Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208,
and Rugjer Bošković Instutute, 41001 Zagreb, Croatia, Yugoslavia

# Inorganic Aromatic Rings: The π-Electronic Structure of B_8S_{16}

BENJAMIN M. GIMARC* and NENAD TRINAJSTIĆ

Calculations Krebs and Hürter[1] have reported the synthesis and structure of B_8S_{16}. This interesting molecule is composed of four five-membered B_2S_3 rings linked through boron atoms by sulfur atom bridges to form a planar macrocycle. Thus, the structure of B_8S_{16} is the same as that of porphine, although the two systems are not isoelectronic, B_8S_{16} having 32 π electrons while porphine has only 26. Calculations of Hückel π-electron densities show that the arrangements of atoms in these macrocycles are topologically determined: with atoms of different electronegativities being located in just the right positions to give up or accept π-electron density as distributed by the connectivity of the molecule and the electron-filling level and independent of the choice of heteroatom parameters for the calculation. Patterns of π-electron density can suggest other possible molecules or ions with 32 or 26 π-electrons as well as systems with 24 or 30 electrons. The Hückel HOMO–LUMO gap (π–π* transition energy) in B_8S_{16} is large compared to that in porphine, a result consistent with the observations that porphyrins are intensely colored compounds while the crystals of B_8S_{16} are white. Again, the relative sizes of the HOMO–LUMO separations are determined by topology, orbital symmetry, and electron-filling level and not by semiempirical heteroatom parameters. As might be expected, the extra electrons in "electron-rich" B_8S_{16} occupy molecular orbitals that are more antibonding than bonding, giving this molecule both a smaller π-delocalization energy and a smaller topological resonance energy than porphine. Finally, speculations concerning the ability of B_8S_{16} to act as a ligand suggest that B_8S_{16} is not likely to be as effective as the porphyrins in binding either simple cations or transition metals.

Introduction

The molecule B_8S_{16} (**1**) has recently been synthesized and

32 pi e   **26 pi e**

1   **2**
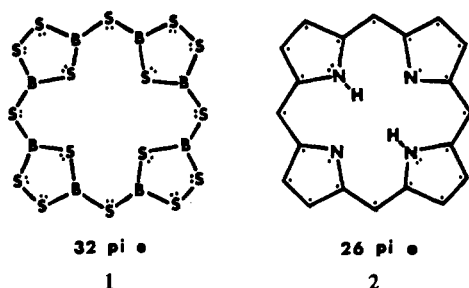
characterized by Krebs and Hürter.[1] This interesting molecule is composed of four five-membered B_2S_3 rings linked through boron atoms by sulfur bridges to form a planar macrocycle. Thus, the structure of B_8S_{16} is the same as that of porphine (**2**). The two systems are not isoelectronic, however. When an electron pair from each sulfur atom and no electrons from the borons are counted, the π-electron system of B_8S_{16} has 32 electrons. In porphine, with one electron from each carbon and each of the two unsubstituted nitrogens and an electron pair from each of the two substituted nitrogens, the π system contains 26 electrons. Therefore, B_8S_{16} can be described as being "electron rich".[2] The two molecules could be expected to have similar σ molecular orbital systems, except for possible differences in the energy ordering among the occupied orbitals.

There is considerable evidence for earlier preparations of B_8S_{16}. The $B_8S_{16}^+$ ion has unusually high abundances in the mass spectra of the vapor over partially decomposed $(HBS_2)_3(s)$ and among the products formed in the reaction of $(HBS_2)_3$ with sulfur.[3]

We wish to report the results of simple Hückel MO calculations and other qualitative considerations for B_8S_{16} and to contrast those results with the related quantities and properties for porphine. In these comparisons we attempt to explain or predict only the rough, qualitative differences in relative stabilities, molecular structures and spectra, and the potentials for these two macrocyclic systems to bind central metal atoms.

Figure 1 compares experimental bond distances in pyrrole[4] and porphine[5] and in $B_2S_3Cl_2$[6] and B_8S_{16}.[1] Notice that the

distances in the isolated B_2S_3 ring are much closer to the related distances in the B_8S_{16} macrocycle than those in pyrrole bear to the comparable distances in porphine.

Charge Densities and Bond Orders. Figure 2 shows calculated π-electron charge densities and bond orders in pyrrole and porphine and in B_2S_3 and B_8S_{16}. The bond orders in B_8S_{16} are remarkably like those in the isolated B_2S_3 fragment. Note particularly the very small value of the S–S π bond orders in B_2S_3 and B_8S_{16}, correlating well with the experimental distances that indicate essentially S–S single bonds.

One of the limitations of Hückel calculations for heteroatomic systems is the necessity to include empirical parameters. The values of these parameters are based on our knowledge of these atoms and bonds in other molecules, and, therefore, they introduce into the calculations something of our expectations of the results for the molecules under study. For the calculations, the results of which are reported in Figure 2, the following Coulomb and resonance integrals were assumed:

$$\alpha_N = \alpha + 1.0\beta$$

$$\alpha_S = \alpha + 1.5\beta$$

$$\alpha_B = \alpha - 1.0\beta$$

$$\beta_{BS} = \beta_{SS} = \beta_{CN} = \beta$$

where α and β represent the values for carbon atoms and CC bonds. It is interesting to repeat the calculations neglecting heteroatom parameters to see to what extent the results are determined by choices of parameters or by the underlying topology of the molecules. Figure 3 shows charge densities of C_{24}^{8-} (**3**) and C_{24}^{2-} (**4**), the carbon analogues of B_8S_{16} (**1**) and porphine (**2**), respectively. In 1950, Longuet-Higgins, Rector, and Platt pointed out that the stability of porphine is topological.[7] With the results of a calculation for **4**, they showed that resultant charge densities on the internal vertices

(1) B. Krebs and H.-U. Hürter, *Angew. Chem., Int. Ed. Engl.*, **19**, 481 (1980).
(2) A. J. Banister, *Nature (London), Phys. Sci.*, **237**, 92 (1972).
(3) J. G. Edwards, J. M. Leitnaker, H. Wiedemeier, and P. W. Gilles, *J. Phys. Chem.*, **75**, 2410 (1971); A. S. Gates and J. G. Edwards, *Inorg. Chem.*, **16**, 2248 (1977).
(4) B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Anderson, *J. Chem. Phys.* **24**, 720 (1956).
(5) B. M. L. Chen and A. Tulinsky, *J. Am. Chem. Soc.*, **94**, 4144 (1972).
(6) A. Almenningen, H. M. Seip, and P. Vassbotn, *Acta Chem. Scand.*, **27**, 21 (1973).
(7) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

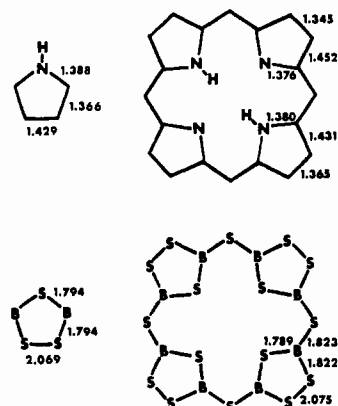*To whom correspondence should be addressed at the University of South Carolina.

Figure 1. Comparisons of experimental bond distances (in Å) in pyrrole and porphine and B_2S_3Cl and B_8S_{16}. Bond distances are from ref 1, 3, 4, and 5.
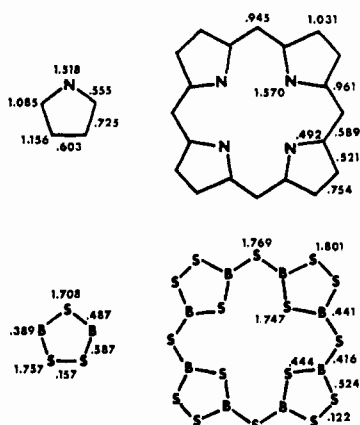

Figure 2. Comparisons of calculated π charge densities and bond orders in pyrrole and porphine and in B_2S_3 and B_8S_{16}.
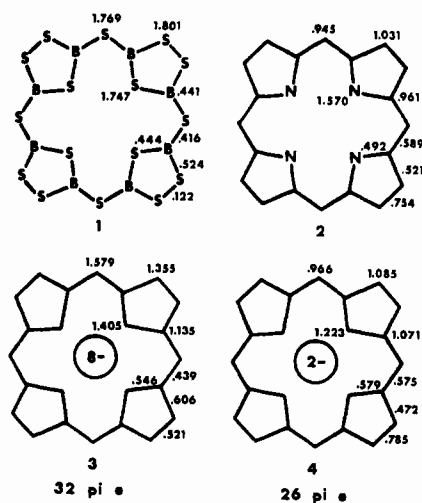

Figure 3. Calculated π charge densities and bond orders for porphine (**2**), B_8S_{16} (**1**) and their respective isoelectronic hydrocarbon analogues C_{24}^{2-} (**4**) and C_{24}^{8-} (**3**). Similar patterns of charge densities for isoelectronic species indicate that charge densities are topologically determined.

of the five-membered rings were significantly larger than those at other atoms even though no parameters in the calculations weighted those locations more heavily. Thus, they concluded that the stability of porphine must be due in part to the fact that the more electronegative nitrogens are located at positions where the topology of the molecule produces large electron densities. Large charge densities coincide with the locations of atoms capable of accepting that charge. Similar calculations
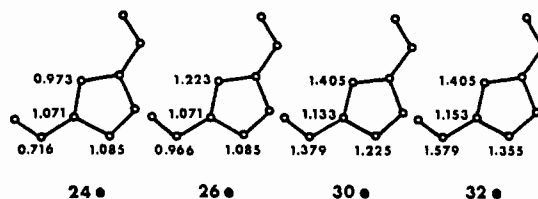

Figure 4. Calculated π charge densities for the hydrocarbon analogue of the porphine structure filled with 24, 26, 30, and 32 electrons. Only a fragment of the full structure is shown.

and arguments explain the stability of B_8S_{16}. Results for the 32-electron carbon analogue **3** show that the smallest electron densities occur at those five-membered ring sites that connect to the bridges. The charges at the other locations, including the bridge vertices, are much larger. The pattern of electron densities in **3**, without any heteroatom parameters, is the same as that in B_8S_{16}. Thus, B_8S_{16} is topologically stabilized because the more electronegative sulfurs are in positions where they can accept the electron charge that the connectivity of the molecule tends to pile up at those locations.
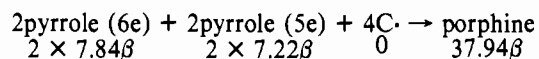
If the patterns of electron densities in B_8S_{16} and porphine are topologically determined, then isoelectronic species with the same topology should exist in which constituent atoms follow the same patterns noted here. Furthremore, electron density patterns may stabilize similar series of macrocycles with 24 and 30 π electrons. (The 28-electron system has been omitted because it would involve an open-shell or diradical electron configuration with a half-filled e_g orbital.) Figure 4 catalogs the electron density patterns for 24, 26, 30 and 32 π-electron systems. Predictions of possible macrocycles that follow these electron density patterns and a search for other systems that support or fail to conform to this model are under way.

Relative Stabilities. We can compare the relative stabilities of B_8S_{16} and porphine using two semiquantitative measures: the π delocalization energy[8] and the topological resonance energy.[9]

Here, we intend the delocalization energy to mean that energy lowering achieved on forming the molecule from its separated, component parts. Consider the process of assembling B_8S_{16} from four B_2S_3 rings and four isolated sulfur atoms:

$$4B_2S_3 \quad + \quad 4S: \quad \rightarrow \quad B_8S_{16}$$
$$4 \times 11.66\beta \quad 8 \times 1.5\beta \quad 62.32\beta$$
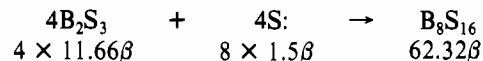
The energy difference between products and reactants is 3.68β, the energy lowering due to the delocalization of 32 π electrons from isolated rings and bridge atoms over the macrocycle. The comparable process for porphine is

$$2\text{pyrrole (6e)} + 2\text{pyrrole (5e)} + 4\text{C} \cdot \rightarrow \text{porphine}$$
$$2 \times 7.84\beta \quad 2 \times 7.22\beta \quad 0 \quad 37.94\beta$$

Here the π delocalization energy is 7.82β, a larger value than for B_8S_{16}. Since the two macrocycles contain different numbers of π electrons, it might be more reasonable to normalize the two delocalization energies by dividing each by the number of π electrons. The delocalization energies per electron for B_8S_{16} and porphine are 0.115β and 0.301β, respectively.

The topological resonance energy (TRE) of a molecule is calculated by means of the relation[9]

$$\text{TRE} = \sum_{i=1}^{N} g_i(x_i - x^{ac}_i)$$

where x_i and x^{ac}_i are the eigenvalues of the characteristic

(8) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, p 239.
(9) I. Gutman, M. Milun, and N. Trinajstić, *J. Am. Chem. Soc.*, **99**, 1692 (1977).
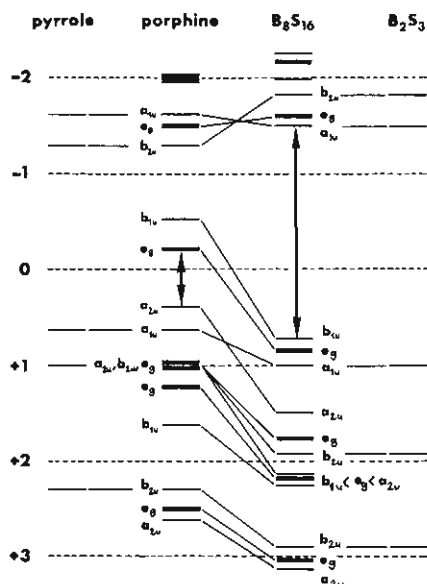
Figure 5. π-Electron energy levels in porphine and B_8S_{16}. The HOMO–LUMO separations are indicated by double-headed arrows. At each side are the levels for the component five-membered rings which are subspectral with the macrocycle.

(Hückel) polynomial and acyclic polynomial,[10] respectively, while g_i is the orbital occupancy number. This expression quantifies the π-electron energy differences between the conjugated cyclic system and a well-defined reference structure. The numerical result (in units of β) for B_8S_{16} is TRE-(B_8S_{16}) = 0.2350. Compare this value to that of porphine: TRE(porphine) = 0.3925. Again, because the two macrocycles differ in the number of π electrons, we normalize the corresponding TRE values according to the relation[12]

$$TRE(PE) = TRE/N$$

where N is the number of π electrons in the system. The TRE(PE) values of B_8S_{16} and phorphine are as follows: B_8S_{16}, TRE(PE) = 0.2350/32 = 0.007; porphine, TRE(PE) = 0.3925/26 = 0.015. These values indicate B_8S_{16} to be a nonaromatic species and less stable than the aromatic molecule porphine. This result is in fine agreement with the delocalization energy analysis.

The lower stability of B_8S_{16} is not unexpected. Because of lower energy atomic orbitals on the sulfurs, the molecular orbital system of B_8S_{16} is lower in energy than that of porphine, allowing more MOs to be occupied in B_8S_{16} than in porphine and explaining the "electron-rich" character of B_8S_{16}.[13] Those extra occupied MOs possess both bonding and antibonding properties, but they are more antibonding than bonding; hence, one might expect total and per electron values of the delocalization and the topological resonance energy to be smaller for B_8S_{16} than for porphine.

Energy Levels. Figure 5 compares the π-energy levels of porphine and B_8S_{16}. The heavy, double-headed arrows mark the gaps separating highest occupied and lowest unoccupied orbitals in each system. The most remarkable feature in Figure 5 is the enormous HOMO–LUMO gap in B_8S_{16} (2.23β) compared to that in porphine (0.60β). The extent of this gap in B_8S_{16} is due both to a lower lying HOMO and a higher LUMO. Porphyrins are intensely colored compounds. The

(10) I. Gutman, M. Milun, and N. Trinajstić, *Math. Chem. (Müheim/Ruhr)*, **1**, 171 (1975).
(11) P. Ilić and N. Trinajstić, *Croat. Chem. Acta*, **53**, 591 (1980).
(12) P. Ilić, B. Dzonova-Jerman-Blazic, and N. Trinajstić, *Croat. Chem. Acta*, **52**, 35 (1973).
(13) B. M. Gimarc and N. Trinajstić, *Pure Appl. Chem.*, **52**, 1443 (1980).
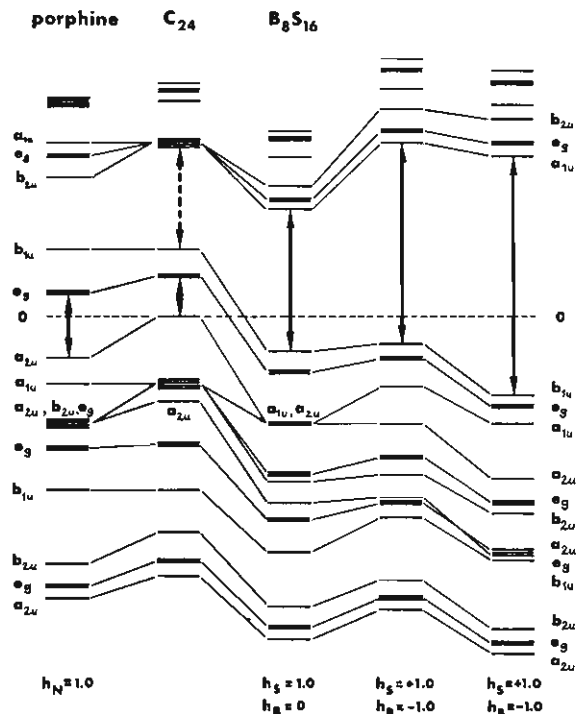
Figure 6. π-Energy levels for B_8S_{16} with the assumption of different sets of heteroatom parameters. Comparisons among these levels and with those of C_{24} and porphine demonstrate that the relative sizes of HOMO–LUMO separations are not determined solely by heteroatom parameter choices. Notice how the energy levels tend to occur in groups or blocks of four.
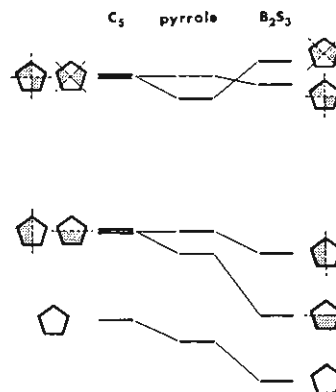

Figure 7. π-Energy levels and nodal properties of molecular orbitals of C_5^-, pyrrole, and B_2S_3 rings.

large gap in B_8S_{16} is consistent with the observation that its crystals are colorless.

To the sides of the energy level schemes for the macrocycles are displayed those of the component five-membered rings. In both cases the energy levels of the fragments match exactly one or more of the levels of the related macrocycles. Thus, the macrocycles and their constituent rings are subspectral.[14] Finally, note that the energy levels of the macrocycles usually occur in sets of four: nondegenerate a and b levels and a degenerate e pair.

Energy levels in Hückel MO calculations are strongly dependent on the choice of heteroatom parameters. Figure 6 contains levels for three different combinations and choices of sulfur and boron Coulomb integrals. These levels are correlated with one another and with those of C_{24} (3 or 4) and porphine. Although the HOMO–LUMO gap in B_8S_{16} varies

(14) T. Živković, N. Trinajstić, and M. Randić, *Croat. Chem. Acta*, **49**, 89 (1977); S. S. D'Amato, *Mol. Phys.*, **37**, 1363 (1979).
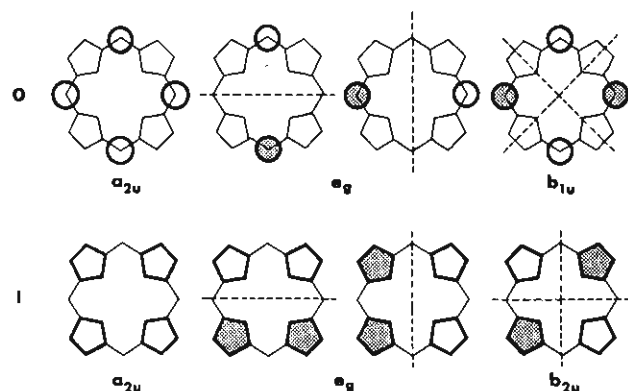
Figure 8. Combinations of five-membered ring nodeless MOs and bridging atom p-π AOs adapted to the symmetry of the macrocycle.
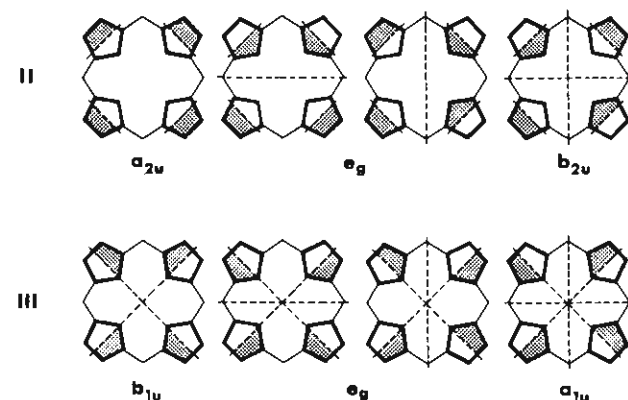

Figure 9. Symmetry-adapted macrocyclic combinations of the single-noded ring MOs.

Figure 10. Symmetry-adapted macrocyclic combinations of the double-noded ring MOs.

in width, it is uniformly broad, as is the gap between the corresponding levels of C_{24} and porphine. On the other hand, the HOMO–LUMO gap at the 26-electron level is uniformly smaller. Thus, the relative sizes of HOMO–LUMO gaps in B_8S_{16} and in porphine do not appear to be entirely artifacts of heteroatom Coulomb integral choices or even the presence of heteroatoms.

Molecular Orbitals. Figure 7 compares π-energy levels and nodal properties of MOs for the cyclopentadienyl anion, pyrrole, and the B_2S_3 ring. It is convenient to imagine the MOs for B_8S_{16} and porphine as constructed from linear combinations of the π MOs of the four component rings and the p-π AOs of the four bridging atoms that link the rings to form the macrocycle. For example, set 0 of Figure 8 consists of the four possible combinations a_{2u}, e_g, and b_{1u}, of the four p-π AOs of the bridging atoms. Set I is the four combinations a_{2u}, e_g, and b_{2u}, of the nodeless MOs of the four five-membered rings. Figures 9 and 10 contain sets II–V formed from the remaining small ring MOs of Figure 7. The 24 combinations of sets 0–V demonstrate that the 24 π MOs of the macrocycle must consist of four orbitals of a_{2u} symmetry, two of a_{1u}, three of b_{2u}, three of b_{1u}, and six degenerate e_g pairs.

The lowest energy MO of the macrocycle must be the in-phase combination of the a_{2u} members of sets 0 and I. Just above a_{2u}, 0 + I, must be the degenerate pair composed of in-phase combinations of the 0 and I set e_g members. The b_{1u} and b_{2u} members of sets 0 and I cannot mix. For the next higher macrocycle level, the b_{2u} member of set I is clearly the best choice. This nonbonding combination of nodeless orbitals of the five-membered rings must have the same energy as an individual isolated ring orbital, as reference to Figure 5 confirms. Each set I–V contains one and only one member that is a nonbonding combination of the small ring MOs, explaining the subspectrality of the small ring and the macrocycle.
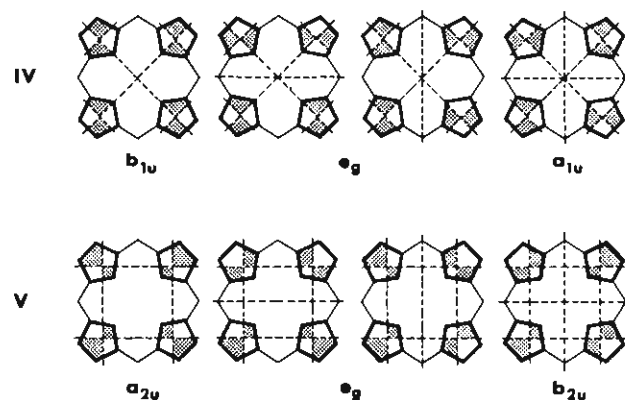
The four members (a, b, and e) of each set (0–V) rationalize the groupings of macrocycle energy levels into blocks of four, although the details of this picture are somewhat more complicated. Now we interpret the large HOMO–LUMO separation in B_8S_{16} compared with that in porphine. The 32 π electrons of B_8S_{16} completely fill four sets of four MOs with a relatively large gap between these filled sets and the empty set above. The 26 electrons of porphine do not completely fill the fourth set of four orbitals, and the HOMO–LOMO separation is the relatively smaller gap within members of the fourth set.

Potential for Binding with Metals. No complexes of B_8S_{16} have been reported and it is interesting to speculate about what kinds of complexes this molecule might form. Two factors should make B_8S_{16} a poorer ligand than porphine. First, the B_8S_{16} molecule is uncharged while porphyrins form complexes as dianions. A neutral B_8S_{16} could not be expected to form electrostatically stabilized complexes as easily as porphyrins which readily complex a number of simple alkali-metal and alkaline-earth cations. Second, because the vacant π orbitals of B_8S_{16} are so high in energy it seems unlikely that they could be involved in bonding with the partially filled d AOs on central transition-metal atoms or ions. Such d-π interactions have been invoked to explain the extra stability of complexes between transition metals and porphyrins in which the vacant π orbitals lie rather low in energy.[15]

Although uncharged and with little possibility for d-π stabilizing interactions with a central metal, B_8S_{16} should still be capable of forming complexes with metal ions, though less effectively than the porphyrins. Here we speculate about what those complexes might be like using analogies. Many examples are known in which sulfurs on uncharged ligands form bonds to metal ions. The bonds are formed from lone-pair electrons on the sulfurs. In the σ electronic structure of B_8S_{16}, each sulfur would have a lone pair orbital in the plane of the macrocycle. (With use of molecular orbital terminology, these are MOs that can be described as linear combinations of localized lone-pair orbitals.[16]) An interesting feature of B_8S_{16} is that there are three different kinds of sulfurs: internal, adjacent peripheral, and bridging. Because of the macrocyclic effect,[17] the most likely site for metal binding would be at the center of macrocycle, where four lone pairs point from the four internal sulfurs. Examples of similar complexes are the tetrathiacyclotetradecane complexes[18,19] **5**. The four sulfurs and

(15) B. Pullman and A. Pullman, "Quantum Biochemistry", Interscience, New York, 1963, p 406.
(16) B. M. Gimarc, "Molecular Structure and Bonding", Academic Press, New York, 1979, p 211.
(17) D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, **91**, 6540 (1969); R. D. Hancock and G. J. McDougall, *ibid.*, **102**, 6551 (1980).
(18) M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacker, *Inorg. Chem.*, **15**, 1190 (1976).

5
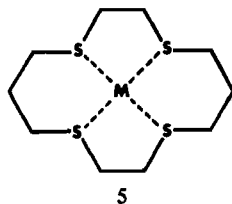
the metal M form a nearly perfect square plane. The macrocyclic thioether ligand is uncharged. M might be Cu^{2+} or Ni^{2+}. Note that the M–S distance in the Cu^{2+} complex is 2.303 Å,[18] very close to half the 4.667-Å S---S hole diameter in B_8S_{16}. The Ni–S distance in **5** is a little smaller at 2.176 Å.[19]

It is possible, though less likely, that B_8S_{16} might form complexes through bonds from one of the bridging sulfurs to a metal. Ru(II) complexes with the analogues thiophene (**6**) and tetrahydrothiophene (**7**) have been prepared.[20]

6   **7**
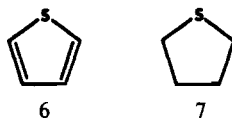
The least likely binding sites of B_8S_{16} would be the adjacent or peripheral sulfurs of the five-membered rings. Neutral molecules of the type R–S–S–R rarely form complexes in which both sulfurs participate in bonding. A few examples have been documented such as the binuclear rhenium complex **8** with bridging bromines and a disulfide.[21]

8
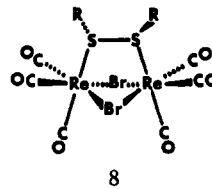
Another analogue is the 1,2-dithiolium cation **9**, which forms unidentate complexes.[22]

9
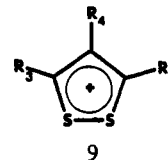
The closest analogue of B_8S_{16} would be the trithiadiborolanes, $S_3B_2R_2$, which have long been known. Apparently, there have been no reports of complex formation involving these small rings as ligands.

Studies are in progress on the σ electronic structure of B_8S_{16} to gain insight into the complex-forming potential of this interesting new macrocycle. As part of this work we find that the results of extended Hückel calculations show that B_8S_{16} has 16 occupied π molecular orbitals arranged in sets of four, supporting our simple electron-counting procedure and the results of the Hückel molecular orbitals analysis reported above.

Registry No. B_8S_{16}, 73825-17-9.

(19) P. H. Davis, L. K. White, and R. L. Bedford, *Inorg. Chem.*, **14**, 1753 (1975).
(20) C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, **98**, 689 (1976).
(21) I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *Isr. J. Chem.*, **15**, 153 (1977).
(22) T. N. Lockyer and R. L. Martin, *Prog. Inorg. Chem.*, **27**, 223 (1980).

Contribution from the Departments of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and the University of Durham, Durham DH1 3LE, United Kingdom

Incorporation of Unsaturated Hydrocarbons into a Borane Cage. A Model for the Irreversible Adsorption of Alkynes

R. L. DeKOCK,[1a] T. P. FEHLNER,*[1a] C. E. HOUSECROFT,[1b] T. V. LUBBEN,[1a] and K. WADE*[1b]

It is demonstrated that a series of boranes and carboranes may be used to model the way in which the carbon–carbon multiple bonds of unsaturated hydrocarbons are progressively weakened, and ultimately cleaved, on interaction with an array of electropositive atoms. Specifically, molecular orbital and bond energy calculations are used to probe the changes that occur when tetraborane(10) reacts with ethylene or acetylene to form hydrogen and the *closo*-carboranes 1,2- and 1,6-$C_2B_4H_6$ via arachno and nido precursors. The driving force for the stepwise cluster oxidation is provided by a progressive increase in the boron–carbon bonding, which is accompanied by transfer of electronic charge to the carbon atoms. The results provide a rationale for the behavior of unsaturated hydrocarbons on surfaces and argue strongly against a carbonium ion like model for the adsorbed state.

The discovery that alkynes could be incorporated into borane cages to yield carboranes led to the production of a class of compounds whose unique properties have been exploited by numerous research groups.[2,3] Carboranes are generally prepared by the reaction of unsaturated hydrocarbons with boranes, and although a variety of intermediate products are known, ultimately the reaction yields carbyne units ($\equiv CR$) in a borane framework. One of the advantageous features of the carboranes (and boranes) is the existence of series of well-characterized compounds. These have provided insight into the systematics of cluster structure and provide the primary experimental evidence for the cluster-electron counting rules.[4] We now point out that the series of compounds illustrated in Figure 1 provides a vehicle for studying the in-

(1) (a) University of Notre Dame. (b) University of Durham.
(2) Onak, T. "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 10.
(3) Grimes, R. N. "Carboranes"; Academic Press: New York, 1970. Williams, R. E. *Prog. Boron Chem.* **1969**, *2*, 51. Hawthorne, M. F. "The Chemistry of Boron and its Compounds"; Muetterties, E. L., Ed.; Wiley: New York, 1967; Chapter 5. Stanko, V. I.; Chapovskii, A.; Brattsev, V. A.; Zakharkin, L. I. *Russ. Chem. Rev. (Engl. Transl.)* **1965**, *34*, 424.
(4) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Williams, R. E. *Ibid.* **1976**, *18*, 67. Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446.
(5) Although the series in Figure 1 is not necessarily a real synthetic route to 1,6-$C_2B_4H_6$, it is known that 2 yields some 5, 5 yields 6, and 6 yields 7.[2,6]
(6) Franz, D. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 1438. Franz, D. A.; Miller, V. R.; Grimes, R. N. *Ibid.* **1972**, *94*, 412.