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A comparative study of the bonding in heteroatom analogues of benzene*

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Summary. Inorganic benzenes $X_3Y_3H_6$ are investigated, with X and Y chosen from Zn, B, Al, Ga, C, Si, Ge, N, P, As, O, and S such that there are a total of 6 π electrons. Geometries and bond orders are used to qualitatively assess the degree of aromatic π bonding in these species. Bond orders are extracted from the CI density matrix over localized molecular orbitals, using methods pioneered by Ruedenberg. Second row elements C, N, O are found to be more effective at this bonding. The aromatic bonding is poorest when X and Y have a large electronegativity difference.

Key words: Benzene heteroatom analogues – Bonding – Bond orders

1. Introduction

Much attention has been focused on the bonding in the main group analogues of benzene such as borazine ($B_3N_3H_6$). Power has reviewed the examples which exist [1]. Many of these compounds have properties which make them similar to benzene. For example, analogous benzene and borazine transition metal complexes have been synthesized [2]. However, the main-group analogues differ in many respects from benzene, most notably in their kinetic instability. We consider here compounds of the general formula $X_3Y_3H_6$, where X and Y are chosen from Group IIB (Zn) with Group VI (O, S), Group III (B, Al, Ga) with Group V (N, P, As), or Group IV (C, Si, Ge). Throughout this paper X will refer to the more electropositive of the two elements.

Benzene itself is the only such group IV $X_3Y_3H_6$ molecule extant, although singly substituted silatoluene has been known for some time [3]. Silabenzene [4], disilabenzene [5], and germabenzene [4], along with similar species have been considered previously by this group, as well as others [6, 7]. The literature of these molecules is well developed, with several reviews available [8, 9, 10]. Of

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* Dedicated to Prof. Klaus Ruedenberg

** *Current address*: Elvis Presley Professor of Chemistry, Memphis State University, Memphis, TN 38152, USA course, a good deal of attention has been paid to the nature of the π bonding in benzene. We mention here only two studies, both using localized orbitals at the SCF level. Edmiston and Ruedenberg have proven that if only the π orbitals are localized, there are in fact an infinite number of equivalent localized orbitals [11]. Pictures of these were later published [12], showing how the two equivalent Kekulé structures can be evolved into each other. Interestingly, when England and Gordon also included the σ orbitals in the localization [13], the resulting orbitals were 3 alternating CC σ bonds, and 3 pairs of banana bonds between the other CC pairs.

In addition to borazine [14], the Group III–Group V analogues of benzene synthesized thus far are the B–P, Al–N, and Ga–P systems. The trimeric B–P compound $[MesBPPh]_3$ was first synthesized by Power and coworkers [15]. Its main structural features include a coplanar ring with equal B–P bond lengths, which are significantly shorter than typical B–P single bond values. Delocalization of the π electrons is suggested by ^{31}P and ^{11}B NMR chemical shifts in which the phosphorus peaks appeared 70 ppm further downfield and the boron peaks 40–50 ppm upfield in comparison with the corresponding dimer. Power and coworkers [16] have also synthesized and structurally characterized an alumazene, $[MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$, in which the ring is also planar. As for the boraphosphazene, a slight upfield shift of the Group III metal (^{27}Al NMR), relative to polyiminoalane was observed. Although the ring is not planar (slightly twisted boat conformation), the Ga–P system, $[(2,4,6\text{-}Ph_3C_6H_2)GaP(\mathit{cyclo}\text{-}C_6H_{11})]_3$, has been isolated by Power and coworkers [17]. Fink and Richards [18] used homodesmic reactions to calculate the resonance energies of some of these species. Their results, in kcal/mol, are:

$$\text{C–C}(22.1) > \text{B–P}(12.7) > \text{B–N}(11.1) > \text{Al–N}(1.9)$$

Not surprisingly, benzene is found to be more aromatic than the other three inorganic benzenes, with aluminum found to be particularly poor. It is interesting that there is little apparent difference between N and its heavier congener P.

Known Group IIB–Group VI species include Zn–S trimers [19] $(R'ZnSR'')_3$, with $R' = Me_3SiCH_2$ and $R'' = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$ or $2,4,6\text{-}t\text{-}Bu_3C_6H_2$. Both of these species are approximately planar. Solution phase trimeric Zn–O compounds were reported some years ago [20], but otherwise Zn–O trimers have proven elusive [19]. A six-membered ring with tetra-coordinate Zn atoms was reported recently [21], but since this molecule cannot be aromatic, it has alternating Zn–O bond lengths. Group IIB–VI compounds (e.g. ZnO, ZnS) have received attention in connection with their use as electronics materials [22].

The interest in the bonding in the main-group benzene analogues has of course focused on the bonding in the π orbitals, in particular the existence or lack of aromaticity. It is the purpose of this paper to use *ab initio* wavefunctions in an attempt to analyze the electronic structure of main-group inorganic benzenes.

2. Calculational methods

All calculations described herein were performed with the GAMESS *ab initio* quantum chemistry program package [23]. The calculations were performed using the Stevens–Basch–Krauss (SBK) effective core potentials and basis sets

[24] for all heavy atoms, and the −31G basis [25] for hydrogen. These bases were augmented with a single *d* polarization function [26] for all elements except hydrogen and zinc. The SBK basis for Zn includes a triple *zeta* valence *d* basis, as well as a double *zeta* valence *s* and *p* set. All geometry optimizations were carried out at the restricted Hartree–Fock (RHF) level of theory, within the constraints of D_{3h} or D_{6h} symmetry for heteronuclear and homonuclear analogues, respectively. The energy hessian was calculated numerically at the resulting planar geometries, in order to verify them as minima (all real frequencies), transition states (one imaginary frequency), or higher order saddle points (more than one imaginary frequency).

Our study of the bonding combines ideas from Ruedenberg's Full Optimized Reaction Space MCSCF model [27] with his orbital self-energy localization method [28]. In order to perform the analysis, the LOCL program from the ALIS program system [29] has been incorporated within GAMESS. As shown by Ruedenberg [30], the first-order density matrix for a CI wavefunction, expressed in terms of localized orbitals, reveals atomic populations and information about bond orders in a directly interpretable way.

The CI calculation requires 6 localized orbitals, since the rings possess 6 atoms. The simplest way to obtain the necessary 6 π orbitals is a high spin calculation, placing one electron in each of them. These heptet state calculations are carried out at the ground state RHF/SBK(*d*) geometries. The resulting ROHF canonical π orbitals are then localized so as to maximize their self repulsion energy sum. The localization yields 6 atom-like *p* orbitals, referred to as "AO-like" MOs, one located on each atom within the ring. It is important to note that these orbitals, although similar to atomic orbitals, are in fact orthonormal MOs, not valence bond hybrids [30]. A full π CI calculation, including excitations up to 6 electrons, is then performed based on these 6 localized ROHF orbitals, *for the singlet ground state*. The first-order density matrix of this localized orbital CI (LMO/CI) has the following two interpretations: (a) The diagonal elements are the electron populations of the atom, and in the present case these necessarily sum to 6; and (b) the off-diagonal elements of the density matrix correspond to bond orders, with a large positive number meaning strong bonding, and a negative value indicative of an antibonding interaction. For this reason, Ruedenberg usually refers to such a density matrix constructed over localized MOs as the charge/bond order matrix.

An alternative to the foregoing procedure is to obtain the necessary orbitals from FORS-MCSCF calculations on the ground state. These include 6 active electrons within an active space consisting of the 6 π and π^* orbitals. Optimizing the orbitals for the singlet ground state of course yields a lower energy than a CI using orbitals optimized for a heptet excited state, but we encountered two difficulties. The first is that in a number of instances, it is not possible to carry out the desired MCSCF calculation. Some of the π orbitals are so polarized that the best correlating orbitals for them are not π^* orbitals. Instead they are $(n+1)p$ orbitals providing in-out correlation on the electronegative element Y. This difficulty is encountered for the Al–N, Al–P, Ga–N, Zn–O, and Zn–S cases. Secondly, even when the calculation does converge to π^* orbitals which are left-right correlating, the bond order matrix for the corresponding localized orbitals is less easily interpreted.

Because our prime interest here is a comparison of benzene analogues with the reference compound benzene itself, only the planar rings are considered. A later work will examine all possible isomeric structures.

3. Results and discussion

3.1. *Geometries and frequencies*

The $X_3Y_3H_6$ species considered here possess only alternating electropositive X, and electronegative Y atoms. Choosing X, Y = C, Si, Ge; or X from B, Al, Ga with Y from N, P, As; or X = Zn with Y = O, S ensures that the rings are valence isoelectronic with benzene. Thus, each is potentially aromatic in its planar geometry.

The calculated planar geometries for the species of interest are in excellent agreement with the available experimental values (Table 1). Apart from Zn–S, errors in bond lengths are less than 0.03 Å. The deviations of the inner-ring angle from 120°, where experimentally available, are also quite well reproduced by the

Table 1. RHF/SBK(*d*) geometries of inorganic benzenes[a]

$X_3Y_3H_6$	R_{X-Y}	R_{X-H}	R_{Y-H}	θ_X	θ_Y
C_6H_6[b]	1.406 (1.396)	1.091 (1.083)		120.0 (120.0)	
$Si_3C_3H_6$	1.766	1.483	1.094	118.7(Si)	121.3(C)
$Ge_3C_3H_6$	1.828	1.527	1.080	121.4(Ge)	118.6(C)
Si_6H_6	2.223	1.483		120.0	
$Si_3Ge_3H_6$	2.262	1.475	1.523	119.2(Si)	120.8(Ge)
Ge_6H_6	2.306	1.521		120.0	
$B_3N_3H_6$[c]	1.434 (1.44)	1.209 (1.20)	1.008 (1.00)	117.5 (118.)	112.5 (112.)
$B_3P_3H_6$[d]	1.868 (1.84)	1.198	1.397	116.6 (115.)	123.4 (124.)
$B_3As_3H_6$	1.956	1.186	1.482	116.0	124.0
$Al_3N_3H_6$[e]	1.787 (1.78)	1.584	1.016	114.2 (115.)	125.8 (125.)
$Al_3P_3H_6$	2.275	1.578	1.405	112.8	127.1
$Al_3As_3H_6$	2.359	1.573	1.489	112.4	127.6
$Ga_3N_3H_6$	1.814	1.564	1.006	114.0	126.0
$Ga_3P_3H_6$	2.264	1.556	1.393	113.4	126.6
$Ga_3As_3H_6$	2.345	1.554	1.489	112.8	127.2
$Zn_3O_3H_6$	1.956	1.567	0.952	102.4	137.6
$Zn_3S_3H_6$[f]	2.394 (2.31 $\sim$ 2.32)	1.560	1.327	99.1 ($\approx$100.)	140.9 ($\approx$140.)

[a] X refers to the more electropositive elements. θ_X and θ_Y are internal ring angles. Bond lengths are in Å and angles are in degrees. The values in parenthesis are experimental geometries

[b] see Ref. [31] (p 717)

[c] see Ref. [14] (references therein)

[d] see Ref. [15]

[e] see Ref. [15]

[f] see Ref. [19]

Table 2. Three lowest calculated frequencies[a]

Species	a_2''	e''
C_6H_6	637	441
$Si_3C_3H_6$	313	230
$Ge_3C_3H_6$	208	197
Si_6H_6	70 (*i*)	101
$Si_3Ge_3H_6$	126 (*i*)	59
Ge_6H_6	145 (*i*)	57 (*i*)
$B_3N_3H_6$	395	294
$B_3P_3H_6$	225 (*i*)	183 (*i*)
$B_3As_3H_6$	267 (*i*)	247 (*i*)
$Al_3N_3H_6$	219	148
$Al_3P_3H_6$	145 (*i*)	155 (*i*)
$Al_3As_3H_6$	173 (*i*)	219 (*i*)
$Ga_3N_3H_6$	187	132
$Ga_3P_3H_6$	178 (*i*)	218 (*i*)
$Ga_3As_3H_6$	175 (*i*)	259 (*i*)
$Zn_3O_3H_6$	68	34
$Zn_3S_3H_6$	78 (*i*)	66 (*i*)

[a] The harmonic frequencies are calculated at the RHF/SBK(*d*) level of theory. The values are in cm^{-1}. The (*i*) indicates an imaginary frequency

calculations. The distortion from a hexagon is small in the main group analogues ($\approx 5°$), but much larger for the zinc-containing rings ($\approx 20°$).

The three lowest vibrational frequencies of all species discussed here belong to the a_2'' and e'' representations of D_{3h}. The a_2'' modes lead to chair conformations, while the doubly degenerate e'' modes lead to two equivalent boat conformations. The calculated harmonic frequencies at the RHF/SBK(*d*) level are presented in Table 2. Note that apart from benzene and borazine, all of the rings are rather easily made nonplanar, as the largest frequency calculated for these motions is barely larger than 300 cm^{-1}. In fact, many of the species are not minima on the potential energy surface, as they possess imaginary frequencies for the a_2'' or e'' modes, indicating their aromaticity is insufficient to maintain planarity. Replacing any second row atom with a third row atom decreases the a_2'' and e'' frequencies. There is a similar but smaller decline when a third row atom is replaced by a fourth row atom. These are indicative of the decreasing rigidity of the planar rings.

Table 2 shows that all rings containing the second row elements C, N, or O are minimum energy structures. This is consistent with results for isolated π bonds obtained previously in this group [32]: the ability to form a π bond was found to be in the order $O \approx N > C \gg S > P > Si$. Note however that the presence of the second row atom B is not sufficient to ensure a planar minimum.

Although many of these species are first- or third-order transition states, the frequencies are small enough that they remain of chemical interest. Steric or electronic effects caused by substituents can perhaps stabilize the planar structures. For example, the B–P system has three small imaginary frequencies when the substituents are hydrogen, but nonetheless a planar B–P ring has been

Table 3. Comparison of X–Y bond lengths

X–Y	Exp. single[a]	This work aromatic[b]	 double[b]	Exp. double[a]
C–C	1.534[c]	1.406	1.350	1.339
Si–C	1.869	1.766	1.703	1.702[d]
Ge–C	1.945	1.828	1.759	1.803[e] 1.827[f]
Si–Si	2.327	2.223	2.134	2.140[g]
Si–Ge	2.357	2.262	2.175	
Ge–Ge	2.403	2.306	2.224	2.213[h] 2.347[i]

[a] experimental values, taken from Ref. [31] unless specified
[b] calculated
[c] see Ref. [33]
[d] see Ref. [34]
[e] see Ref. [35]
[f] see Ref. [36]
[g] see Ref. [37]
[h] see Ref. [38]
[i] see Ref. [39]

reported with bulky groups [15]. Similary, the Zn–S trimeric ring which has been reported [19] is close to planarity.

As previously noted by Nagase [7], hexasilabenzene is a transition state leading to a chair conformation, provided the basis is of double *zeta* plus polarization quality. The Si–Ge analogue is the only other true transition state, with an imaginary frequency of 126 cm^{-1}. The remaining species all have three imaginary frequencies, and are thus unstable to both boat and chair distortions. Note that in all cases if the planar geometry is not stable, the vibrational distortion is always with respect to out of plane motions, rather than towards unequal bond lengths. Thus, each of the molecules seems to have at least some ability to participate in aromatic binding in its planar arrangement.

The most revealing feature of Table 1 is that each species possesses six equal bond lengths in the planar geometry. The Group IV X–Y bond lengths are intermediate to the corresponding single and double bond lengths, shown in Table 3. A similar comparison for the other inorganic benzenes is complicated due to the paucity of experimental data and ambiguities in defining a typical single bond. For the Group III–V case, it is not clear whether this should be H_3B–NH_3 (which has a weak dative bond) or H_2B–NH_2 (which has a partial dative π bond).

3.2. Bond separation reactions

A quantitative measure of aromatic stabilization, relative to isolated single and double bonds, is the energy of a bond separation reaction [40]. For these isodesmic reactions, one conserves bond type (identical numbers of XH, YH, X–Y, and X=Y bonds), but compares the conjugated π system in the ring to separated molecules. The bond separation reactions, along with their energetics

Table 4. Energy differences ($\Delta H_{\text{reaction}}$) of bond separation reactions (kcal/mol)

Reaction	RHF[a]	MP2[b]
$C_6H_6 + 6CH_4 \rightarrow 3H_2C{=}CH_2 + 3H_3C{-}CH_3$	61.4	74.7
$Si_3C_3H_6 + 3SiH_4 + 3CH_4 \rightarrow 3H_2Si{=}CH_2 + 3H_3Si{-}CH_3$	60.2	62.0
$Ge_3C_3H_6 + 3GeH_4 + 3CH_4 \rightarrow 3H_2Ge{=}CH_2 + 3H_3Ge{-}CH_3$	58.7	65.3
$Si_6H_6 + 6SiH_4 \rightarrow 3H_2Si{=}SiH_2 + 3H_3Si{-}SiH_3$	42.3	57.8
$Si_3Ge_3H_6 + 3SiH_4 + 3GeH_4 \rightarrow 3H_2Si{=}GeH_2 + 3H_3Si{-}GeH_3$	41.0	60.2
$Ge_6H_6 + 6GeH_4 \rightarrow 3H_2Ge{=}GeH_2 + 3H_3Ge{-}GeH_3$	40.3	59.9

[a] The corrected zero-point energies (multiplied by 0.89) are used

[b] Second order Møller–Plesset energies at the RHF/SBK(*d*) geometries, using the corrected RHF zero-point energies

are shown in Table 4. For reasons noted above, these are examined only for the Group IV compounds.

The Group IV species show a trend that is consistent with the frequency results presented above. Benzene is the most aromatic species by this measure, and the molecules containing 3 carbon atoms are the next most aromatic. Those rings which do not contain carbon are slightly less aromatic. While there is a considerable drop in the calculated MP2 bond separation energy upon replacing carbons in benzene, there is little variation among the benzene analogues themselves. Even so, those with no carbons are not minima on the potential energy surfaces.

3.3. Electronic structure

The degree of covalency in the inorganic benzenes can be assessed from the charge, or electron population in the localized orbital located on each of the 6 atoms. These π atomic populations n_X and n_Y are given in Table 5. When the atoms X and Y are identical, or very similar in electronegativity (e.g., Si–Ge), the 6 π electrons are equally shared. Si–C and Ge–C are also close to full delocalization ($n_Y \approx 1.15$ electrons). The Group III–V rings are noticeably more ionic, with $n_Y \approx 1.3$ for B rings, and 1.5 for Al or Ga rings. The orbitals for the two Zn compounds are from approximately converged ROHF calculations (due to orbital symmetry breaking problems), but indicate an even higher degree of ionicity, $n_Y \approx 1.8$.

The *ortho*, two different *meta*, and *para* bonding interactions are also given in Table 5. The nearest neighbor *ortho* interaction is always the largest, and represents partial bonding. It is largest for benzene itself (0.614) and is only slightly smaller ($\approx$0.59) for the remainder of the Group IV rings and for the boron-containing rings. This bonding interaction drops off slightly for the aluminum- or gallium-containing rings, to 0.55, and dramatically for the very ionic zinc rings, to 0.40.

In order to calibrate these bond orders, consider the analogous quantities for the ehtylene $H_2X{=}YH_2$, presented in Table 6. The bond order for a full π bond in C=C is 0.897, and there is a small decrease in bond order, in the range 0.83–0.85, for the other Group IV compounds. The bond order index is therefore not very sensitive to the π bond energy, which is 65 kcal/mol for C=C,

Table 5. LMO/CI populations and bond orders for the π orbitals[a]

$X_3Y_3H_6$	n_X	n_Y	ϱ_o(XY)	ϱ_m(XX)	ϱ_m(YY)	ϱ_p(XY)
using ROHF orbitals						
C_6H_6	1.000		0.614	−0.001		−0.271
$Si_3C_3H_6$	0.835	1.165	0.599	0.071	−0.067	−0.250
$Ge_3C_3H_6$	0.869	1.131	0.590	0.061	−0.056	−0.245
Si_6H_6	1.000		0.590	0.061		−0.249
$Si_3Ge_3H_6$	0.992	1.008	0.593	0.004	−0.007	−0.247
Ge_6H_6	1.000		0.590	−0.001		−0.244
$B_3N_3H_6$	0.614	1.386	0.589	0.116	−0.110	−0.220
$B_3P_3H_6$	0.681	1.319	0.596	0.051	−0.053	−0.247
$B_3As_3H_6$	0.714	1.286	0.595	0.038	−0.041	−0.251
$Al_3N_3H_6$	0.507	1.493	0.552	0.139	−0.125	−0.170
$Al_3P_3H_6$	0.452	1.548	0.544	0.104	−0.103	−0.168
$Al_3As_3H_6$	0.471	1.529	0.549	0.098	−0.098	−0.178
$Ga_3N_3H_6$	0.567	1.433	0.562	0.128	−0.112	−0.193
$Ga_3P_3H_6$	0.489	1.511	0.555	0.100	−0.098	−0.184
$Ga_3As_3H_6$	0.508	1.492	0.559	0.092	−0.092	−0.193
$Zn_3O_3H_6$	0.235	1.765	0.434	0.098	−0.095	−0.060
$Zn_3S_3H_6$	0.171	1.829	0.384	0.077	−0.077	−0.034
using MCSCF orbitals						
C_6H_6	1.000		0.620	−0.001		−0.279
$Si_3C_3H_6$	0.891	1.109	0.620	0.114	−0.109	−0.286
$Ge_3C_3H_6$	0.905	1.095	0.614	0.103	−0.097	−0.282
Si_6H_6	1.000		0.603	−0.001		−0.259
$Si_3Ge_3H_6$	0.991	1.009	0.601	0.006	−0.009	−0.257
Ge_6H_6	1.000		0.598	−0.001		−0.254
$B_3N_3H_6$	0.862	1.138	0.640	0.105	−0.099	−0.306
$B_3P_3H_6$	0.643	1.356	0.600	0.086	−0.087	−0.241
$B_3As_3H_6$	0.667	1.333	0.600	0.071	−0.073	−0.246
$Al_3As_3H_6$	0.689	1.311	0.624	0.106	−0.103	−0.269
$Ga_3P_3H_6$	0.721	1.279	0.630	0.098	−0.095	−0.280
$Ga_3As_3H_6$	0.656	1.343	0.616	0.113	−0.111	−0.255

[a] The orbital populations (n) and *ortho*, *meta*, and *para* bond orders (ϱ) are calculated using two orbital sets (see text)

and is much smaller for Si=C and Si=Si, 37 and 23 kcal/mol, respectively [32]. Note that the bond orders for all of the rings are somewhat less than these full π bonds, indicative of the delocalization. The majority of the nearest neighbor bond orders in Table 5 fall in the range 0.55–0.61, so that the nearest neighbor interaction in the rings is a significant percentage of the 0.83–0.90 value typical of Group IV π bonds.

The large density matrix elements for the non-nearest neighbor π interactions are also indicative of the delocalized interactions in these molecules. There is a fairly substantial bonding interaction (up to 0.11) between the electropositive XX atoms, which is canceled by an approximately equal antibonding interaction between the electronegative and hence electron-rich YY pairs (up to −0.11).

Table 6. Populations and bond orders in ethylenes $H_2X{=}YH_2$

X–Y	n_X	n_Y	$\varrho(XY)$
C–C	1.000		0.897
Si–C	0.875	1.125	0.849
Ge–C	0.870	1.130	0.833
Si–Si	1.000		0.852
Si–Ge	0.977	1.023	0.847
Ge–Ge	1.000		0.841

When X and Y are the same element, or have similar electronegativities, the values for the XX and YY bond orders are much smaller. In all cases, the net *meta* interactions are essentially zero.

The XY *para* interaction is quite substantially antibonding, ranging up to about -0.25. Thus, the density matrix tells us that while all nearest neighbor XY pairs have a bond order that is a substantial fraction of a full π bond, there is a smaller antibonding interaction across the ring. It is this additional antibonding contribution that yields the chemist's perception that benzene's π bond order is 0.5, as the nearest neighbor interactions themselves are stronger than a half bond. We can define an overall π bond order by summing the *ortho*, *meta*, and *para* interactions:

$$(6\varrho_o(XY) + 3\varrho_m(XX) + 3\varrho_m(YY) + 3\varrho_p(XY))/6$$

In all cases except the two Zn compounds, this average bond order lies in the range 0.46–0.48. The poorly delocalized Zn compounds have values of 0.41 for Zn–O, and 0.37 for Zn–S.

Many other chemists have tried to assign a bond order in benzene. Coulson's simple consideration [41] of the two Kekulé structures of benzene leads to a bond order of 0.5; inclusion of Dewar benzene and other valence bond structures leads to a lower value. Pauling [42] used valence bond calculations and bond length-bond order considerations to obtain a π bond order of 0.5. Streitweiser [43] used simple Hückel MO theory to assign a bond order of 2/3 for benzene.

The *para* element of the LMO/CI bond order matrix is just one way of presenting the partial antibonding inherent in a 6 π electron aromatic system. Two possibly more familiar ways involve the ground-state SCF orbitals. The canonical MOs of benzene consist of a completely bonding a_{2u} orbital, and a degenerate e_{1g} pair. Each of these e_{1g} orbitals has one node, and this antibonding reduces their formal bond order to just 2/6 of that in the a_{2u} orbital. A pictorial way to display the same antibonding is with the localized closed shell SCF orbitals. In the present $X_3Y_3H_6$ compounds, the localized π orbitals center themselves on Y, with equivalent delocalization towards each neighboring X. As may be seen in Fig. 1, there is always an antibonding tail on the Y atom in the *para* position!

The orbitals for the LMO/CI calculation can be obtained directly from MCSCF calculations on the ground state in a number of cases. Where available these values are also included in Table 5. The same trends in ionic character are observed for n_X and n_Y. The bond orders are even closer to each other than when

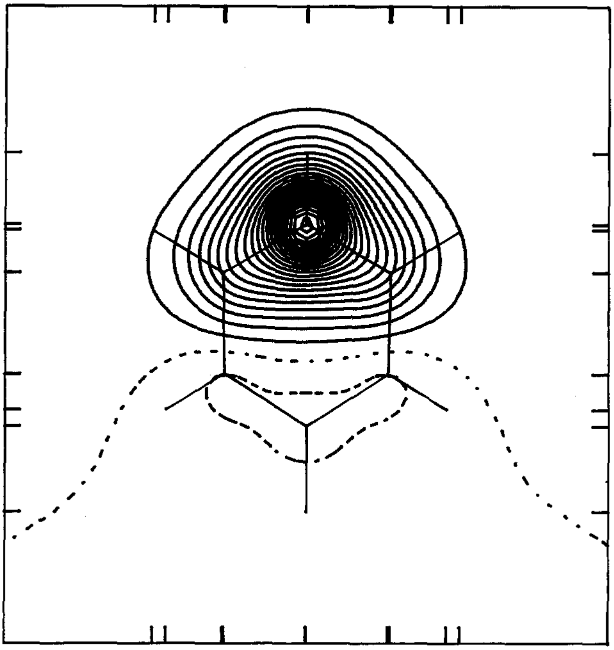

Fig. 1. One of three equivalent localized SCF orbitals for borazine, drawn 0.75 Å above the plane with a contour increment of 0.010 $\text{bohr}^{-3/2}$. Note bonding from nitrogen to each *ortho* boron, and antibonding to the *para* boron

obtained from a CI based on the high spin ROHF orbitals. This close correspondence between the MCSCF and ROHF orbital optimization approaches is encouraging, in the light of their intrinsic N^5 versus N^4 computational expense.

4. Conclusions

The present calculations consider a number of existing and hypothetical inorganic benzenes. The ionic character increases in the order Group IV–IV < Group III–V < Group IIB–VI, in line with chemical intuition and basic electronegativity arguments. A number of these compounds possess one or three small imaginary frequencies, but each must still be regarded as a potential synthetic target, as planar B–P and approximately planar Zn–S compounds already exist. Inclusion of the second period atoms C, N, or O is a way to stabilize the rings, as all such rings are minimum energy structures, even with H substituents. This is true even for the Zn–O ring, which has so far proven elusive in the laboratory [19].

The bond orders presented here are very similar for many of the compounds, and are the same as those previously obtained from valence bond or bond length-bond order calculations. They probably do not closely track the bond energies (or "aromaticity"), as AB bonds of the same order *n* always have different bond strengths (compare $H_3C–CH_3$ with F–F). Since the bond orders for all rings not containing Zn are actually very similar, it is possible that one day all of them will be isolated in the laboratory.

In closing, we call attention to the beautiful work on localized orbitals for benzene (and many polycyclic aromatic hydrocarbons) by Professor Ruedenberg and his students [12]. That paper shows how the SCF localized orbitals for benzene can be evolved from set of Kekulé-like orbitals, to orbitals like that shown here for borazine, to the other equivalent set of Kekulé-orbitals. Figure 12 of that paper deserves to be included in every introductory organic chemistry text.

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