

An Evaluation of the Aromaticity of Inorganic Rings: Refined Evidence from Magnetic Properties

Paul von Ragué Schleyer,*† Haijun Jiao,†
 Nicolaas J. R. van Eikema Hommes,†
 Vladimir G. Malkin,‡ and Olga L. Malkina‡

Computer Chemistry Center, Institut für
 Organische Chemie, Universität Erlangen-Nürnberg
 Henkestrasse 42, D-91054 Erlangen, Germany
 Institut of Inorganic Chemistry
 Slovak Academy of Sciences
 Dubravska Cesta, SK.84236, Bratislava, Slovakia

Received June 11, 1997

Revised Manuscript Received October 8, 1997

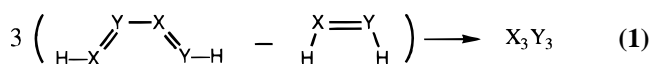
Aromaticity, a concept generally associated with organic compounds, results in exceptional geometric, energetic and magnetic properties.¹ However, the conventional criteria are often difficult to apply to inorganic analogues. Equal ring bond lengths (as in benzene **1**) are found frequently in stable inorganic six π electron ring systems, e.g., in borazine (**2**) and boroxine (**3**), but the highly polar character of the bonding rather than electron delocalization could be responsible. Benzene analogues such as N₆ (**4**) and Si₆H₆ (**5**) are unstable.

Cyclic delocalization of mobile electrons, σ or π , proposed as the defining characteristic of aromaticity,^{1–5} results in ring currents which are responsible for abnormal magnetic properties, e.g., exalted magnetic susceptibilities, anisotropies, and displaced chemical shifts (especially $\delta^1\text{H}$ in organic compounds). However, these do not serve well for inorganic compounds which often have no proton substituents. Few magnetic susceptibility measurements have been reported, and reference increments necessary to evaluate the exaltations are not available.⁶

We show here how computational data, easily obtainable, can be used effectively to assess the aromaticity and to provide a more detailed analysis. Several theoretical studies of the inorganic (or heteroatom) analogues of benzene have been reported already. Using homodesmotic reactions, but with trans configurations of the reference molecules, Fink and Richards⁷ calculated the following aromatic stabilization energies (ASE, kcal/mol): benzene (**1**, 22.1) \gg boraphosphabenzene (**6**, 12.7) > borazine (**2**, 11.1) \gg alumazene (**7**, 1.9) (derivatives of **6** and **7** are known only with bulky substituents).⁸ On this basis, **6** and **2** are less aromatic than **1**, and **7** is not aromatic. This behavior was ascribed mainly to the electronegativity differences between the ring atoms. Using the calculated charge densities and Mulliken population analysis, Boyd et al.⁹ demonstrated the substantial decrease of the π -electron delocalization relative to benzene (**1**) and the increase in ring bond polarities of

s-triazine (**8**), borazine (**2**), and boroxine (**3**). This quantitative ordering (ca 3:2:1:0, respectively) agrees with the ASEs calculated by Haddon.¹⁰ Using the RCI (ring current index), Jug suggested that s-triazine (**8**) has nearly the same aromatic character as benzene (**1**) and that borazine (**2**) and boroxine (**3**) are moderately aromatic.¹¹ Fowler and Steiner^{4b} agree that **8** has a delocalized ring current similar to benzene, but find **2** and **3** to be π localized on the electronegative atoms.

For Si₆H₆ (**5**), Nagase computed an ASE approximately half that of benzene.¹² Gordon et al. also found that both Si₆H₆ (**5**) and Ge₆H₆ (**9**) are less stabilized than benzene (**1**) (57.8, 59.9, and 74.7 kcal/mol, respectively).¹³ Hexagonal N₆ (**4**) is highly unstable toward dissociation into 3 N₂,¹⁴ whereas P₆ (**10**) is lower in energy than 3 P₂,¹⁵ but these reveal nothing about the degree of electron delocalization of the two six-membered rings. Estimates of aromatic stabilization energies vary significantly and depend strongly on the equations used (isodesmotic, homodesmotic, hyperhomodesmotic), the reference molecules adopted, and the computational levels and basis sets.^{16,17} For example, Nagase¹⁵ found that both **4** and **10** are stabilized and have ca. 60% of the benzene ASE by eq 1 with X = Y = N for **4** and X = Y = P for **10** as reference molecules. However,



when the trans isomers of these models are employed, **4** and **10** are destabilized by 17.6 and 7.2 kcal/mol, respectively, rather than stabilized.¹⁴ The procedure used to define stabilization energies is arbitrary; no choice is free from objection.

We now employ magnetic criteria to assess the degree of aromaticity of a series of inorganic ring systems (Table 1, D_{6h} or D_{3h} symmetry facilitates direct comparisons but data for D_{3d} forms also are given). B3LYP/6-311+G** optimized geometries, energies, and CGST magnetic susceptibilities and anisotropies were computed with the Gaussian 94 program.¹⁸ The nucleus-independent chemical shift (NICS)¹⁹ values reported here calculated at the SOS-DFPT-IGLO level using the Perdew-Wang-91 exchange-correlation functional and the IGLO-III TZ2P basis set as implemented in the deMon NMR program.²⁰ Since the IGLO method provides the contributions from the individual localized MOs,²¹ the total NICS values can be divided into contributions from the π bonds, NICS(π), from the ring σ

(10) Haddon, R. C. *Pure Appl. Chem.* **1982**, *54*, 1129.

(11) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344.

(12) Nagase, S.; Kudo, T.; Aoki, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1121. (b) Sax, A.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651. (c) Sekiguchi, A.; Sakurai, H. In *Studies in Inorganic Chemistry 14, The Chemistry of Inorganic Ring Systems*; Elsevier: Amsterdam, 1992; Chapter 7, p 101, and cited references.

(13) Matsunaga, N.; Cundari, T. R.; Schmidt, M. W.; Gordon, M. S. *Theor. Chim. Acta* **1992**, *83*, 57.

(14) (a) Glukhovtsev, M. N.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *198*, 547. (b) Schleyer, P. v. R.; Jiao, H. Unpublished results.

(15) (a) Nagase, S.; Ito, K. *Chem. Phys. Lett.* **1986**, *126*, 43. (b) Warren, D. S.; Gimarc, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 5378.

(16) Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* **1988**, *152*, 402.

(17) Jiao, H.; Hommes, N. v. E.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1996**, *61*, 2826.

(18) Gaussian 94; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian Inc.: Pittsburgh, PA, 1995.

(19) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(20) (a) Malkin, V. G.; Malkin, O. L.; Eriksson, L. A.; Salahub, D. R. *Modern Density Functional Theory*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; p 273. (b) Malkin, V. G.; Malkin, O. L.; Eriksson, L. A.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898.

(21) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR: Basic Principles and Progress*, Springer: Berlin, 1990; Vol. 23, p 165.

* Universität Erlangen-Nürnberg.

† Slovak Academy of Sciences.

(1) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *28*, 209.

(2) Jiao, H.; Schleyer, P. v. R. Glukhovtsev, M. N. *J. Phys. Chem.* **1996**, *110*, 12299.

(3) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. In *Non-Benzenoid Aromatics*; Synder, J., Ed.; Academic Press: New York, 1971; Vol. 2.

(4) (a) Fleischer, U.; Kutzelnigg, W.; Lazzarotti, P.; Müllenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298 and private communications. (b) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **1997**, *101*, 1409. (c) Bader, R. F. W.; Keith, T. A. *J. Chem. Phys.* **1993**, *99*, 3683.

(5) Elvidge, J. L.; Jackman, L. M. *J. Chem. Soc.* **1961**, 859.

(6) (a) Lonsdale, K. *Nature* **1959**, *184*, 1060. (b) Watanabe, H.; Ito, K.; Kubo, M.; *J. Am. Chem. Soc.* **1960**, *82*, 3294. (c) Muszkat, K. A. *J. Am. Chem. Soc.* **1964**, *86*, 1250. (d) Kubo, M.; Watanabe, H.; Ito, K. *J. Am. Chem. Soc.* **1964**, *86*, 1251. (d) For a summary of magnetic susceptibilities, see: Hellwege, K.-H.; Hellwege, A. M. *Diamagnetic Susceptibilities*; Landolt-Börnstein, New Series, II/16; Springer-Verlag: Berlin 1986.

(7) Fink, W. H.; Richards, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 3393.

(8) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

(9) Boyd, R. J.; Choi, S. C.; Hale, C. C. *Chem. Phys. Lett.* **1984**, *112*, 126.

Table 1. Computed ASE (kcal/mol), Λ Based on Eq 1, and Magnetic Susceptibility Anisotropies (χ_{anis})

	ASE ^a	Λ^b	χ_{anis}^b
benzene (1)	-34.1	-13.9 (-13.7) ^c	-67.5 (-59.7) ^d
borazine (2)	-10.0	-3.7	-25.7
Si ₆ H ₆ , <i>D</i> _{6h} (5)	-15.6	-32.8	-114.6
Si ₆ H ₆ , <i>D</i> _{6d} (5a)	-17.9	-26.0	-107.9
Ge ₆ H ₆ , <i>D</i> _{6h} (9)	-15.3	-40.8	-130.8
Ge ₆ H ₆ , <i>D</i> _{3d} (9a)	-29.8	-17.0	-144.6

^a At B3LYP/6-311+G**. ^b CSGT-B3LYP/6-311+G**. ^c Experimental value in ref 3. ^d Experimental value in ref 4a.

Table 2. NICS(tot), NICS(π), and NICS(σ) at Points 0.5 Å above and at the Ring Centers^{a,b}

molecules	R	NICS(π)	NICS(σ)	NICS(tot)
C ₆ H ₆ , <i>D</i> _{6h} (1)	1.396	-16.8 (-20.7)	+8.8 (+13.8)	-10.7 (-8.9)
B ₃ N ₃ H ₆ , <i>D</i> _{3h} (2) ^c	1.431	-8.7 (-12.0)	+7.8 (+11.4)	-3.2 (-2.1)
B ₃ O ₃ H ₃ , <i>D</i> _{3h} (3) ^c	1.377	-6.3 (-9.6)	+10.2 (+9.6)	-2.2 (-0.8)
N ₆ , <i>D</i> _{6h} (4)	1.319	-15.9 (-20.4)	+13.3 (24.6)	-7.0 (+0.2)
Si ₆ H ₆ , <i>D</i> _{6h} (5)	2.217	-14.1 (-15.0)	+0.3 (+0.6)	-12.8 (-13.1)
Si ₆ H ₆ , <i>D</i> _{3d} (5a)	2.240			-11.4 (-11.2)
B ₃ P ₃ H ₆ , <i>D</i> _{3h} (6)	1.837	-13.2 (-15.0)	+4.2 (+5.4)	-8.7 (-8.7)
Al ₃ N ₃ H ₆ , <i>D</i> _{3h} (7) ^c	1.803	-4.8 (-6.0)	+3.6 (+4.8)	-2.2 (-2.4)
C ₃ N ₃ H ₃ , <i>D</i> _{3h} (8)	1.334	-15.3 (-19.5)	+11.4 (+18.6)	-8.6 (-4.8)
Ge ₆ H ₆ , <i>D</i> _{6h} (9)	2.305	-14.4 (-15.0)	-1.8 (-1.5)	-14.5 (-14.6)
Ge ₆ H ₆ , <i>D</i> _{3d} (9a)	2.384			-9.9 (-10.0)
P ₆ , <i>D</i> _{6h} (10)	2.133	-14.7 (-15.9)	+1.2 (+3.0)	-15.8 (-15.2)
B ₃ S ₃ H ₃ , <i>D</i> _{3h} (11)	1.810	-8.7 (-10.8)	+8.4 (+11.4)	-3.3 (-2.5)
Al ₃ P ₃ H ₆ , <i>D</i> _{3h} (12) ^c	2.265	-7.2 (-8.1)	+0.6 (+1.2)	-5.4 (-5.8)

^a The remaining contributions, due to core orbitals, X-H bonds, and in-plane lone pairs, are small. ^b The NICS values computed at the ring centers are given in parentheses for comparison. ^c See the text.

bonds, NICS(σ), and from the other contributions (bonds to hydrogen, in-plane lone pairs, core orbitals). We implemented the Pipek and Mezey localization procedure²² in the deMon NMR program for this purpose. The NICS(σ) and NICS(π) data for points 0.5 Å above and in the ring centers are summarized in Table 2.

Not only ASE values but also exalted magnetic susceptibilities (Λ) can be evaluated using the homodesmotic reaction (eq 1).²³ The ASE ordering of benzene (**1**, 34.1 kcal/mol) > Si₆H₆ (**5**, 15.6 kcal/mol) \approx Ge₆H₆ (**9**, 15.3 kcal/mol) is qualitatively in line with the results of Nagase¹² and those of Gordon.¹³ The computed Λ of **5** and **9** are larger than that of benzene. However, Λ depends on the square of the ring area, which increases from C₆H₆ and Si₆H₆ to Ge₆H₆. The ring-size-adjusted aromaticity index (ρ)²⁴ gives an aromaticity ordering of C₆H₆ (1.00) > Si₆H₆ (0.37) \approx Ge₆H₆ (0.36), in agreement with the ASE results.

The NICS(tot) values of **5** and **9** are larger than the benzene value. However, such NICS values computed in the ring centers of first row compounds are known to be influenced by the local paramagnetic contributions of the σ bonds, which counteract the diamagnetic π ring current effects.⁴ Consequently, we have employed the dissected NICS(π) and the NICS(σ) contributions at points 0.5 Å over the ring centers (Table 2). The lower benzene NICS(tot) value, -10.7, relative to those of Si₆H₆ (-12.8) and Ge₆H₆ (-14.5), is due to the large paratropic effect

of the C-C σ bonds (NICS(σ) = 8.8). In contrast, Si₆H₆ (0.3) and Ge₆H₆ (-1.8) have negligible NICS(σ) components, since the ring diameters are larger. NICS(π) decreases from C₆H₆ (-16.8) to Si₆H₆ (-14.1) and Ge₆H₆ (-14.4). This order agrees with the ASE and the ρ aromaticity indexes. Benzene is more aromatic than its sila and germa homologues on the basis of these three criteria even in *D*_{6h} symmetry, and both Si₆H₆ and Ge₆H₆ prefer nonplanar geometries. These *D*_{3d} cyclic hexasila (**5a**) and hexagerma (**9a**) minima are 2.3 and 14.5 kcal/mol lower in energy than their planar *D*_{6h} structures (**5** and **9**). Due to the reduced strain, **5a** and **9a** have larger ASE values, but smaller NICS(tot) and Λ than **5** and **9**. This shows that the degree of cyclic delocalization is decreased in the *D*_{3d} forms despite their increased stability.

We also have analyzed the magnetic properties of *D*_{6h} N₆ (**4**) and P₆ (**10**) similarly. The very small total NICS at the ring center of **4** (0.2) is due to the nearly complete diatropic and paratropic compensation. The NICS(π) and NICS(σ) of N₆ (**4**) are both larger than those of benzene (Table 2), due to the smaller ring radius. As expected, P₆, like Si₆H₆, has a larger NICS(π), but a negligible NICS(σ). Both N₆ and P₆ have quite large NICS(π) values at 0.5 Å above the ring centers.

Although computed to have about 29% of the benzene ASE by eq 1, borazine (**2**) is nonaromatic as indicated by its modest χ_{anis} and negligible Λ (Table 1). This conclusion is also supported by the calculated NICS values (Table 2). The Pipek-Mezey localization results only in localized lone pair (LP) electrons on nitrogens, and these are responsible for the NICS(π) values given in Table 2. Thus, the magnetic criteria show little or no evidence of ring currents.^{4b} Borazine is not aromatic due to the polar BN bonds. The same is true for Al₃N₃H₆ due to the even greater ionic character of the Al-N bonds. Since B and P have nearly equal electronegativities, B₃P₃H₆ is moderately aromatic. Our NICS(π) criterion gives a somewhat modified aromaticity order, C₆H₆ > B₃P₃H₆ \gg B₃N₃H₆ > Al₃N₃H₆, from that deduced earlier.^{7,9}

Our NICS(π) criterion supports Jug's suggestion that s-triazine (**8**) has nearly the same aromatic character as benzene but, like Fowler and Steiner,^{4b} does not agree with his conclusion that B₃N₃H₆ and B₃O₃H₃ are moderately aromatic. In addition, NICS(π) of B₃S₃H₃ (**11**, *D*_{3h}) is half that of benzene, and Al₃P₃H₃ (**12**, *D*_{3h}) has localized lone pairs at phosphorus due to the highly polarized Al-P bonds.

In conclusion, electron delocalization of "inorganic" benzene analogues can be analyzed using the magnetic criteria of aromaticity, especially NICS values separated into the NICS(π) and NICS(σ) contributions. Without delocalization, the NICS(π) and NICS(σ) tend to cancel, and NICS(tot) (e.g., **2**, **3**, and **7**) are near zero. Cyclic delocalized systems have enhanced NICS(π) contributions, and appreciably negative NICS(tot) values result. As the NICS(σ) above the ring fall off faster than the NICS(π), the NICS(tot) at the ring centers are usually less than those 0.5 Å away. Both NICS(π) and NICS(σ) decrease with increase of the ring size (bond length), e.g., benzene > Si₆H₆ \approx Ge₆H₆ and N₆ > P₆. The NICS(π) values agree well with the other magnetic criteria of aromaticity for this set of molecules. While often called "the inorganic benzene", borazine has a localized electronic structure and is not aromatic.^{4b}

(22) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.

(23) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222. Planar reference molecules were used for simplicity in this equation.

(24) The aromaticity index (ρ) is defined as $\rho = k[n\Lambda/S^2]$ which presents the relationship among the number of delocalized electrons (n), the ring size (S), and Λ , k is a scaling factor, see: Maoche, B.; Gayoso, J.; Ouamerah, *Rev. Roum. Chem.* **1984**, *26*, 613.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. G. Subramanian and Prof. W. Kutzelnigg for discussions.