

## AROMATIC INORGANIC RINGS

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**Abstract** - General properties of aromaticity are discussed with regard to inorganic rings. Qualitative MO arguments are used to explain the variations in ring bond distances in inorganic analogs of the cyclopentadienyl anion. Examples discussed include  $H_2B_2O_3$  and  $HR_2BN_4$ . Next, electronic and structural properties are reviewed for the series of aromatic rings composed only of sulfur and nitrogen:  $S_2N_2$ ,  $S_3N_2^+$ ,  $S_3N_3^-$ ,  $S_4N_2$ ,  $S_4N_3^+$ ,  $S_4N_4^{2+}$ , and  $S_5N_5^+$ . Finally, the relationship between the sigma MO framework and the pi MOs is discussed for the cyclic states of  $N_3^+$  and  $O_3$  and their substituted analogs  $C_3H_3^+$  and  $N_3H_3$ .

### INTRODUCTION

Many of the experimental comparisons which are used for elucidating or describing aromaticity in conjugated hydrocarbons are not possible in inorganic systems. For example, although many cyclic inorganic compounds are believed to have electronic structures analogous to those of benzene or other aromatic hydrocarbons and which therefore presumably are aromatic also, the corresponding noncyclic or saturated systems are unknown, ruling out comparisons of relative thermodynamic stabilities or NMR shifts. Furthermore, the preference of aromatic rings to undergo substitution rather than addition reactions is an inappropriate consideration for those inorganic rings which have no substituents at all. For the purpose of this paper the term aromatic will be applied to those planar monocyclic inorganic molecules and ions that have electronic structures in which  $4n+2$  valence electrons occupy molecular orbitals (MOs) which are antisymmetric with respect to reflection in the plane of the ring. We will refer to these as the pi MOs. Those MOs that are symmetric in the ring plane will be the sigma MOs. The pi MOs will not involve bonding to exocyclic groups which are out of the plane of the ring. In several cases it is known that inorganic aromatic structures exhibit the generally accepted aromatic property of having ring bonds that are intermediate in length between those of normal single and double bonds. The object of this paper is to review the electronic and structural properties of some simple inorganic ring systems using the qualitative results of simple Hückel and extended Hückel calculations.

The simplest explanation of the origin of the Hückel  $4n+2$  rule for monocyclic aromatic compounds comes from the solution of the quantum mechanical problem of a particle of mass  $m$  on a ring of constant radius  $R$  and constant (zero) potential:

$$-\frac{\hbar^2}{2mR^2} \frac{d^2\psi}{d\phi^2} = E\psi; \quad \begin{array}{ccc} \vdots & \vdots & \vdots \\ \text{---} & \text{---} & k = \pm 2 \end{array}$$

$$\psi = A \exp(ik\phi); \quad E \pm \text{---} \text{---} \quad k = \pm 1$$

$$E = \frac{k^2\hbar^2}{2mR^2}, \quad k = 0, \pm 1, \pm 2, \dots \quad \text{---} \quad k = 0$$

The factor  $k^2$  in the energy  $E$  and the allowed value of  $k = 0$  produce a pattern of energy levels in which the lowest level ( $k = 0$ ) is discrete and all higher levels are doubly degenerate corresponding to + and - values of  $k$ . If  $4n+2$  electrons occupy the lowest available energy levels in such a system then all electrons will be paired for a closed

unperturbed MOs as being composed of two sets of functions:  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  at low energy and  $\phi_4$  and  $\phi_5$  at higher energy, as simple Hückel calculations show for  $H_2B_2O_3$ . The calculations, however, reveal a reversal of the energies of  $\phi_4$  ( $=\psi_5$ ) and  $\phi_5$  ( $=\psi_4$ ). Presumably, the mixing of three S functions pushes the highest ( $\psi_5$ ) of the S MOs above the energy of the higher ( $\psi_4$ ) of the A MOs which result from the perturbation mixing of only two functions.

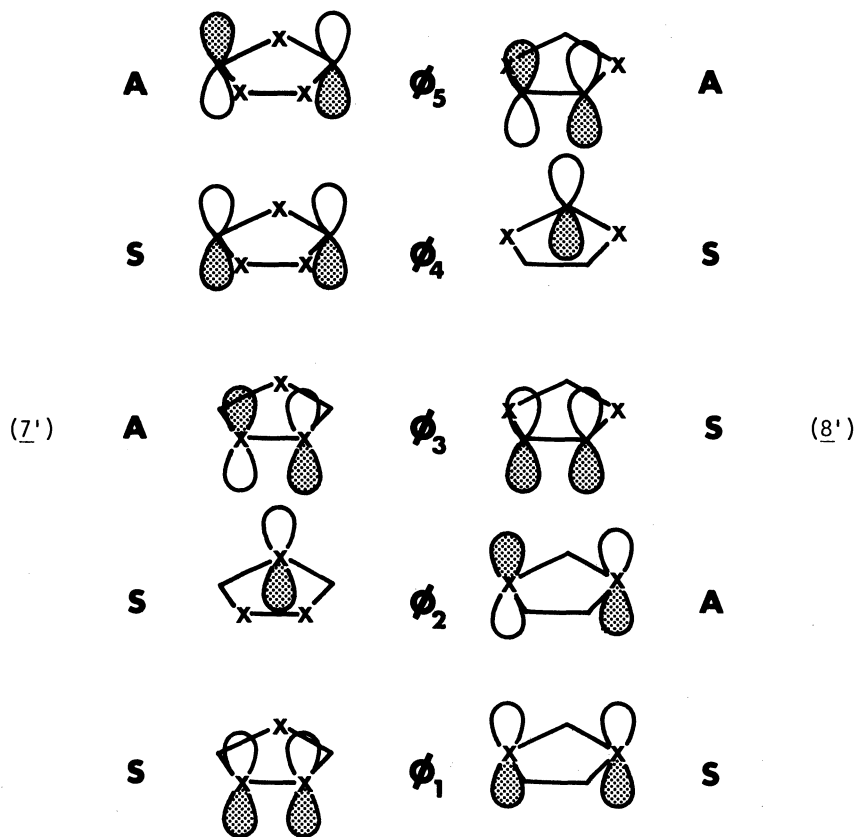
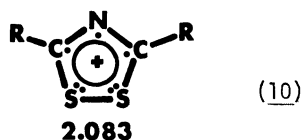
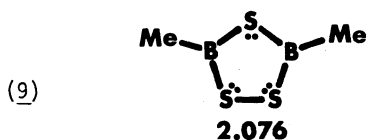


Figure 1. Symmetry adapted basis functions for model 5-membered ring systems.

Suppose that 6 pi electrons occupy  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  (or  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$ ) in (7'). The functions  $\phi_1$  and  $\phi_3$  have large coefficients on the equivalent X atoms. The X-X antibonding interactions in  $\phi_3$  cancel the X-X bonding interactions of  $\phi_1$  giving a negligible pi bond order for the unique X-X bond, in agreement with the Hückel calculations and the long O-O bond distance observed in (7).

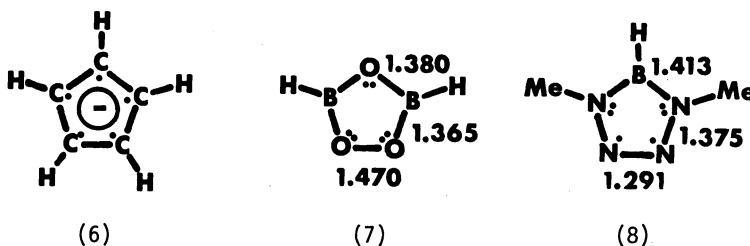
Similar arguments apply to the functions  $\{\phi_i\}$  and the MOs  $\{\psi_i\}$  of Ring (8'). The two lowest energy MOs,  $\psi_1$  and  $\psi_2$ , are mainly the in-phase and out-of-phase combinations of the two X atom p AOs. Next in energy is  $\psi_3$ , the bonding combination of p AOs of the unmarked atoms on opposite sides of the symmetry plane. Mixing gives an extra boost to the highest S MO, placing the MO that is mainly  $\phi_4$  above that which is mainly  $\phi_5$ . With 6 pi electrons occupying  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$ , it is the in-phase combination  $\phi_3$  that gives a large pi-bond order to the unique bond, in agreement with the short bond distance observed in (8).

If the pattern of atoms of high electronegativity makes the unique bond long in (7') but short in (8'), then similar trends should be noted in related structures. In (9) and (10) the unique bond is essentially a single bond (10,11). A long unique bond should be found in



## INORGANIC CYCLOPENTADIENYL SYSTEMS

There are many inorganic analogs of the cyclopentadienyl anion (6). Examples shown here are (7) and (8). In the parent compound (6) all ring bonds are equivalent. In (7), however,



the unique O-O bond has a length that resembles a normal single bond (7). Compare the O-O bond distance of 1.470 Å in (7) with 1.467 Å in hydrogen peroxide. See Table 2. A different situation occurs in (8); the unique N-N bond (1.291 Å) is shorter than the two

Table 2. Some normal single and double bonds.

Type/Bond	N-N	O-O	S-S
Single	1.45	1.47	2.07
Double	1.25	1.21	1.89

equivalent N-N bonds (1.375 Å) on either side (8) and comparable to the double bond in HN=NH (1.25 Å). The structures of (7) and (8) have  $C_{2v}$  symmetry. The unique bond that crosses the symmetry plane is long in (7) but short in (8). This pattern of bond distances is reflected in the calculated Hückel  $\pi$  bond orders: the O-O bond order in (7) is small while that of the unique N-N bond in (8) is large. All  $\pi$  bond orders in (7) are equal. The success of the Hückel bond orders in following the trends in observed bond distances suggests that the trends might be explained using qualitative MO arguments (9).

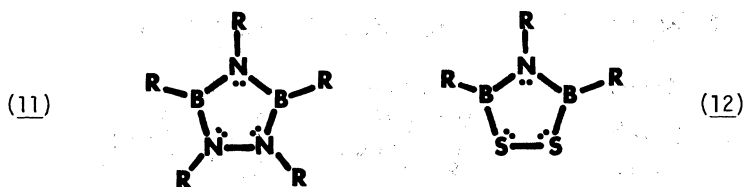
Consider the following model structures for 5-membered rings of  $C_{2v}$  symmetry, where X designates an atom with electronegativity larger than that of the unmarked atoms. Ring (7') is a perfectly reasonable description of (7) while Ring (8') is a rough approximation of (8). In the latter case, the two atoms marked X are the two "double dot" nitrogens.



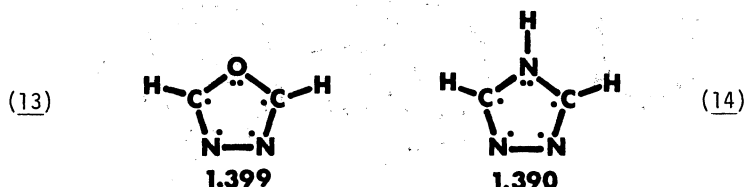
Presumably, these nitrogens would be more electronegative than those which introduce individual  $\pi$  electrons.

Fig. 1 shows the symmetry adapted basis functions for the two ring systems (7') and (8'). Symmetry adapted basis functions are those combinations of AOs in which symmetry requires that the AOs enter with coefficients of exactly the same absolute value. The functions labeled  $\phi_1, \phi_2, \dots, \phi_5$  in Fig. 1 are arranged from bottom to top in the increasing energy order they might be expected to have standing alone as independent functions. For instance, in Ring (7') the lowest energy function  $\phi_1$  is the bonding combination of the two X atom p AOs on opposite sides of the molecular symmetry plane. Higher in energy would be  $\phi_2$ , the p AO of the unique X atom on the symmetry plane. Next in energy is  $\phi_3$ , the out-of-phase or antibonding combination of p AOs on the symmetry related X atoms. Functions  $\phi_4$  and  $\phi_5$  are, respectively, the same-phase and opposite-phase combinations of the higher energy AOs on the unmarked atoms. The set of MOs  $\{\psi_i\}$  of (7') can be produced by mixing the symmetry adapted basis functions  $\{\phi_i\}$  under the restriction that only S (symmetric with respect to the vertical plane) functions mix with each other and A (antisymmetric) functions mix together. In fact, the set of MOs  $\{\psi_i\}$  turns out to be very closely related to the set of symmetry adapted basis functions  $\{\phi_i\}$ ; one of the functions in  $\{\phi_i\}$  is the principal component of each of the MOs in  $\{\psi_i\}$ . In particular,  $\psi_1$  is mainly  $\phi_1$ ,  $\psi_2$  is primarily  $\phi_2$  and so on. MO perturbation theory can rationalize this arrangement. If there is a large energy difference between AOs on the X and the unmarked atoms then we can consider the

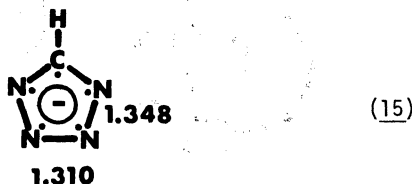
triazadiborolidines (11) and dithiadiborolidines (12). The unique bond is shortened in



cases where the equivalent X atoms are not significantly more electronegative than the unmarked atoms. For example, in (13) and (14) the equivalent X positions of (7') are occupied by "single dot" nitrogens and the N-N bond distances are in the aromatic range



(12,13). Following the pattern of Ring (8') is (15) which has a short unique N-N bond across the plane of symmetry and longer adjacent N-N bonds (14).



#### AROMATIC SN RINGS

Fig. 2 displays the structures and averaged bond distances for the collection of known, planar, cyclic molecules and ions composed of sulfur and nitrogen only (15-21). In these SN rings each sulfur atom can be considered to be contributing a pair of electrons to the pi system while each nitrogen provides only one electron. Consider the planar ring  $S_xN_yq$ , where the charge  $q$  could be plus, minus or zero. For such a system to be aromatic the total number of pi electrons,  $2x+y-q$ , must equal  $4n+2$ . With the exception of the radical cation  $S_3N_2^+$ , all of the SN rings in Fig. 2 follow the Hückel rule even in those cases where lowered molecular symmetry removes the energy level degeneracy that presumably gives rise to that rule. Notice that except for  $S_4N_4^{2+}$  (isoelectronic with  $C_8H_8^{2-}$ ) the SN rings have more pi electrons than the aromatic hydrocarbons with the same size ring. Banister (22) has called these SN systems "electron rich". For example,  $S_3N_3^-$  has 10 pi electrons compared to 6 for benzene. Compared to the hydrocarbons, the deeper energy AOs on sulfur and nitrogen pull MO energies lower to accommodate a larger number of bound electrons in the SN rings. Because these electrons occupy MOs that are nonbonding or mainly antibonding, the pi bond orders of the SN ring bonds turn out to be no greater and usually smaller than those for conjugated hydrocarbon rings of the same size. Some comparisons appear in Table 3. Despite different numbers of pi electrons in  $C_4H_4$  and  $S_2N_2$  their bond orders are very nearly equal because the higher occupied MOs in these cases are exactly nonbonding at the simple Hückel level. The small difference results from different heteroatom parameter choices for N and S. The bond orders of  $S_3N_3^-$  are considerably lower than those of  $C_6H_6$  because the extra electrons in  $S_3N_3^-$  occupy mainly antibonding pi orbitals.

Chapman and Waddington (23) have plotted S-N bond distances as a function of formal bond order which they defined as the number of bond pairs, including both sigma and pi electrons, divided by the number of bonds. Fig. 3 is an attempt to correlate Hückel bond order with experimental S-N bond distances from the S-N rings. The choices of 1.75 Å and 1.50 Å as standard single and double bond distances, respectively, were taken from the work of Kalman, Argay, Fischer, and Rembarz (24). The correlation in Fig. 3 is about as good as

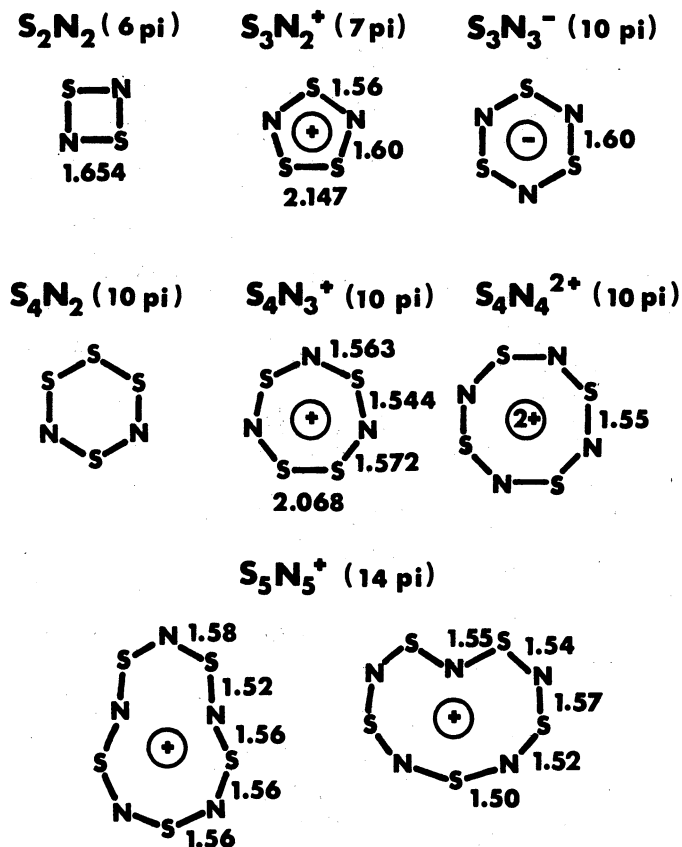


Figure 2. Structures of known planar aromatic SN rings.

Table 3. Hückel bond orders for SN rings and comparable aromatic hydrocarbons.

Compound	pi electrons	Hückel bond order
$C_4H_4$	4	0.500
$S_2N_2$	6	0.496
$C_6H_6$	6	0.667
$S_3N_3^-$	10	0.331
$S_4N_2$	10	0.244, 0.343, 0.400
$C_7H_7^+$	6	0.642
$S_4N_3^+$	10	0.505, 0.527, 0.540
$C_8H_8^{2-}$	10	0.604
$S_4N_4^{2+}$	10	0.596
$C_{10}H_{10}$	10	0.647
$S_5N_5^+$	14	0.518

that found by Coulson and Dingle (25) in a similar study of B-O bonds. The point for  $S_2N_2$  deviates considerably from the trend of the others. The 1.65 Å distance for the S-N bond in  $S_2N_2$  is the value obtained from the x-ray structural analysis of  $S_2N_2$  itself (15b).

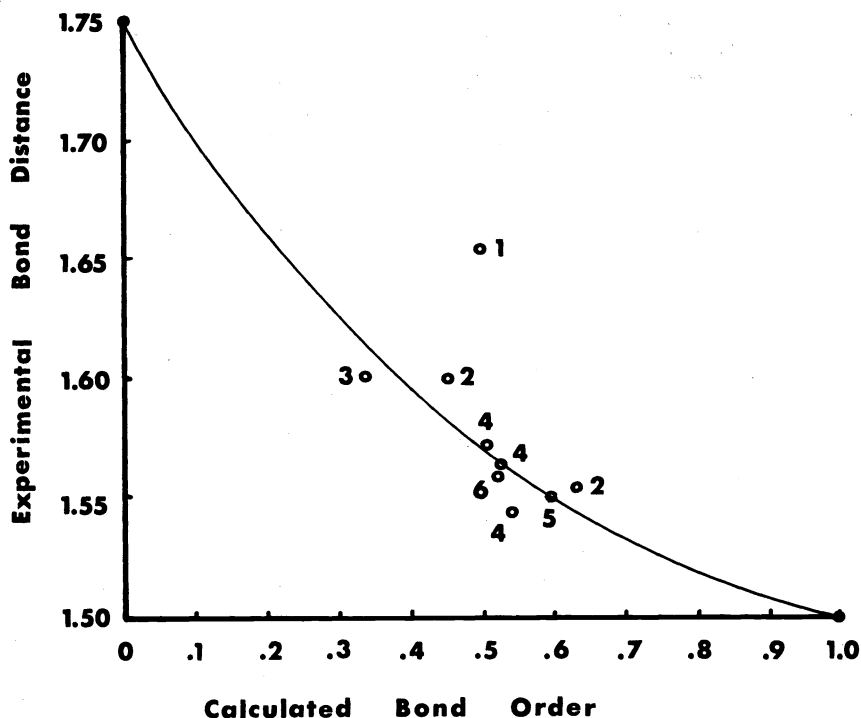


Figure 3. Correlation of experimental S-N bond distances with calculated pi bond orders. 1:  $S_2N_2$ ; 2:  $S_3N_2^+$ ; 3:  $S_3N_3^-$ ; 4:  $S_4N_3^+$ ; 5:  $S_4N_4^{2+}$ ; 6:  $S_5N_5^+$ .

A better fit would have resulted from the choice of the shorter distance, 1.62 Å, found in the addition compound  $S_2N_2(SbCl_5)_2$  (15a).

Simple Hückel energy levels for the known SN rings are compared in Fig. 4. In  $S_3N_2^+$ ,  $S_3N_3^-$ , and  $S_4N_2$  the highest occupied energy levels are slightly above  $\alpha_C$ , the carbon p AO energy arbitrarily chosen as the zero of energy. Stable systems must have highest occupied MOs that are neither too low nor too high. Since the rings in Fig. 4 are known, the highest occupied levels must fall within acceptable limits. Parameter choices strongly influence the calculated energy levels. Those used in these calculations are the recommended heteroatom values of Streitwieser (26) and those used by Johnson, Blyholder, and Cordes (27) for  $S_4N_3^+$ . The simple Hückel results are supported by those of extended Hückel calculations. In each case the highest occupied MO is a pi level rather than a sigma level. Inclusion of sulfur d AOs in the basis set does not alter these properties.

$S_2N_2$ . Disulfur dinitride is planar and essentially square with nearly equal S-N bonds. Fig. 5 compares Hückel energy levels of cyclobutadiene and  $S_2N_2$ . The lower energy of the AOs on S and N make the  $S_2N_2$  MOs of lower energy than the corresponding orbitals of  $C_4H_4$ . Since the symmetry of  $S_2N_2$  is not  $D_{4h}$ , the upper occupied pi levels are not degenerate as they are in  $C_4H_4$ . Still, the square geometry of  $S_2N_2$  and the similar values of Hückel parameters for S and N make the splitting between the two nonbonding levels small. In  $C_4H_4$  the doubly degenerate nonbonding levels would be half-filled for an open-shell configuration. In  $S_2N_2$  the comparable levels are completely filled for a closed shell.

Fig. 6 contains schematic pictures showing the AO compositions of the  $S_2N_2$  MOs. Coulomb integral choices cause the nonbonding MO containing only S AOs to have lower energy than that containing only N AOs. This order is reversed in the extended Hückel calculations, where the valence state ionization potential for the nitrogen 2p AOs is slightly larger than that for the sulfur 3p AOs.

The polycations  $S_4^{2+}$ ,  $Se_4^{2+}$ , and  $Te_4^{2+}$ , all isoelectronic with  $S_2N_2$ , are also known to be square and planar (28-30).

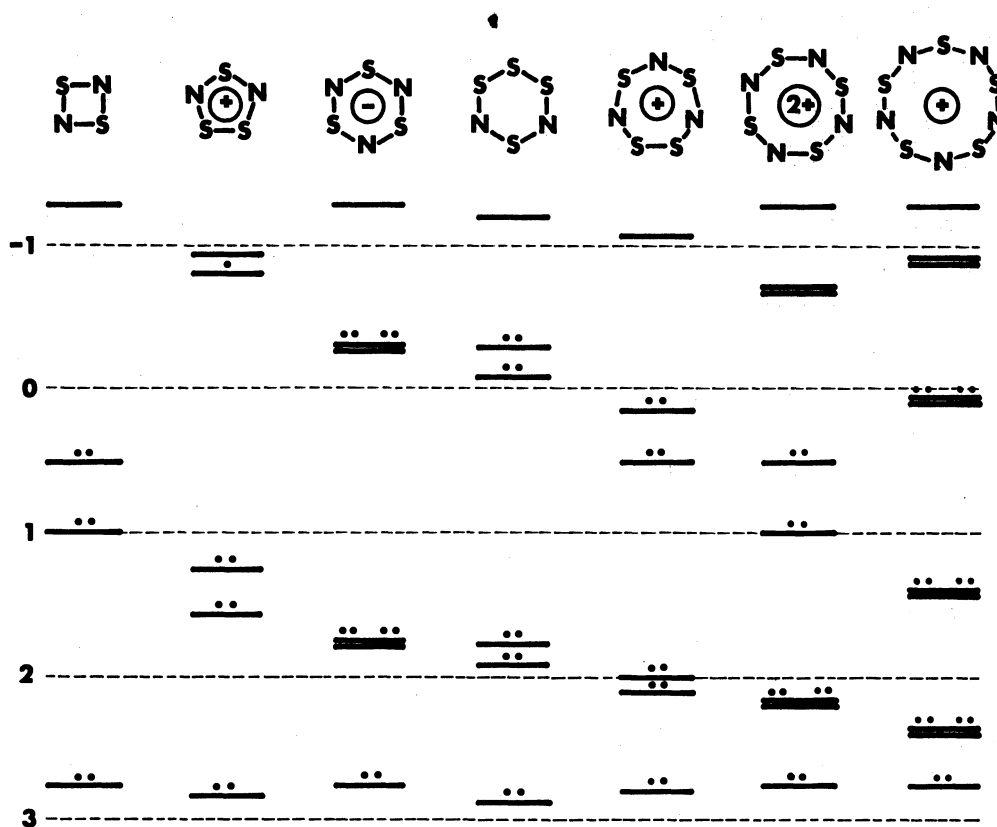


Figure 4. Comparison of Hückel energy levels of known SN rings.

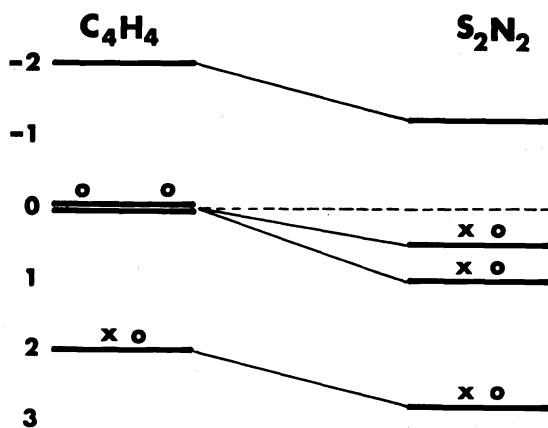


Figure 5. Comparison of Hückel energy levels of  $C_4H_4$  and  $S_2N_2$

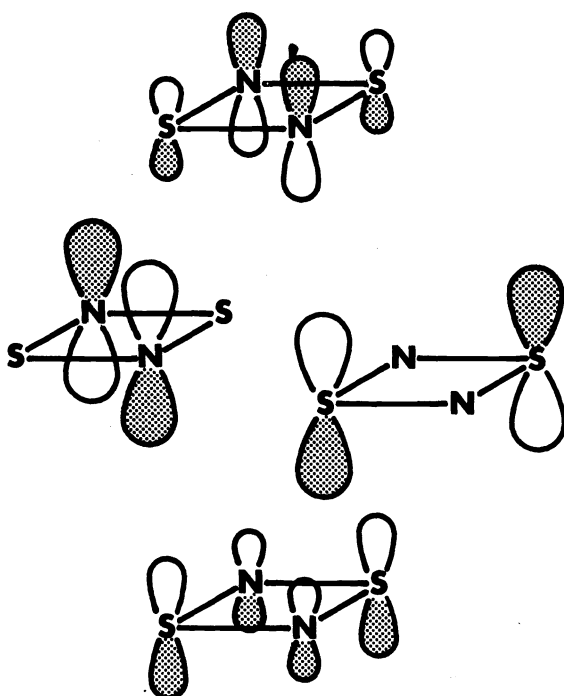
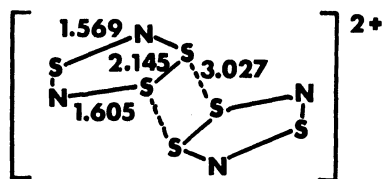


Fig. 6. The AO compositions of the pi MOs of  $S_2N_2$ .

$S_3N_2^+$ . The radical cation  $S_3N_2^+$  has 7 pi electrons. Fig. 4 shows the small splittings of those pairs of energy levels that are degenerate in the 5-fold symmetric cyclopentadienyl anion. The odd electron of  $S_3N_2^+$  occupies a MO of energy higher than that of any other occupied MO in any of the known SN rings. However, if the odd electron were absent, the highest occupied MO of the resulting  $S_3N_2^{2+}$  cation would be below that of the HOMO of any other ring.

The unique S-S bond in  $S_3N_2^+$  exceeds the length of a normal S-S single bond. This is in accord with the picture of one electron occupying the  $\psi_4$  orbital ( $\phi_5$ , A) of the Ring (7') model in Fig. 1.

In the structure of  $S_3N_2^+AsF_6^-$  reported by Gillespie, Ireland and Vekris (16a), the  $S_3N_2^+$  ions are isolated from each other and do not interact in any way. In a slightly earlier paper on  $S_3N_2^+S_2O_6Cl^-$ , Banister, Clarke, Raymont and Shearer (16c) describe the ion  $S_6N_4^{2+}$  (16) as being composed of two  $S_3N_2^+$  units loosely bonded between the sulfur edges of the two 5-membered rings which are in parallel planes rather than coplanar. The bond distances



(16)

in the two associated  $S_3N_2^+$  units are almost exactly the same as those reported for the isolated  $S_3N_2^+$  ions in  $S_3N_2^+AsF_6^-$ . Banister and coworkers (16c) describe  $S_6N_4^{2+}$  as two  $S_3N_2^{2+}$  rings linked by way of pairs of S atoms in a 4-center 2-electron bond:





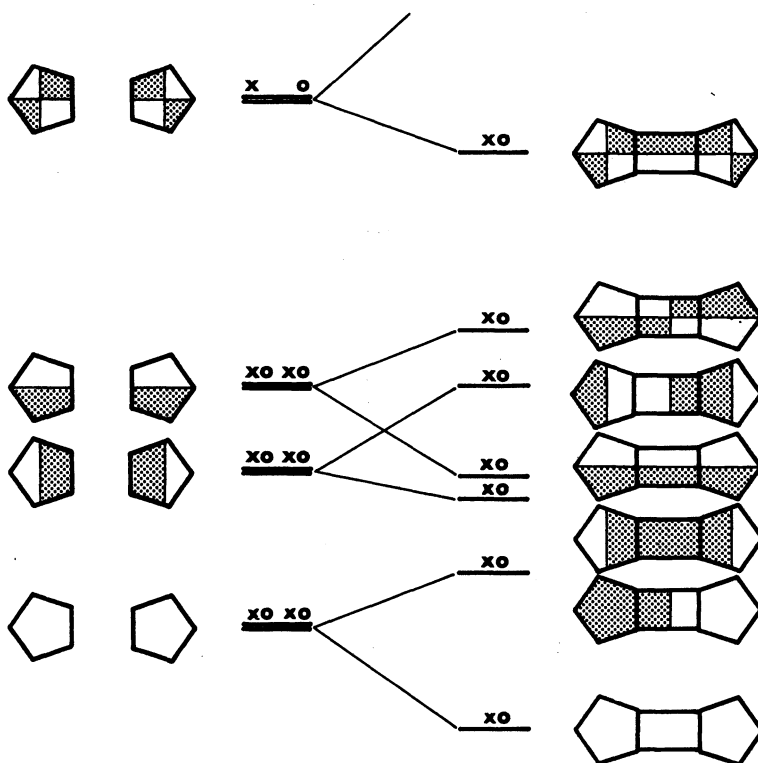
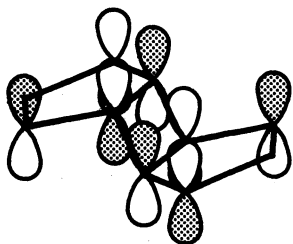


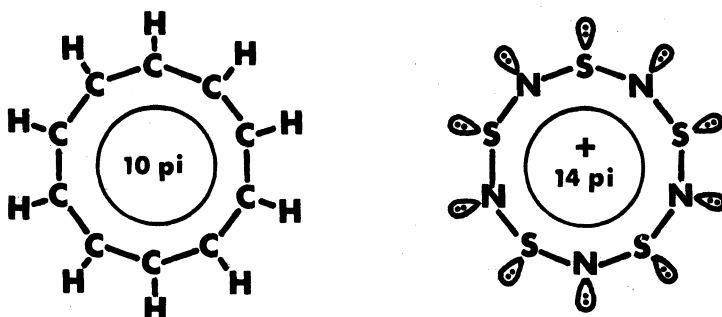
Figure 7. Occupied MOs of  $S_3N_2^+$  and  $S_6N_4^{2+}$ .

The following is a qualitative MO rationalization of the bonding of this dimer. Each  $S_3N_2^+$  ring has 27 valence electrons: 7 pi electrons and 20 electrons in sigma bonds and lone pairs. In molecular orbital terms these electrons would occupy 3 filled and one half-filled pi MOs and 10 filled sigma MOs. Imagine the formation of a coplanar dimer. The two sets of 10 filled sigma MOs would combine to form 20 filled MOs, half of which would be with the same phase or bonding between the two rings and half would be antibonding between the two rings for no net sigma bonds between rings. In fact, if overlap is included, the destabilizing effect of antibonding interactions is always greater than the stabilization provided by an equal number of comparable bonding interactions (9). Therefore net sigma interactions would be repulsive. Similarly, the two sets of filled pi MOs would combine to form six filled pi MOs, half from in-phase combinations and half from out-of-phase combinations of monomer ring pi MOs, again, with no net stabilization. The two half-filled monomer pi MOs would also form in-phase and out-of-phase combinations but only the bonding or in-phase combination would be filled with electrons forming a net pi bond between the rings. Fig. 7 shows the Hückel energy levels and nodal properties of the monomer and dimer pi MOs and their interactions. Although this model indicates that net pi bonding occurs, the effect might still be too weak to overcome the net repulsive interaction among the sigma orbitals or perhaps even crystal packing forces. The ion might compensate for these effects by dissociating or by shifting to a noncoplanar conformation. Naively, the interaction among the highest occupied MOs of  $S_3N_2^+$  monomers in the parallel planes conformation would be more effectively bonding because of the shift from pi- to approximately sigma-type overlap;

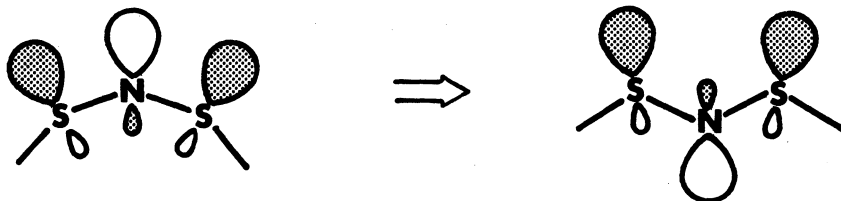


However, removal of coplanarity of the two rings would allow mixing of sigma and pi orbitals and the loss of distinction between these two classifications.

$S_4N_4^{2+}$  and  $S_5N_5^+$ . The  $S_4N_4^{2+}$  cation is known to exist in the same crystal in three different conformations of 8-membered rings, one of which is planar with equivalent S-N bonds as depicted in Fig. 2. The other two forms, one of which deviates from planarity, have S-N bonds of alternant lengths. The planar  $S_5N_5^+$  ring can adopt either heart-shaped or pear-shaped conformations. Bartetzko and Gleiter (31) have performed extended Hückel calculations which indicate that the pear-shaped form is more stable than the heart-shaped conformation which in turn is more stable than the ring with full  $D_{5h}$  symmetry. These authors also give the following qualitative MO arguments to account for the results of their calculations. The conformations of  $S_5N_5^+$  and [10] annulene are similar despite the fact that these rings contain different numbers of pi electrons. The ring shapes are determined by the properties of the underlying sigma MOs which are related. A change of planar conformation does not change the overlaps between bonded p-pi AOs around the ring. The conformation of [10] annulene is apparently determined by repulsions among substituent hydrogens while that of  $S_5N_5^+$  is governed by repulsions among exocyclic lone pairs:



The particular MO involved is composed largely of lone pair orbitals of alternant phase around the ring. Inversion of angles relieves out-of-phase interactions among neighboring lone pairs and lowers the energy:



The heart-shaped conformation involves one such inversion; the pear-shaped form contains two inversions.

Stabilities of planar SN rings. Banister (22) has attempted to systematize our knowledge of the planar SN rings and to infer something about the stabilities of unknown, hypothetical rings relative to those of the known examples. He notes that the ratio of number of sulfur to number of nitrogens is always equal to or greater than unity but not too much greater. There are no known SN Hückel rings that contain N-N bonds. In the more stable SN rings each sulfur atom is bonded to at least one nitrogen ( $S_4N_2$  is probably an exception.) Only one anion is known while there are 4 cations including one dication, indicating that positive charges seem to be preferred.

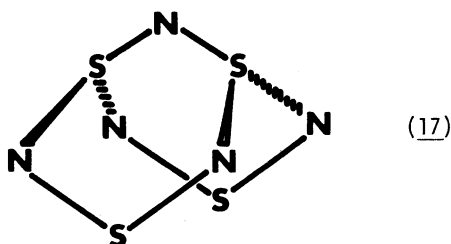
Table 4 contains formulas and numbers of pi electrons for the known and some hypothetical Hückel SN rings. Those formulas in crosshatched squares represent rings which have never been reported. In selecting these we have taken rings with charges between +2 and -1 which satisfy the  $4n+2$  rule and for which the number of pi electrons is equal to or greater than the number of atoms in the ring. The circles around the formulas  $S_4N_5^-$  and  $S_6N_4^{2+}$  indicate that these ions have been prepared but are not planar rings. The structure of  $S_4N_5^-$  (17) is similar to that of  $S_4N_4$  but with a nitrogen atom bridging two sulfurs in the  $S_4N_4$  cage (32).  $S_6N_4^{2+}$  is the previously discussed dimer of two  $S_3N_2^+$  rings.

Fig. 8 presents relative Hückel pi energy levels for several hypothetical Hückel SN rings. It is interesting to compare these levels with those of the known SN rings in Fig. 4.

Table 4. Known and proposed planar SN rings. The number of pi electrons appears beneath each formula.

#S \ #N	1	2	3	4	5	6
1	$\text{SN}^+$ 2	$\text{S}_2\text{N}^-$ 6	$\text{S}_3\text{N}^+$ 6			
2	$\text{SN}_2^{2+}$ 2	$\text{S}_2\text{N}_2$ 6	$\text{S}_3\text{N}_2^+$ 7	$\text{S}_4\text{N}_2$ 10	$\text{S}_5\text{N}_2^{2+}$ 10	
3	$\text{SN}_3^-$ 6	$\text{S}_2\text{N}_3^+$ 6	$\text{S}_3\text{N}_3^-$ 10	$\text{S}_4\text{N}_3^+$ 10	$\text{S}_5\text{N}_3^-$ 14	
4		$\text{S}_2\text{N}_4^{2+}$ 6	$\text{S}_3\text{N}_4$ 10	$\text{S}_4\text{N}_4^{2+}$ 10	$\text{S}_5\text{N}_4$ 14	$\text{S}_6\text{N}_4^{2+}$ 14
5			$\text{S}_3\text{N}_5^+$ 10	$\text{S}_4\text{N}_5^-$ 14	$\text{S}_5\text{N}_5^+$ 14	$\text{S}_6\text{N}_5^-$ 18
6					$\text{S}_5\text{N}_6^{2+}$ 14	

Matching rings of the same size we see the same arrangement of levels in  $\text{S}_5\text{N}^+$  as for  $\text{S}_2\text{N}_2$ . The 7-membered ring  $\text{S}_5\text{N}_2^{2+}$  compares favorably with  $\text{S}_4\text{N}_3^+$ . The highest occupied MO in



$\text{S}_5\text{N}_3^-$  is higher than that in any of the known rings in Figure 4 with the exception of the  $\text{S}_3\text{N}_2^+$  radical cation, suggesting that  $\text{S}_5\text{N}_3^-$  may not be stable. Removing 4 electrons from the highest levels of  $\text{S}_5\text{N}_3^-$  would produce  $\text{S}_5\text{N}_3^{3+}$ , with a charge higher than that of any known ring and a highest occupied MO that is probably too deep in energy to allow a stable ion. The higher filled levels of  $\text{S}_5\text{N}_4$  differ little from those of the known 6-membered rings  $\text{S}_4\text{N}_2$  and  $\text{S}_3\text{N}_3^-$ . The higher filled levels of  $\text{S}_6\text{N}_4^{2+}$  are comparable to those of  $\text{S}_5\text{N}_5^+$ , yet  $\text{S}_6\text{N}_4^{2+}$  takes on the noncoplanar, polycyclic conformation (16). Notice the stabilization of higher filled levels with ring expansion from  $\text{S}_5\text{N}_3^-$  to  $\text{S}_5\text{N}_4$  to  $\text{S}_6\text{N}_4^{2+}$ . Obviously, stability results from more effects than a reasonable energy for the highest occupied orbital, but the energy level comparisons suggest that several additional SN rings might be prepared;  $\text{S}_3\text{N}^+$ ,  $\text{S}_5\text{N}_2^{2+}$ , and  $\text{S}_5\text{N}_4$  are possibilities.

Since each sulfur contributes two electrons to the pi system, rings having a large ratio of number of sulfur atoms to number of nitrogens are unlikely since such rings would be particularly electron rich and several antibonding MOs would be occupied. An example is  $\text{S}_5\text{N}_3^-$  just discussed. Consider the following examples of molecules and ions composed only of sulfur atoms. The ion  $\text{S}_6^{2-}$  is known to be a nonlinear chain (33). Planar, cyclic  $\text{S}_6^{2-}$  would be impossible because  $2 \times 6 + 2 = 14$  pi electrons (satisfying Hückel's rule) could not be accommodated in the 6 pi MOs available to them. The chair-shaped (34) ring  $\text{S}_6$  would not be an aromatic system; 12 pi electrons would fill all antibonding and bonding pi MOs. On the other hand,  $\text{S}_6^{2+}$  (10 pi electrons and isoelectronic with the known rings  $\text{S}_3\text{N}_3^-$  and  $\text{S}_4\text{N}_2$ ) is a reasonable prospect. However, 4 of the pi electrons would occupy MOs that are mainly

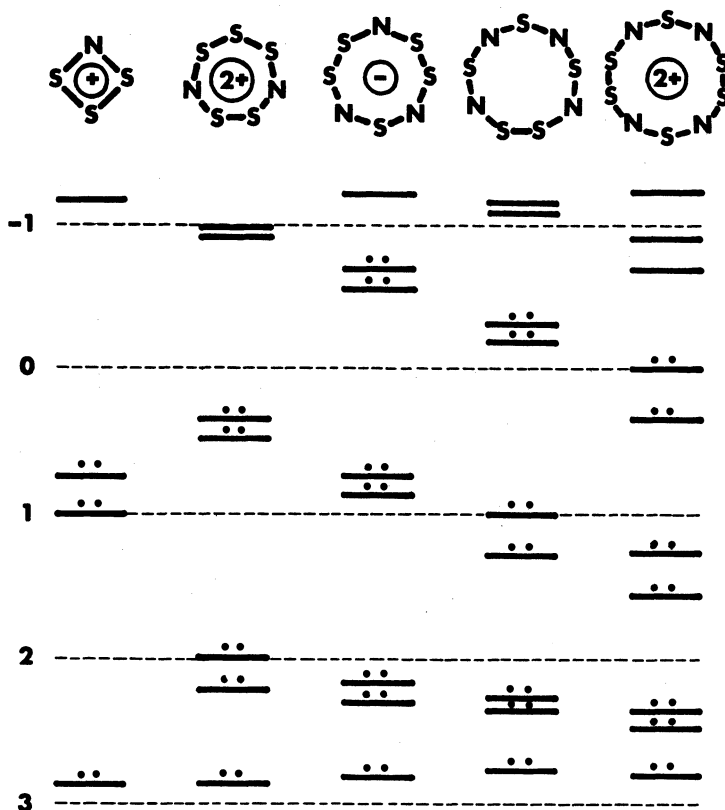


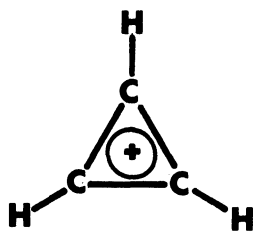
Figure 8. Comparison of Hückel energy levels for some hypothetical SN rings.

antibonding, making  $S_6^{2+}$  less likely than the known  $S_4^{2+}$  cation, for which higher occupied MOs are nonbonding. As in  $S_6^{2-}$ , a hypothetical cyclic  $S_4^{2-}$  would have more pi electrons than the pi MOs could hold. The  $S_4^{2-}$  ion is a nonlinear chain rather than a ring (35).

#### RING STATES FOR $N_3^+$ , $O_3$ , AND $S_3$

It has been suggested that aromaticity might be a property of the sigma framework rather than of the pi MOs (36). In some special cases, at least, this seems to be true.

Cyclopropenyl cation,  $C_3H_3^+$  (18), is known to be cyclic and aromatic (37). Of 14 valence electrons in  $C_3H_3^+$ , two are pi electrons and this ion belongs to the  $n=0$  case of the  $4n+2$  rule. Cyclic  $N_3^+$  (19) would be the inorganic analog of (18). Naively, we could expect the lower energy nitrogen p AOs to stabilize the pi system.  $N_3^+$  has been observed



(18)



(19)

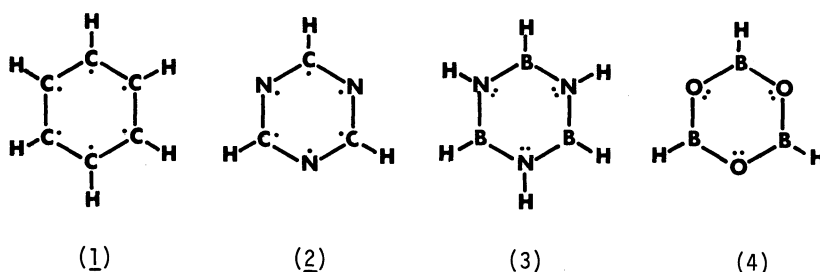
in mass spectral studies (38) but no experimental structural information has been reported. Ab initio calculations indicate that a linear structure is the most stable form of  $N_3^+$ , about 250 kJ/mole more stable than the equilateral triangular cyclic state (4,39). Even though the bonding pi MO might be expected to have lower energy in cyclic  $N_3^+$  than that of  $C_3H_3^+$ , overall stability must depend on the sigma structure as well and the sigma MOs of

shell electron configuration.

Symmetry requires that the pi-energy levels of cyclic hydrocarbons, under the Hückel approximation, follow a similar pattern with an additional discrete level at high energy for even-membered rings. Unlike the hydrocarbons, the inorganic aromatic rings are not uniform; they are formed by joining different kinds of atoms around the ring. The lowered symmetry resulting from such structures may remove the degeneracy from some or all of the energy levels. (In terms of the particle-on-the-ring model, the potential is no longer constant around the ring.) Since the semiempirical heteroatom parameters for some atoms are nearly the same the splitting of formerly degenerate levels may turn out to be small and the  $4n+2$  rule may still be followed.

#### INORGANIC BENZENE ANALOGS

The most familiar inorganic aromatics are analogs of benzene (6 pi electrons). Consider the series benzene (1), s-triazazine (2), borazine (3), and boroxine (4). This isoelectronic series shows a steady progression from organic to inorganic constituents. In each of these molecules all ring bonds are equivalent and of intermediate length between normal single



and double bonds as shown in Table 1. The rings (1)-(4) are planar with  $D_{3h}$  symmetry. Equivalent ring bonds and planar molecular structures (1-3) suggest that the electronic structures of (2)-(4) are similar to that of benzene, but with perhaps greater localization

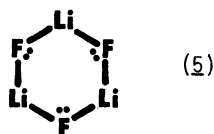
Table 1. Comparisons of aromatic bond distances ( $\text{\AA}$ ) with those of normal single and double bonds.

Type/Bond	C-C	C-N	B-N	B-O
Single	1.54	1.48	1.56	1.61
Aromatic	1.40	1.32	1.44	1.38
Double	1.34	1.27	1.38	1.33

of electrons on the more electronegative ring atoms. Notice that nitrogen occurs in (2) and (3) in different ways. Each N in (2) contributes a single electron to the pi MO system of the ring while each N in (3) offers an electron pair. We will refer to these as "single dot" and "double dot" nitrogens, respectively.

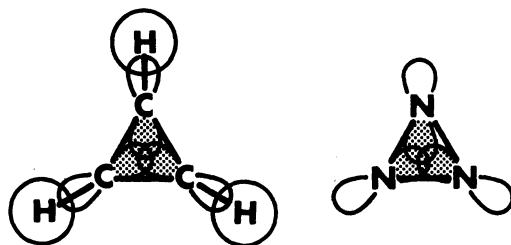
In formulating rings (2)-(4),  $\cdot\text{C-H}$  is replaced by  $\cdot\text{N}$  or for each  $\cdot\text{C-H}$  replaced by  $:\text{N-H}$  or  $:\text{O}$  another  $\cdot\text{C-H}$  must be replaced by B-H. Apparently, not all logical substitutions are possible. For example, the  $\text{N}_6$  ring is unknown, presumably because of the unusual stability of  $\text{N}_2$  (4). On the other hand, planar  $\text{P}_6$ , with equivalent ring bonds, is known in solid  $\text{Rb}_4\text{P}_6$  (5).

Extrapolation of these ideas to cases involving atoms with large electronegativity differences can lead to the absurd. The LiF trimer (5) has a planar  $D_{3h}$  shape with six equivalent Li-F bonds (6). Although (5) is not isoelectronic with (1)-(4), extended

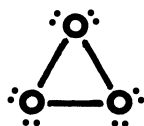


Hückel calculations show that (5) has six electrons in MOs that are antisymmetric with respect to the plane of the ring. However, these MOs are the linear combinations of three lone pair orbitals localized on the fluorine atoms. The ratios of coefficients of F AOs to those of Li AOs are more than 100 to 1. No one would call  $\text{Li}_3\text{F}_3$  aromatic.

$C_3H_3^+$  are stabilized by hydrogen substitution which is lacking in  $N_3^+$ .



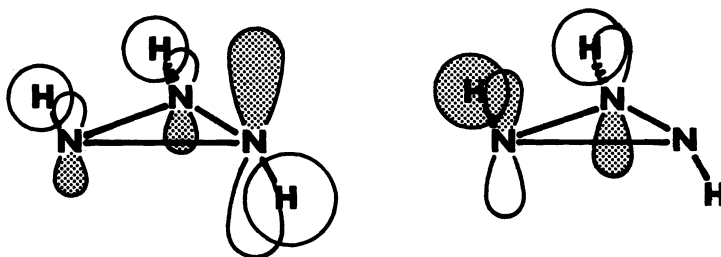
The  $n=1$  or 6 pi electron case of a 3-membered ring would be cyclic  $O_3$  with 18 valence electrons. In earlier days, ozone was believed to be cyclic (40) and, in fact, an excellent Lewis diagram can be drawn for cyclic  $O_3$ :



The normal bent form, which ozone is known to have in the ground state, requires resonance pictures:



As in  $N_3^+$ , one might expect the lower energy of oxygen p AOs to lower the energy of the pi MO system. Again, ab initio calculations show that the cyclic state of  $O_3$  lies above that of the bent ground state by about 125 kJ/mole (41). The ring state of  $S_3$  is only about 18 kJ/mole above the bent ground state (42). The cyclic, isoelectronic analog of  $O_3$  is cyclotriazane,  $N_3H_3$ , which has been isolated only as a complex with  $Ag^+$  (43). The x-ray crystal structure shows an equilateral triangle of nitrogen atoms. As in  $C_3H_3^+$ , the sigma MOs of  $N_3H_3$  are stabilized by hydrogen substitution, an effect that is not possible in  $O_3$  or  $S_3$ . It is unlikely that the hydrogens of  $N_3H_3$  lie in the plane of the nitrogens. Additional stabilization would accrue from the hydrogen 1s AOs moving off the nodal plane of the pi MOs to overlap lobes of the adjacent p AOs on nitrogens as shown below in the antibonding pi orbitals:



Cyclopropane,  $C_3H_6$  (isoelectronic with  $O_3$  and  $N_3H_3$ ) has even more hydrogen substituents to stabilize the sigma structure. Clearly, the cyclic states of  $O_3$ ,  $N_3H_3$ , and  $C_3H_6$  are not aromatic but saturated. Bonding and antibonding pi MOs are completely filled and the pi bond orders of the equivalent ring bonds would be zero in these systems and no extra stability should arise from satisfying the  $4n+2$  rule.

#### CONCLUSIONS

A large number of planar inorganic rings are known that have some properties similar to those of aromatic hydrocarbons. These inorganic systems generally follow the Hückel  $4n+2$  rule even where lack of 3-fold or higher symmetry eliminates the energy level

degeneracy frequently invoked to account for that rule. Still unknown are the general principles which govern ring stability in inorganic systems. Furthermore, no planar polycyclic inorganic ring systems have been reported. Our state of knowledge of aromatic inorganic systems is still very meagre. We cannot claim to understand the concept of aromaticity until this area has been developed.

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