Aromaticity in X₃Y₃H₆ (X = B, Al, Ga; Y = N, P, As), X₃Z₃H₃ (Z = O, S, Se), and Phosphazenes. Theoretical Study of the Structures, Energetics, and Magnetic Properties

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A systematic estimation of aromaticity in $X_3Y_3H_6$, **1**, (X = B, Al, Ga; Y = N, P, As), $P_3N_3H_6$, **2**, and $X_3Z_3H_3$, **3** (Z = O, S, Se), has been conducted using structural, energetic, and magnetic criteria. Estimates based on aromatic stabilization energy (ASE) calculations predict that **1BN** (**1**; X = B, Y = N) and **1BP** are equally aromatic. Contrary to this, we have found, from magnetic susceptibility exaltation (MSE) and from the nucleus independent chemical shift (NICS) data at the B3LYP/6-31G* level, that **1BN** is not aromatic while **1BP** is. This emphasizes the fact that energetic and magnetic criteria need not be parallel. On the basis of MSE and NICS values, all **1XP** compounds show strong aromatic character; **1XAs** are borderline aromatic while **1XN** compounds are nonaromatic. Despite being aromatic, all **1XP** and **1XAs** compounds are found to prefer nonplanar geometries. MSE and NICS criteria can also diverge quite strongly; this has been observed in the $X_3Z_3H_3$ family. MSE values for **3BS**, **3BSe**, **3AlO**, **3AlS**, and **3GaS** are more than half of the MSE value for benzene, indicating substantial aromatic character. However, NICS estimates point to the contrary; none of the type **3** compounds are aromatic. The problem with the ASE and MSE is that both depend on the choice of the reference systems while NICS, which avoids the need for reference molecules, is impossible to vary experimentally. In spite of this epistemological deficiency of NICS, we find it complementary to the ASE and MSE criteria. Despite the existence of a large number of well-established structures and substantial aromatic stabilization energy, phosphazenes, **2**, are not aromatic according to NICS data.

Introduction

Inorganic cyclic ring systems that are isoelectronic with benzene have been known for many years. Borazine, **1BN** (**1**; X = B, Y = N) and phosphazene, **2**, are textbook examples.[1]

1   **2**   **3**

4   **5**

6   **7**
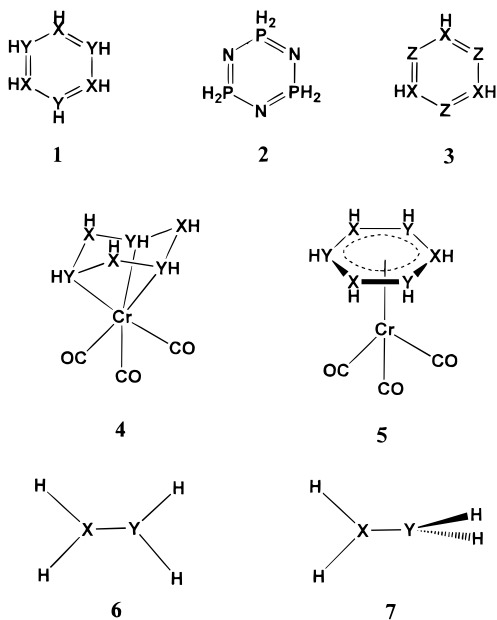
Numerous derivatives of **1BN** have been synthesized and well

characterized.[2] Planarity, equal bond lengths, and the similarity in physical properties to benzene gave the name "inorganic benzene" to borazine. However, the chemical properties of borazine are quite different from those of benzene.[1,3] Borazine readily undergoes several polar addition reactions which are extremely difficult with benzene. Theoretical calculations have shown that the π electrons are localized on nitrogen atoms, making it basic; boron, as expected, is acidic in nature.[3] Power's group has synthesized several heavier analogues of borazine: **1BP**, **1GaP**, **1AlN**, and **1GaN**.[4] A few of the group 16 analogues of the borazine family, $X_3Z_3H_3$ (X = B, Al, Ga; Z = O, S, Se), **3**, are also known; boraxine, **3BO**, and the B−S analogue, **3BS**, are well-characterized examples.[5] Phosphazenes, **2**, represent another class of inorganic benzenes where the hypervalent phosphorus is involved in the delocalization.[6] The extent of aromaticity in these systems is of current interest.

Several attempts have been made to estimate the aromaticity in these systems.[7,8] Aromatic stabilization energy (ASE)

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calculations based on homodesmotic equations (eq 1) have
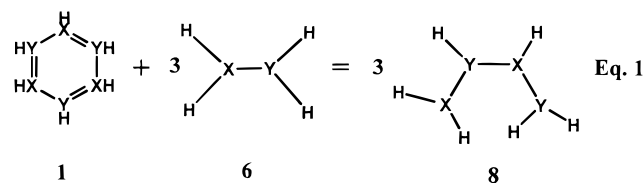
shown that **1BN** and **1BP** have nearly equal stabilization energies (10.1 and 11.2 kcal/mol, respectively) which are close to half of the value for benzene (22.2 kcal/mol) (at MP4/6-31G*//HF/6-31G*).[7b] However, magnetic susceptibility exaltation (MSE) data, based on group increment values, indicate that **1BN** is not aromatic (-1.7), compared to benzene (-13.7).[8] No MSE data exist for **1BP**. Both **1BN** and **1BP** form metal complexes of the type $(B_3Y_3H_6)Cr(CO)_3$, but they differ substantially in the mode of bonding.[9,10] Borazine metal complex **4BN** is puckered, indicating the preference for σ bonding where the lone pairs of N interact with the metal. The phosphorus analogue **5BP** is more like benzene complex **5CC**. This is an indication that the π delocalization is more than that in **1BN**, which is not reflected in ASE estimates. Are aromatic stabilization energies good indicators of aromaticity?

Phosphazenes, $P_3N_3R_6$, **2**, present a similar dilemma.[6] The planarity, equal and short PN bond distances, high stability, and extreme resistance to reduction resemble those of aromatic compounds. But there exists a significant difference. The delocalization here is from $d\pi-p\pi$ overlap. Can this overlap be sufficient to make the derivatives of **2** aromatic? What is the extent of delocalization present in these systems?

Aromaticity is not an experimentally observable quantity. Hence, despite its common usage in chemistry, there is no acceptable definition which can be applied to a wide range of chemical systems. Conventionally, aromaticity is identified with high stability, near planarity, small bond length alternation, unusual magnetic properties, and preference for substitution over addition in chemical reactions. Though usually there exists good correlation between these criteria, this is not universal. The criterion of high stability is true for benzene but not for Si_6H_6; the aromatic hexasilabenzene isomer is less stable than the

nonaromatic [3]-hexasilaprismane.[11] Recently, Schleyer and co-workers found that the most stable isomer in some heterobicyclic aromatic systems is the least aromatic.[12] Many benzenoid systems have significant differences in bond lengths and undergo addition reactions rather than substitution.[8] Abnormal ^{1}H chemical shifts are often used as a good indicator of aromaticity, but this is restrictive in many examples.

Nevertheless, the criteria based on aromatic stabilization energy and "ring current" are shown to be very effective in quantifying aromaticity. Aromatic stabilization energies derived from homodesmotic equations have been used quite successfully for a long time in quantifying aromaticity.[13] A prudent choice of the reference molecules ensures a reliable estimate of aromaticity in most systems. Another criterion used as a measure of aromaticity is the magnetic susceptibility exaltation (MSE) arising from the ring current. This exaltation, Λ, is defined as the difference between the susceptibility (χ_m) calculated from the theory or measured experimentally and that estimated using an additivity rule.[14] This index was tested by Dauben and co-workers over a wide range of molecules and was found to work satisfactorily.[15] Schleyer and co-workers have used this criteria for several systems. Recently, a new magnetic criterion, viz. nucleus-independent chemical shift (NICS), has been used to probe aromaticity in planar rings.[16] It is defined as the negative of the absolute magnetic shielding computed at the geometrical center of the ring. Aromatic rings are characterized by negative NICS values (diatropic) and nonaromatic compounds by positive NICS values (paratropic). The chemical shift value at the midpoint of the molecule will have the π contribution to the out-of-plane tensor from the diamagnetic part only; paramagnetic contributions are minimum at this point.[17] Thus, for NICS, no reference systems need to be calculated, and therefore, unlike MSE, it is not sensitive to the choice of the reference systems. NICS has been found to be very useful for planar rings.[16] However, NICS is not an experimentally observable quantity and with it are all the uncertainties attached to experimentally unverifiable parameters. Any one of these criteria of aromaticity provides a spectrum of values. How do we draw the line of demarcation between aromatic and nonaromatic compounds? To make the discussion tractable, we arbitrarily assign the convention that if a molecule has less than half the magnitude of property in comparison to that of benzene, it is not aromatic. Currently there exists no comparison of aromaticity based on these three criteria for the inorganic benzenes. Theoretical studies that are directed to address aromaticity in **3** are almost nonexistent. Several theoretical studies exist in the literature on **2** to understand the

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Table 1. Total Energies of $X_3Y_3H_6$ (**1**) Along with Zero-Point Energies (ZPE) Calculated at the B3LYP/6-31G* Level

structure	tot. energy (au)	ZPE (kcal/mol)	structure	tot. energy (au)	ZPE (kcal/mol)
1BN	−242.67016	58.63	1AlAs	−7432.31683	29.60
1BP	−1102.24107	43.25	1GaN	−5936.79088	43.64
1BAs	−6779.43801	40.12	1GaP	−6796.52559	31.79
1AlN	−895.37568	43.58	1GaAs	−12473.80812	29.11
1AlP	−1755.04751	32.04			

Table 2. Total Energies of $X_3Z_3H_3$ (**3**) Along with Zero-Point Energies (ZPE) Calculated at the B3LYP/6-31G* Level

structure	tot. energy (au)	ZPE (kcal/mol)	structure	tot. energy (au)	ZPE (kcal/mol)
1BO	−302.31918	34.71	1AlSe	−7927.56413	17.16
1BS	−1271.08422	26.62	1GaO	−5996.45424	21.14
1BSe	−7274.64758	26.60	1GaS	−6965.39015	17.71
1AlO	−955.09713	22.42	1GaSe	−12969.03532	16.57
1AlS	−1923.94340	18.36			

Table 3. Important Parameters for Benzene (**1CC**), Ethylene (**6CC**) and 1,3-butadiene (**8CC**) Calculated at the B3LYP/6-31G* Level

	1CC	**6CC**	**8CC**
energy (au)	−232.24886	−78.58746	−155.99214
susceptibility ϵ_1	92.56	19.35	34.24
ϵ_2	22.82	10.18	18.00
ϵ_3	22.82	9.53	16.18
ASE (kcal/mol)	21.9		
MSE (Λ_{av})	−16.7		
NICS	−11.5		

bonding and the role of d orbital participation in bonding.[18] But relatively little work has been done on the aromaticity of these classes of compounds.

In this paper, structural, energetic, and magnetic criteria are used to ascertain the relative aromaticity of $X_3Y_3H_6$ (X = B, Al, Ga; Y = N, P, As), $X_3Z_3H_3$ (X = B, Al, Ga; Z = O, S, Se), and $P_3N_3H_6$.

Computational Details

Hybrid HF−Density functional calculations using the Becke, Yang, and Parr correlation functional and 6-31G* basis set (B3LYP/6-31G*) are used for all the molecules considered here.[19] Full geometry optimizations were done for all molecules, and vibrational frequencies were calculated to establish the nature of stationary points. All calculations were performed using the Gaussian 94 series of programs.[20] The total energies of $X_3Y_3H_6$ and $X_3Z_3H_3$ along with benzene are given in Tables 1−3. We have used the energies and properties of the optimized planar form of the rings in establishing the aromaticity index. This is because, for most systems, the experimentally known structures are planar. Comparisons can be easily made across the ring systems if all of them have planar geometries.

NBO analysis is used to gain further insight into the bonding in these molecules, using the standard routine given in Gaussian 94

programs.[21] The non-NRT (natural resonance theory) bond indices, namely Wiberg bond indices (WBI), have been used to gauge the bond strengths.[21]

The NMR shielding tensors were computed by two different methods: (1) the gauge-independent atomic orbital (GIAO) and (2) the continuous set of gauge transformations (CSGT) methods.[22,23] The magnetic susceptibility tensors were computed with CSGT-B3LYP/6-31G*//B3LYP/6-31G* and the NICS values with the GIAO−HF/6-31G*//B3LYP/6-31G* method by placing a ghost atom (symbol Bq for Gaussian 94 input) at the geometrical center of the molecule.[16]

Results and Discussion

$X_3Y_3H_6$ Systems. (a) Structural Criteria. In the discussion of relative aromaticity of inorganic benzenes, it is useful to start with the structural data. The bond length equalization, which is the hallmark of aromaticity for hydrocarbons, has also been observed in borazine and related systems. In borazine, the B−N bond length is intermediate between single and double bond lengths. For comparison, X−Y bond lengths in XH_2YH_2 (**6**) and XH_2YH_2 (**7**) as well as WBI are given in Table 4.[21]

In general, the X−Y distance in $X_3Y_3H_6$ systems is calculated to be intermediate between single and double bond lengths for all the X and Y considered here (Table 4). As the size of the atoms increases, the X−Y distances tend to increase. Thus, the structural data point to a delocalized description for six-membered rings. To gain further insight into the bonding between the X−Y bond pairs, Wiberg bond orders have been calculated.[21] For polar bonds, the bond orders will be less than the corresponding covalent bond orders. The WBI indicates that the bond order decreases with the increase in the electronegativity difference between X and Y (Table 4). For most of the compounds in the present study, the X−Y single bond order, as modeled by $XH_2YH_2\perp$, **7**, is less than 1. For X=Y (**6**) double bonds, WBI is much less than 2. The WBI for **1BP** is highest of all, reflecting the enhanced delocalization in comparison with other compounds. This indicates **1BP** to be the most aromatic among the systems considered here. However, the bond-length criterion alone is not sufficient to probe aromaticity.[8]

(b) Energetic Criteria. Traditionally, aromatic stabilization energy is associated with the aromaticity of the chemical systems under consideration. Homodesmotic equations, which preserve similar bond types on both sides, have been widely used to estimate aromatic stabilization energies.[12] The accuracy of the ASE calculation depends on the reference systems considered. For benzene, a homodesmotic equation consisting of ethylene and *cis*-1,3-butadiene is found to give the best results.[8] Similar equations were applied to several inorganic ring systems such as Si_6H_6 and P_6 with considerable success.[b,24]

Earlier, aromatic stabilization energy calculations using eq 1, were performed on **1BN**, **1BP**, and **1AlN**.[7b] As anticipated from the electronegativity difference between the bond pairs, **1AlN** has very low aromatic stabilization energy. Surprisingly,

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Table 4. X−Y Bond Lengths (Å) and Wiberg Bond Indices (WBI) of $XH_2YH_2\|$ (**6**), $X_3Y_3H_6$ (**1**), and $XH_2YH_2\perp$ (**7**) Systems

structure	Z = N	Z = P	Z = As
7BZ	1.473 (0.88)	1.967 (1.05)	2.060 (1.05)
1BZ	1.431 (1.00) [1.429]^a	1.841 (1.35) [1.840]^d	1.915 (1.35)
6BZ	1.393 (1.26)	1.796 (1.63)	1.871 (1.64) [1.926]^e
7AlZ	1.809 (0.57)	2.371 (0.82)	2.439 (0.84)
1AlZ	1.801 (0.56) [1.782]^b	2.268 (0.92)	2.325 (0.95)
6AlZ	1.780 (0.77)	2.235 (1.07)	2.281 (1.04)
7GaZ	1.897 (0.65)	2.352 (0.86)	2.423 (0.87)
1GaZ	1.848(0.72) [1.859]^c	2.234 (1.01)	2.296 (1.04)
6GaZ	1.832 (0.87)	2.208 (1.19)	2.265 (1.23)

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Table 5. Aromatic Stabilization Energies (ASE) (kcal/mol) and Magnetic Susceptibility Exaltation (Λ) Values (cgsu) Calculated at the B3LYP/6-31G* Level and Nucleus-Independent Chemical Shift (NICS) Values of $X_3Y_3H_6$ Systems at the GIAO-Hf/6-31G*//B3LYP/6-31G* Level

structure		Y = N	Y = P	Y = As
1BY	ASE	9.6	10.4	8.7
	Λ	−5.9	−17.8	−20.3
	NICS	−2.1	−7.9	−8.3
1AlY	ASE	2.0	2.8	−0.7
	Λ	−4.5	−9.7	−12.1
	NICS	−2.2	−4.9	−5.6
1GaY	ASE	5.7	3.2	2.4
	Λ	−1.3	−10.0	−12.9
	NICS	−1.5	−5.3	−6.0

Table 6. Magnetic Susceptibility Data (in ppm cgsu with the Signs Reversed) for $X_3Y_3H_6$ (**1**), **6**, and **8**, Calculated at CSGT-B3LYP/6-31G* Level

structure	ϵ_1	ϵ_2	ϵ_3	χ_{av}
6BN	17.22	13.17	9.76	13.38
8BN	31.90	22.19	18.65	24.25
1BN	57.48	29.03	29.03	38.51
6BP	25.89	19.23	18.31	21.14
8BP	46.25	34.55	33.15	37.98
1BP	113.17	45.87	45.87	68.30
6BAs	35.44	29.51	28.93	31.29
8BAs	65.34	55.09	52.49	57.64
1BAS	147.57	75.25	75.25	99.36
6AlN	23.63	17.65	17.33	19.34
8AlN	41.15	35.33	32.25	36.24
1AlN	57.54	57.54	48.79	54.62
6AlP	31.28	25.52	22.69	26.50
8AlP	56.10	49.48	44.10	49.89
1AlP	86.76	76.36	76.36	79.83
6AlAs	43.38	35.65	32.62	37.22
8AlAs	78.92	69.25	63.53	70.56
1AlAs	121.25	107.53	107.53	112.10
6GaN	31.63	29.84	28.90	30.12
8GaN	58.90	57.73	56.06	57.78
1GaN	83.69	83.59	83.59	83.62
6GaP	42.06	38.30	34.94	38.77
8GaP	77.22	74.65	68.03	73.30
1GaP	121.52	111.15	111.15	114.61
6GaAs	52.12	48.20	45.16	48.49
8GaAs	96.18	92.56	87.06	91.94
1GaAs	157.22	136.24	136.24	143.23

despite the different bond polarities, both borazine and boraphosphabenzene possess very similar aromatic stabilization energies. We used similar equation (eq 1) for estimating the aromaticity for $X_3Y_3H_6$. The calculated energy values are depicted in Table 5. In the estimation of energies, planar geometries were used for all of the reference systems for an across-the-board comparison.

In agreement with the earlier work, both **1BN** and **1BP** have very similar aromatic stabilization energies.[7b] **1AlN** has very small ASE in accordance with the electronegativity difference between the aluminum and nitrogen. In general, as the electronegativity difference between the X−Y pairs increases, the ASE decreases. This is in tune with the observation that overlap of orbitals centered on atoms decreases with increasing electronegativity difference. However, the delocalization is not the only factor that contributes to the final value of the aromatic stabilization energy. Strain and other factors would also have influence. It is extremely difficult to delineate these contributions from the total value of eq 1. The next section considers studies based on magnetic properties of $X_3Y_3H_6$ systems.

(c) Magnetic Criteria. Aromatic compounds have very large out-of-plane susceptibilities in comparison to the in-plane components. The magnetic susceptibility data for $X_3Y_3H_6$ systems along with the values for **6** and **8**, which are necessary for the increment scheme, are given in Table 5. Almost all compounds have large out-of-plane susceptibilities (ϵ_1) except for **1AlN**. The magnetic susceptibility exaltation was successfully applied by Dauben and co-workers for a large number of hydrocarbons. For the present systems, the MSE, Λ, is defined according to eq 1 (Table 6). This can be compared to the MSE value of −16.7 calculated for benzene (Table 3). According to this, **1BN** is not aromatic, which is in accordance with earlier results (Table 5).[8] This contrasts with the comparable ASE values of **1BN** and **1BP**. Further estimates of aromaticity can be made from NICS.[16] These are given along with the exaltation

data (Table 5). The NICS values reflect the same trends as that of MSE. Large NICS values can be seen for **1BP** and **1BAs** compounds. The compounds involving Al, Ga, P, and As are borderline aromatics. Though not exact, there is a good correlation between the electronegativity difference between the heavy atoms involved in the ring and various parameters of aromaticity. Thus the top right side of the Table 5 gives the systems with highest aromaticity. The bottom left has the least aromatic candidates. These are also the ones with extreme electronegativity differences. There is a progressive increase in aromaticity from nitrogen to phosphorus to arsenic in these systems. According to the yardstick of a 50% value of benzene, all the $X_3Y_3H_6$ systems except X = N are aromatic.

(d) Planarity vs Nonplanarity. We have noticed in the previous section that the phosphorus and arsenic compounds of B, Al, and Ga are aromatic or quasiaromatic. However, all of them are third-order stationary points on the B3LYP/6-31G* potential energy surface, with the imaginary frequencies corresponding to the out-of-plane movement of P or As atoms. These distortions are expected to decrease the π interaction with the neighboring groups. What are the overriding factors responsible for the ring puckering?

Table 7. Total and Relative Energies (with Respect to the Planar Structures, **1XY** of Table 1) of the Optimized Structures of $X_3Y_3H_6$ (**1**) Systems Calculated at the B3LYP/6-31G* Level

structure	tot. energy (ZPE)	RE[a]	structure	tot. energy (ZPE)	RE[a]
9BP	−1102.24108 (43.05)	0.71	9AlAs	−7432.34085 (30.17)	15.07
9BAs	−6779.46291 (41.74)	15.64	9GaP	−6796.55234 (31.11)	16.90
9AlP	−1775.06243 (32.58)	9.36	9GaAs	−12473.84769 (29.95)	24.83

[a] Without ZPE correction.
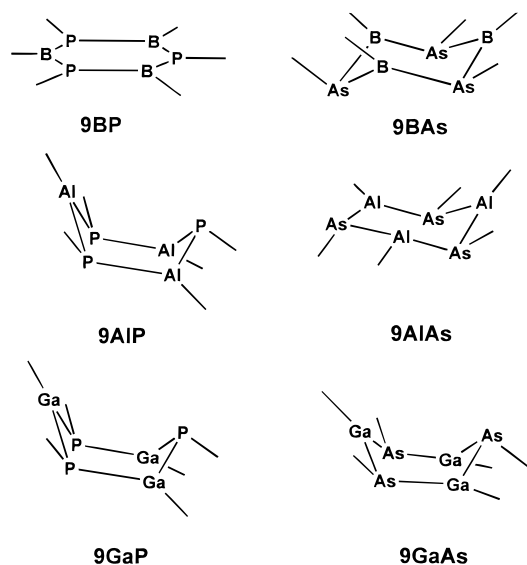
Figure 1. 1. Schematic representation of Becke 3LYP/6-31G* optimized geometries.

Table 8. Inversion Barriers of YH_3 Systems Calculated at the B3LYP/6-31G* Level

Y	TE YH_3 (C_{3v})	TE YH_3 (D_{3h})	RE
N	−56.54795	−56.53773	6.42
P	−343.14028	−343.08361	35.56
As	−2235.53747	−2235.46418	45.99

To understand these factors, we have optimized the structures without any symmetry constraints (C_1 symmetry), **9** (Figure 1). The total and relative energies are given in Table 7. In agreement with the experimentally observed planar geometry of the derivatives of **1BP**, the C_1 symmetry structure is energetically and structurally very close to the planar optimized geometry. This is in contrast to the earlier result (HF/6-31G*) where the nonplanar structure is calculated to be 5 kcal/mol lower in energy than the planar one.[7b]

Except **1BP**, all the structures in Table 7 are puckered to a large extent and substantially lower in energy (Table 7). The solid-state structure of **1GaP** has a boat conformation with average Ga−P distance of 2.310 Å. We have located a similar kind of boat conformation, **9GaP**, with the average Ga−P distance 2.296 Å. The nonplanarity in these compounds is not only due to the small ASE value but also due to the large inversion barriers of PH_3 and AsH_3 (Table 8). The inversion barrier for ammonia is very small in comparison to those for other group members. Therefore, all the nitrogen compounds are planar, whereas the remaining structures are puckered. Additionally, the ASE (Table 5) is small except for that of **1BP**. In other words, the gain in delocalization in the planar geometry is not sufficient to compensate the preference for pyramidalization.

$X_3Z_3H_3$ Systems. $X_3Z_3H_3$, **3** (X = B, Al, Ga; Z = O, S, Se), form another group of six-π-electron systems. One lone pair of the group 16 elements is in the plane of the ring, and the other lone pair is perpendicular to the ring. The well-known

Table 9. X−Z Bond Lengths (Å) and Wiberg Bond Indices (WBI) of $XH_2ZH\|$ (**10**), $X_3Z_3H_3$ (**3**), and $XH_2ZH\perp$ (**11**) Systems Calculated at the B3LYP/6-31G* Level

structure	Z = O	Z = S	Z = Se
11BZ	1.364 (0.94)	1.873 (1.16)	2.006 (1.16)
3BZ	1.377 (0.88) [1.383][a]	1.811 (1.26) [1.795][b]	1.928 (1.29)
10BZ	1.354 (1.08)	1.783 (1.43)	1.899 (1.47)
11AlZ	1.697 (0.58)	2.233 (0.77)	2.342 (0.82)
3AlZ	1.721 (0.56)	2.193 (0.82)	2.305 (0.90)
10AlZ	1.714 (0.64)	2.199 (0.90) [2.194][c]	2.300 (0.98)
11GaZ	1.816 (0.64)	2.256 (0.81)	2.358 (0.86)
3GaZ	1.808 (0.63)	2.204 (0.88)	2.307 (0.95)
10GaZ	1.810 (0.73)	2.207 (0.98) [2.208][c]	2.304 (1.05)

[a] Boese, R.; Polk, M.; Blaser, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 245. [b] Huttner, G.; Kreig, B. *Chem. Ber.* **1972**, *105*, 3437. [c] Wehmschulte, R. J.; Senge, K. R.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 2593.

example in this category is boraxine, $B_3O_3H_3$, **3BO**. The sulfur analogue of boraxine is also experimentally known. However, little work has been done on these systems addressing the question of aromaticity. In quantifying aromaticity here, we have essentially used the same methodology as used for $X_3Y_3H_6$ systems.

Bond lengths along with WBI of $X_3Z_3H_3$, **3**, $XH_2ZH\|$, **10**, and $XH_2ZH\perp$, **11**, are given in the Table 9. Unlike the bond
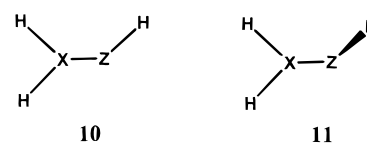
lengths in $X_3Y_3H_6$ systems (Table 4), the X−Z bond lengths fall in a short range. The WBI shows a slightly different picture. The bond orders do not vary linearly with the bond distances. Nevertheless, the differences among various bond types (single, aromatic, and double) are small. It is difficult to categorize these systems as aromatic or otherwise on the basis of bond lengths.

Aromatic stabilization energies have been calculated using eq 2, similar to that used for $X_3Y_3H_6$ systems. Magnetic
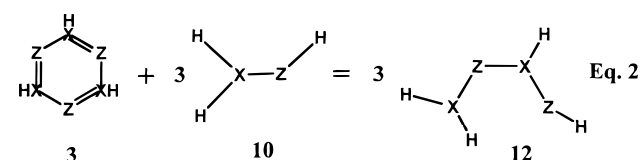
susceptibility data for the reference compounds are given in the Table 10. The exaltation is also calculated using the same equation, and NICS has been calculated similarly. Aromatic stabilization energies, MSE data, and NICS values are given in the Table 11.

Several interesting points emerge from Table 11. Except for that of **1BS**, the aromatic stabilization energies are very small, less than 5 kcal/mol. They are destabilizing (i.e., eq 2 is endothermic) for **3AlO**, **3GaS**, and **3GaSe**. The magnetic

Table 10. Magnetic Susceptibility Data (in ppm cgsu with the Signs Reversed) for **3**, **10**, and **12** Calculated at the CSGT-B3LYP/6-31G* Level

structure	ϵ_1	ϵ_2	ϵ_3	χ_{av}
10BO	13.60	12.46	6.63	10.90
12BO	25.93	20.11	15.97	20.67
3BO	44.04	29.79	29.79	34.54
10BS	26.35	18.20	14.63	19.73
12BS	53.01	35.93	25.17	38.04
3BS	101.08	45.38	45.38	63.95
10BSe	36.77	27.18	23.50	29.15
12BSe	74.02	54.45	43.13	57.20
3BSe	138.50	72.48	72.48	94.49
10AlO	21.96	15.21	14.49	17.22
12AlO	35.99	34.22	24.79	31.67
3AlO	56.54	56.54	45.12	52.73
10AlS	32.00	24.17	23.84	26.67
12AlS	62.14	48.54	46.89	52.52
3AlS	87.77	87.77	87.15	87.56
10AlSe	40.80	35.90	34.14	36.95
12AlSe	83.03	73.59	66.32	74.31
3AlSe	123.02	117.17	117.17	119.12
10GaO	28.97	26.96	25.51	27.15
12GaO	53.29	50.31	48.37	50.67
3GaO	80.19	80.19	69.64	76.67
10GaS	42.01	36.91	34.52	37.81
12GaS	79.18	72.50	67.84	73.17
3GaS	113.48	113.19	113.19	113.29
10GaSe	50.23	48.85	44.16	47.75
12GaSe	97.30	95.46	85.02	92.59
3GaSe	149.79	138.06	138.06	141.97

Table 11. Aromatic Stabilization Energies (ASE) (kcal/mol) and Magnetic Susceptibility Exaltation (Λ) Values (cgsu) Calculated at the B3LYP/6-31G* Level and Nucleus-Independent Chemical Shift (NICS) Values of $X_3Z_3H_3$ Systems at the GIAO$-$HF/6-31G*//B3LYP/6-31G* Level

structure		Z = O	S	Se
3BZ	ASE	4.2	8.1	3.5
	Λ	-5.2	-9.0	-10.3
	NICS	0.4	0.9	0.0
3AlZ	ASE	-5.8	1.2	-0.1
	Λ	-9.4	-10.0	-7.0
	NICS	-2.3	-2.9	-1.9
3GaZ	ASE	3.3	-2.8	-3.3
	Λ	-6.2	-7.2	-7.4
	NICS	-1.8	-1.8	-1.0

susceptibilities of **3**, **10**, and **12** (Table 10) show some unusual properties. As for **1**, the out-of-plane susceptibilities of **3** are also large compared to the in-plane values, except for **1AlN**. For Al$-$O, Ga$-$O, Al$-$S, and Ga$-$S compounds, the out-of-plane values are less than the in-plane values.

The trends in MSE data differ from those obtained from aromatic stabilization energy results. For most compounds the MSE is more than half of the value for benzene, indicating these systems are aromatic according to our operational definition. However, NICS presents a different picture. Almost all the compounds have very low NICS values, indicating that these are not aromatic.

Phosphazenes. Phosphazenes, $P_3N_3R_6$, **2**, represent yet another class of inorganic benzenes where, unlike the case for earlier systems, d$\pi-$pπ interactions are invoked to justify delocalization. Numerous derivatives of **2** have been synthesized and well characterized.[25] The bonding in these compounds has attracted several theoretical studies. One of the successful

Table 12. Important Parameters for $P_3N_3H_6$ (**2**), **13**, and **15** Calculated at the B3LYP/6-31G* Level

	2	13	15
energy (au)	-1191.88320	-398.44640	-795.73584
susceptibility ϵ_1	38.39	20.64	34.13
ϵ_2	38.23	16.69	33.27
ϵ_3	38.23	14.58	24.858
ASE (kcal/mol)	9.3		
MSE (Λ_{av})	-2.1		
NICS	-2.2		

models for bonding in **2** is Dewar's island model.[18a] In this model, the d_{xz} and d_{yz} orbitals are hybridized to give two orbitals which are directed toward the adjacent nitrogen atoms. This allows the formation of three-center bonds about each nitrogen. Trinquier had explained the bonding without the participation of the d orbitals of phosphorus.[18b]

Formally, aromaticity in these compounds arises from the fact that the nitrogen p_z orbital, which is perpendicular to the ring, participates in the delocalization with the phosphorus d_{xz} and d_{yz} orbitals. The important parameters of $P_3N_3H_6$, **2**, along with the reference compounds are given in Table 12. For the single and double bonds, we have taken PH_4NH_2 (**13**) and PH_3NH (**14**). The homodesmotic eq 3 is used to calculate ASE and MSE.

$$\text{2} + 3\ H_3P{=}N{-}H = 3\ \text{15} \qquad \textbf{Eq. 3}$$
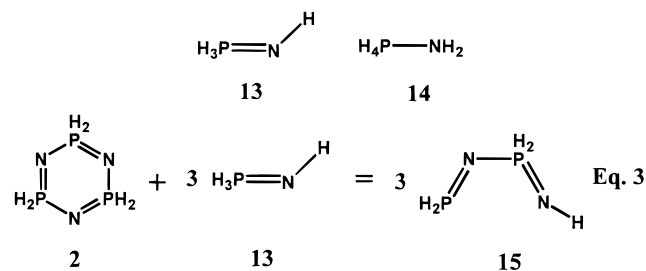
The average P$-$N bond length in the derivatives of **2** is 1.582 Å;[26] the optimized P$-$N bond length for **2** is 1.605 Å. This bond length is intermediate between the P$-$N single bond length of 1.697 Å in PH_4NH_2, **13**, and the P$-$N double bond length 1.574 Å as seen in PH_3NH, **14**. The aromatic stabilization energy from the eq 3 is 9.3 kcal/mol. Since the P$-$N$-$P and N$-$P$-$P bond angles are very close to 120°, the strain energy contribution to the total aromatic stabilization energy will be minimum. Despite the substantial aromatic stabilization energy, the MSE and NICS data do not support aromaticity. Both show that **2** is not aromatic. The magnetic criteria for aromaticity do not always parallel a large value of ASE.

Conclusions

The aromaticities in $X_3Y_3H_6$, $X_3Z_3H_3$, and $P_3N_3H_6$ systems have been studied using structural, energetic, and magnetic criteria. All these criteria can diverge quite strongly from each other. Despite equal aromatic stabilization energies, **1BN** is not aromatic but **1BP** is substantially aromatic according to the MSE and NICS data. The MSE and NICS data also do not always parallel each other. This has been the case for the $X_3Z_3H_3$ systems. While ASE and MSE rely on the choice of reference systems, the NICS values do not require a reference system. On the basis of NICS values, phosphazene (**2**) and $X_3Z_3H_3$ (**3**) are not aromatic. However, NICS is not an

(25) *Phophorus$-$An outline of its Chemistry, Biochemistry and Technology*, 4th ed.; Corbridge, D. E. C., Ed.; Studies in Inorganic Chemistry 10; p 428 and references therein.

(26) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R.; *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

experimentally observable quantity. A judicious use all criteria is needed in gauging aromaticity of these systems.

Supporting Information Available: Listings of the standard orientations of **1**−**3** and **9** optimized at the B3LYP/6-31G* level (8 pages). Ordering information is given on any current masthead page.

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