exo*-substitution on the rings, some rings being completely substituted like benzene with its six *exo* hydrogens while others bear no substituents at all. Substituents interact more directly through the sigma MO's than through the pi MO's leading to a stabilization or lowering of the energies of the occupied sigma MO's. In this paper I have excluded from consideration those planar rings that have substituents that project out of the plane of the ring. Non-ring-plane substituents interact with the pi MO's in a way not possible in comparable aromatic hydrocarbons. Therefore, I have eliminated several classes of planar inorganic rings, such as the cyclic phosphazines, that have been the objects of speculation about aromatic properties.

Most of the annulenes in Fig. 1 follow the Hückel $4n + 2$ rule for numbers of electrons that occupy the pi MO's. To count pi electrons use the following rules: Count none from boron, one electron from each two-coordinate nitrogen, and two electrons from each oxygen, sulfur, and tri-coordinate nitrogen. For ionic structures, add or subtract electrons as appropriate to achieve the overall charge on the ion. Many inorganic species are pi-electron rich, i.e., they hold more pi electrons than the aromatic hydrocarbon of the same ring size. For example, planar hexagonal $S_3N_3^-$ (10) has 10 pi electrons while benzene has only 6. Because many planar inorganic rings contain $4n + 2$ pi electrons or are pi-isoelectronic with aromatic hydrocarbons it is tempting to call them aromatic.

Much of the experimental thermochemical and NMR data that are conventionally used to demonstrate aromaticity (refs. 7,8) in planar conjugated organic rings are not available or not obtainable for the corresponding inorganic rings. For example, measurements of heats of hydrogenation for cyclic and acyclic systems are not possible where hydrogenation reactions do not occur and for which acyclic reference structures are unknown. But there is less direct physical evidence for aromaticity. Molecular structures of planar inorganic rings show equivalent or nearly equivalent ring bonds that are intermediate in length between ordinary single and double bonds just as they are in aromatic hydrocarbons. Furthermore, the MCD spectra of Se_4^{2+} (2), S_2N_2 (3), $S_3N_3^-$ (10), and $S_4N_3^+$ (11) have been successfully interpreted as arising from $n^* - n^*$ transitions of delocalized electrons using a model developed for $4n + 2$ aromatic hydrocarbons (refs. 9-12). In those instances where resonance energies have been calculated for inorganic rings, they turn out to have values comparable to those of aromatic hydrocarbons (ref. 5).

THE $4N + 2$ RULE

Consider the MO's of cyclobutadiene and S_2N_2 (3). S_2N_2 has $4n + 2$ pi electrons while cyclobutadiene contains $4n$. The doubly degenerate, half-filled non-bonding HOMO's of cyclobutadiene split into discrete nonbonding orbitals which are fully occupied in S_2N_2 . One of the S_2N_2 nonbonding orbitals is composed of a pair of nitrogen 2p AO's of opposite phase at diagonal corners of the square structure; the other nonbonding orbital consists of two sulfur 3p AO's of opposite phase. At the simple Hückel level, the energies of these nonbonding MO's are just the values taken for the heteroatom coulomb integral parameters for N and S in the calculation and the energy difference between the two nonbonding MO's is the difference between the S and N heteroatom parameters. If the difference in parameters vanishes the nonbonding levels become degenerate as in cyclobutadiene. For S and N the parameters usually chosen are rather close and the energy splitting is small. This suggests that the stability of many sulfur-nitrogen rings may be related to the diagonal relationship of sulfur and nitrogen in the periodic table. Atoms of two such diagonal elements are more alike in atomic size, AO energy, and electronegativity than are horizontally or vertically related pairs.

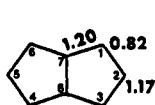
A justification for the Hückel $4n + 2$ rule is based on the solution to the quantum mechanical problem of a particle on a ring of constant potential. The energy levels for such a system are given by $\epsilon_n = (\hbar^2/2mR^2)n^2$, where the quantum number $n = 0, \pm 1, \pm 2, \dots$. The pattern of energy levels is a discrete level $\epsilon_0 = 0$ for $n = 0$ and double degenerate higher levels ϵ_n for $\pm n \neq 0$. For a many-electron system to achieve a stable closed-shell electron configuration requires an odd number of pairs of electrons or a number of electrons that can be expressed as $4n + 2$. The S_2N_2 ring does not have degenerate energy levels but its levels are still filled with $4n + 2$ pi electrons. As we have seen the energy gap between the nonbonding pi levels in S_2N_2 is rather small. Perhaps a system with a larger splitting between the nonbonding MO's would be stabilized by an even number of electron pairs, $4n$. The planar four-membered boron-nitrogen ring (1) is just such an example.

Another rationalization of the Hückel $4n + 2$ rule comes from an examination of the nodal character of the pi MO's for chain and ring (ref. 4). Consider the MO's and energies of butadiene and cyclobutadiene. Imagine joining the end atoms of the chain to form the ring. In the lowest energy MO ψ_1 , the AO's on the terminal atoms of the chain come together with the same phase to form a ring MO of lower energy. In ψ_2 end-end AO's of the chain join out-of-phase to give a ring orbital of higher energy. Next, ψ_3 is ring stabilizing because the even numbers of nodes allow terminal AO's to come together with the same phase. Regardless of the number of atoms in the chain, the number of nodes in the chain MO ψ_m is $m-1$. When m is even, closing of the ring will be destabilizing because the odd number of nodes will bring terminal AO's together out-of-phase. For MO's of odd m , end-end overlap is in-phase and ring formation is stabilizing. Thus stable rings are those filled to odd m . Odd numbers of MO's are filled by odd numbers of electron pairs or a total number of electrons expressed as $4n + 2$, the Hückel numbers.

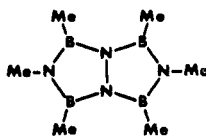
Such a rule may account for the stabilities of hydrocarbon (C_6H_6) or homocyclic (Se_4^{2+} , P_5^-) annulenes but what about heteroatomic rings (e.g., S_2N_2 and the B_2N_2 rings)? In S_2N_2 and $R_2B_2N_2R_2$ the degeneracy of the nonbonding levels is removed. The larger the splitting between these two levels, the more the MO's of the ring are like those of the chain. Because of the large splitting between nonbonding levels in B_2N_2 , the pi destabilization of the ring compared to the chain is small and easily overcome by the sigma bond that closes the ring.

HETEROATOM ARRANGEMENTS

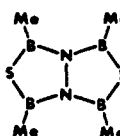
The arrangement of atoms of different kinds in the ring system of Fig. 1 can be rationalized by the rule of topological charge stabilization and the rule of electrostatic stabilization by charge alteration. Electron charge distributions in homoatomic systems such as hydrocarbons are determined by symmetry, topology, and electron count. The 6-fold symmetry of benzene, for example, requires all six carbons to have the same charge density. But several hydrocarbon analogs of the inorganic species illustrated in Fig. 1 have structures for which symmetry does not require uniform charges in non-alternant systems or in alternant systems for which the number of pi-electrons does not equal the number of p AO's involved. The rule of topological charge stabilization says that stable systems are those for which the electronegativities of constituent atoms match the charge distributions established by topology for the isoelectronic, isostructural, homoatomic system (ref. 13). Consider the example of pentalene (19). Pentalene has been prepared but only in substituted form, in which the rings are surrounded by bulky, protecting groups. The simple Hückel charge densities for 8 pi electrons shown in 19 suggest a reason for this instability: topology sets up large separations of charge in this homoatomic system. But the distribution of charge in 19 rationalizes the stabilities of the known isoelectronic inorganic analogs 16 and 17, in which less electronegative boron atoms occupy the positions of low charge density at positions 1, 3, 4, and 6 and more electronegative nitrogens or sulfurs are located at the other sites. The rule of topological charge stabilization has also been successful in explaining the structures of 3-dimensional molecules (ref. 14-17). Aihara has observed that the rule serves as a guiding principle in chemical evolution and general biosynthesis (ref. 18).



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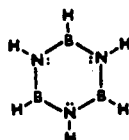
The isoelectronic, isostructural series benzene (20), s-triazine (21), borazine (7), and boroxine (8) form a progression from organic to inorganic planar rings with increasing localization of charge on atoms of the more electronegative element. The rule of topological charge stabilization favors benzene because topology establishes uniform charges around the hexagon. But the alternant arrangement of atoms in 21, 7, and 8 provides electrostatic stabilization through alternation of atoms of greater and lesser electronegativity. Klein has recently reviewed the role of charge alternation in determining stable structures (ref. 19).



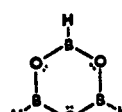
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RESONANCE ENERGIES OF S-N RINGS

The chemistry of sulfur-nitrogen rings has been of considerable interest and has been extensively reviewed (refs. 20, 21). Nenad Trinajstić, Albin Juric, and I collaborated in the calculation of topological resonance energies (TRE's) for a series of known and hypothetical sulfur-nitrogen annulenes containing $4n + 2$ pi electrons (ref. 5). Our object was to try to understand the stabilities of known examples and to predict relative stabilities of other possible members of this class. The TRE method was developed by Gutman, Milun, and Trinajstić (ref. 22). Aihara proposed a similar method independently at about the same time (ref. 23).

In simple Hückel theory the resonance energy (RE) of a cyclic structure can be defined as the difference between the pi energy (E_π) calculated for the cyclic structure and E_π of a suitably defined acyclic reference structure: $RE = E_\pi(\text{cyclic structure}) - E_\pi(\text{acyclic reference structure})$. For the cyclic structure, E_π is just the sum of orbital energies α_i multiplied by the number of

electrons g_i ($= 2, 1, \text{ or } 0$) that occupy each MO i . The characteristic polynomial of the cyclic structure can be generated by means of Sachs' theorem which expresses polynomial coefficients as functions of the numbers of unlinked edges and cycles that make up the structure. The characteristic polynomial for a well-defined acyclic reference structure can be obtained by omitting the cyclic contributions from the Sachs' theorem expressions for the polynomial coefficients for the cyclic structure. The roots x_i^{ac} of the acyclic polynomial can be determined and the topological resonance energy can be expressed as the sum of the difference $x_i - x_i^{ac}$ multiplied by the occupation number g_i . For aromatic hydrocarbons, calculated TRE values have been found to correlate well with physical and chemical properties of aromatic hydrocarbons. For comparisons of structures containing different numbers of pi electrons it is convenient to divide the TRE by the number of pi electrons involved to obtain the topological resonance energy per electron, TRE(PE). Experience with planar hydrocarbons has established the following ranges (ref. 24): TRE(PE) $> + 0.01$: aromatic; $-0.01 < \text{TRE(PE)} < + 0.01$: nonaromatic; TRE(PE) < -0.01 : antiaromatic, where the values are energies in units of the carbon resonance integral β .

TRE(PE) values for some sulfur-nitrogen annulenes appear in Fig. 2. Each block in the matrix contains the formula of the ring, the number of pi-electrons involved, and the calculated TRE(PE) in units of β . Blocks for the known planar rings are enclosed by heavy squares. Circles surround data for three species which are known but which have structures other than planar annulenes. If these three species were planar they would have the numbers of pi electrons and TRE(PE) values as indicated in the blocks. In selecting hypothetical examples and, indeed, in the general layout of Fig. 2, we followed the suggestion of Banister (ref. 25). Five of the six known planar rings have TRE(PE) values greater than 0.01 in the aromatic range. The sixth, $S_5N_5^+$ (13) has TRE(PE) = 0.0090, just below the aromatic threshold. Of the three non-planar structures only S_4N_2 would have TRE(PE) > 0.01 if it had planar geometry. Conformations of S_4N_2 and $S_3N_3^-$ have been discussed elsewhere (ref. 26). Fig. 2 reveals several promising but unknown rings that have TRE(PE) greater than the 0.01 aromatic threshold.: $S_2N_3^+$, S_3N_4 , and $S_2N_4^{2-}$.

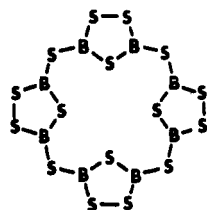
N \ S	2	3	4	5	6
2	S_2N_2 6 .0503	$S_3N_2^{2+}$ 6 .0498	S_4N_2 10 .0127	$S_5N_2^{2+}$ 10 .0174	S_6N_2 14 .0053
3	$S_2N_3^+$ 6 .0472	$S_3N_3^-$ 10 .0135	$S_4N_3^+$ 10 .0175	$S_5N_3^-$ 14 .0053	$S_6N_3^+$ 14 .0075
4	$S_2N_4^{2-}$ 10 .0134	S_3N_4 10 .0174	$S_4N_4^{2+}$ 10 .0180	S_5N_4 14 .0079	$S_6N_4^{2+}$ 14 .0089
5	$S_2N_5^-$ 10 .0178	$S_3N_5^+$ 10 .0179	$S_4N_5^-$ 14 .0079	$S_5N_5^+$ 14 .0090	$S_6N_5^-$ 18 .0042
6	S_2N_6 10 .0182	$S_3N_6^{2+}$ 10 .0171	S_4N_6 14 .0089	$S_5N_6^{2+}$ 14 .0088	S_6N_6 18 .0051

Fig. 2. Topological resonance energies per electron for some known and hypothetical sulfur-nitrogen rings. The number of pi electrons are also included. Energies are in units of β .

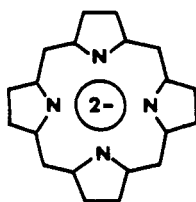
Several trends in TRE(PE) values appear in Fig. 2. Generally, TRE(PE) decreases with increasing numbers of pi electrons. A similar trend is known for hydrocarbon annulenes. A second trend for hydrocarbons is a general decline in TRE(PE) for larger rings with the same number of pi electrons. The SN rings show just the opposite trend. A third observation from Fig. 2 is that SN rings of the same size and same number of pi electrons but with different atomic composition have very nearly the same TRE. Furthermore, TRE values apparently do not distinguish between positional isomers as demonstrated by pairs of annulenes with alternant S and N atoms and alternant S and N pairs. These results demonstrate the truly topological nature of TRE values. Indeed, Gutman, using a first order perturbation treatment of TRE for weighted graphs, has pointed out that hetroatom contributions to TRE should be small (ref. 27).

POSSIBLE TRANSITION METAL COMPLEXES WITH INORGANIC RINGS

In 1980 Krebs and Hürter (ref. 28) reported the preparation and crystal structure of B_8S_{16} (18). This planar inorganic macrocycle has a structure like that of the porphine dianion (22). The two systems are not isoelectronic, however. B_8S_{16} has 32 pi electrons while porphine dianion has 26. The porphyrins have great biological significance because of their ability to bind metals at their centers. It turns out that the central hole in B_8S_{16} is very nearly the same size as that in the porphine dianion. In particular, the hole is about the right size to accommodate a copper ion. In 1983 Zhu and I carried out a study of the hypothetical complex between Cu^{2+} and B_8S_{16} (ref. 3).

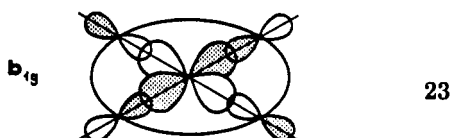


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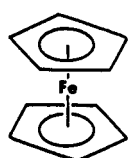
We found that such a complex would be stabilized primarily through the b_{1g} MO (23). This MO consists of the $d_{x^2-y^2}$ AO of the central metal overlapping with the inward-pointing 3p AO's of the unique sulfurs in the 5-membered B_2S_3 rings of the macrocycle.



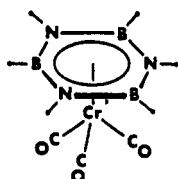
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We concluded that Cu^{2+} should form a complex with B_8S_{16} that might be at least as stable as that known to form between the metal and the tetrathiaether macrocycle 14-ene S_4 and possibly approaching the stability of the porphyrin complex. To date, no B_8S_{16} complexes have been reported.

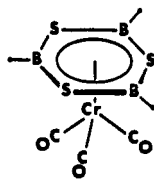
The complex ferrocene, $Cp_2 Fe$ ($Cp = C_5H_5$), was first reported in 1951 by Kealy and Pauson (ref. 29). Wilkinson, Woodward, and coworkers (ref. 30) and Fischer and Pfaff (ref. 31) subsequently showed this complex to have an unprecedented structure: a central iron atom sandwiched between two planar cyclopentadienyl rings (24). Qualitative MO theory describes metal-ring bonding as due to the interaction of 3d valence AO's of the metal with the pi MO's of the rings (ref. 32). What possible pi complexes might be formed between transition metals and inorganic aromatic rings? A few examples have already been reported. The 6-membered rings borazine (7) and trithiaboralene (9) form complexes with transition metal carbonyls (25, 26) (Refs. 33-35). The 4-membered BN ring (1) forms a mixed (ref. 36) metallocene with Co and the Cp ion (27). The complex (28) of the B_2N_3 anion (4) has been reported by Nöth and Regnet (ref. 37). Because 28 is diamagnetic Nöth and Regnet conclude that it has a metallocene structure rather than one



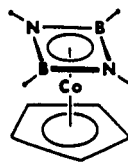
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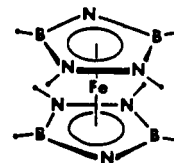
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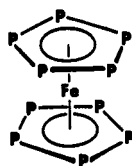


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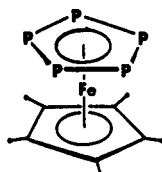


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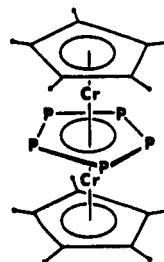
involving sigma bonds to the metal originating from lone pairs on the unsubstituted nitrogen in the ring. The ferrocene complexes (29, 30) of P_5^- (5) and Fe^{2+} have been prepared (refs. 38, 39). No x-ray structures are yet available for 28-30 but the structure of the triple-decker complex 31 related to 29 and 30 has been determined and it clearly shows equivalent interactions between the atoms of the P_5^- ring and the metals (ref. 40). Similar triple-deckers with middle-deck As_5 and P_6 rings have also been prepared. Tremel, Hoffmann, and Kertesz have made a frontier orbital study of these and related complexes (ref. 41).



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No pi complexes of the sulfur-nitrogen rings are known. At this symposium Professor Baiching Dai of Harbin will report on some preliminary theoretical studies of promising but still hypothetical pi-complexes of SN rings with transition metals.

CONCLUSION

The planar inorganic rings enrich the variety of structures and properties exhibited by aromatic systems. The inorganic examples offer another dimension to the concept of aromaticity. A complete understanding of aromaticity will not result from the study of hydrocarbons alone. Systematic consideration of inorganic rings as a group should increase our understanding of chemical bonding in both organic and inorganic chemistry.

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