Is Nucleus-Independent Chemical Shift Scan a Reliable Aromaticity Index for Planar Heteroatomic Ring Systems?

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Density functional theoretical investigation has been performed to explore the reliability of the nucleus-independent chemical shift (NICS) scheme in assessing aromatic behavior of some planar six-membered heteroatomic systems. It has been observed that the NICS scan and the diamagnetic and paramagnetic contributions of the in-plane and out-of-plane components are quite reliable in assessing any aromatic or antiaromatic behavior in borazine. However, for boraphosphabenzene, the aromatic stabilization energy is too small to consider it as an aromatic system but the NICS scans and the homodesmotic reactions suggest an opposite trend. Interestingly, in the case of alumazene, a very shallow minimum is observed for the out-of-plane component, which suggests the presence of weak diamagnetic ring current. However, the diamagnetic and paramagnetic contribution curves to the out-of-plane component for alumazene clearly reveal a net paramagnetic contribution. Thus we may surmise that apart from the single NICS value, the NICS scan also is not a very authentic tool for the assessment of aromaticity of planar six-membered heteroatomic systems.

1. Introduction

Aromaticity is a qualitative phenomenon of utmost importance in the wide realm of chemistry.[1] With the discovery of new molecules exhibiting aromatic or antiaromatic behavior, the theory of aromaticity has gained a momentum in quantum chemical research.[2] Now a days, the concept of aromaticity is not only confined to homoatomic π-electronic systems such as organic molecules, but several heteroatomic systems with σ-electronic framework have also attracted much attention. Recent years have also witnessed the innovation of all metal clusters with σ aromaticity and d-orbital aromaticity.[3,4] The concept of three-dimensional aromaticity is also quite amazing and this theory helps us in elucidating the stability of various apparently unstable molecular complexes[5] and organometallic compounds.[6]

There are several criteria for assessing aromatic behavior in a molecule of which structural, energetic, and magnetic criteria are the ones mostly investigated.[7] While bond-length equalization and harmonic oscillator model of aromaticity (HOMA) index are usually related to the molecular structure, there are several reactions, namely, homodesmotic reactions, isodesmic reactions, aromatic stabilization (ASE), and antiaromatic destabilization energies (ADE), which are strongly associated with the energetic criterion used for the assessment of aromatic behavior in a molecule. Magnetic criteria have gained lot of importance in recent years due to their dependence on the induced ring currents vis-a-vis cyclic delocalization of electrons. In their pioneering work, Schleyer et al.[8] for the first time reported the scheme of Nucleus-independent chemical shift (NICS) to calculate the magnetic shielding tensors of various systems. Since then, the NICS scheme[9,10] has become the most popular and widely used aromaticity index, particularly due to its easy computability. It is calculated as negative magnetic shielding tensors at some selected points in space. The common notion is that compounds with negative magnetic shielding tensors possess diatropic ring current and are usually aromatic and stable whereas those with positive magnetic shielding tensors possess paratropic ring currents and are usually antiaromatic and unstable in nature.

Albeit the NICS scheme[9] is widely used for the evaluation of aromatic behavior in various systems,[11,12] severe questions have already been raised regarding its reliability to predict aromatic behavior of several other systems.[13] It has quite often been observed that a single NICS value fails to predict any aromatic or antiaromatic behavior in a system. A very useful and efficient way to solve this problem is to follow the scanning procedure where NICS values ranging from 0.0 Å, i.e., molecular plane to quite a large distance (say up to 4.0 Å), are observed. Stanger[10] reported such NICS scans for several homoaromatic cyclic systems and predicted the presence of diamagnetic ring current in systems whose NICS scan passes through a minima.

Although there has been a lot of investigation regarding the aromatic/antiaromatic behavior in different homoatomic systems (organic molecules) and their derivatives, the study of the same on heteroatomic inorganic systems is confined mainly to energy analyses.[14−16] Recently, Chattaraj et al.[17] for the first time have reported the aromaticity in the polyacene analogues of several heteroatomic inorganic systems of interest. They have used the NICS values and density functional theory based reactivity descriptors in their analysis. In the present work, we investigated the NICS scans of some planar heteroatomic inorganic analogues of benzene within the framework of density functional theory (DFT). The major objective of the present study is to search how far this NICS scanning procedure is reliable for the appraisal of aromatic or antiaromatic behavior in these systems.

2. Computational Details

All the calculations have been implemented in the Gaussian 03 suite of programs[18] at the spin-restricted level. The geom-

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etries of benzene and its planar heteroatomic inorganic analogues, i.e., borazine ($B_3N_3H_6$), boraphosphabenzene ($B_3P_3H_6$), and alumazene ($Al_3N_3H_6$), are optimized (see the Supporting Information for the optimized bond lengths, bond angles, and zero-point corrected energy values) with use of hybrid B3LYP[19] functional and Pople's 6-311++G(d,p) basis set. Frequency calculations have been performed for all the systems at the same level of theory.

For the NICS scans, we adopted the gauge-independent atomic orbital (GIAO) formalism. This scanning procedure is performed by placing the probe (Bq) at the ring center of the molecule, i.e., at 0.0 Å (molecular plane), and varying its distance up to 4.0 Å at intervals of 0.1 Å. The NICS values obtained are the isotropic values of respective Bqs and the corresponding eigenvalues are separated into in-plane (XX and ZZ) and out-of-plane components (YY). To find out whether the trends observed in the NICS scans for these systems have any basis set/method dependency, we have implemented the scanning procedure using 6-311++G(d,p), 6-311G(d,p), and 6-31G basis sets within density functional theory (DFT) as well as Hartree–Fock (HF) and Møller–Plesset perturbation (MP2) methods. Apart from the NICS scans, diamagnetic and paramagnetic contributions to the in-plane and out-of-plane components have also been extracted from the net magnetic shielding tensors. The separation of the net magnetic shielding tensors to the diamagnetic and paramagnetic components as well as the energetics of homodesmotic reactions and ASE have been thoroughly investigated by using the hybrid B3LYP[12] functional and the 6-311++G(d,p) basis set only.

3. Results and Discussion

The NICS scans of the planar heteroatomic inorganic analogues of benzene, namely, $B_3N_3H_6$, $B_3P_3H_6$, and $Al_3N_3H_6$, have been performed to interpret the extent of reliability of such NICS scanning in assessing aromatic or antiaromatic behavior in these systems. To provide a better picture, the NICS values that are extracted into their out-of-plane (YY) and in-plane components (XX and ZZ) from the net magnetic shielding tensors have been further separated into their corresponding diamagnetic and paramagnetic contributions.[10,13] Of particular relevance to this issue, we took up the gauge-invariance atomic orbital (GIAO) formalism using the so-called London orbitals which eliminates the global gauge origin and ensures rapid basis set convergence for second-order magnetic properties. The magnetic shielding tensor of a nucleus is the second derivative of energy with respect to the magnetic field and magnetic moment of the nucleus. The diamagnetic and paramagnetic contributions can easily be extracted by using the following relation

$$\sigma = \frac{1}{2c^2}\sum_k^{\text{occ}}\left\langle \psi_{k0}\left|\frac{r r_{\text{N}} I - r_{\text{N}} \otimes r}{|r - R_{\text{N}}|^3}\right|\psi_{k0}\right\rangle - \frac{2}{c}\sum_k^{\text{occ}}\left\langle \psi_{k0}\left|\frac{(L_{\text{N}})}{|r - R_{\text{N}}|^3}\right|(\psi_{k1})\right\rangle$$

where $L_N = r_N \times \nabla$ and $r_N = r - R_N$. In the above equation, r refers to the electronic position, R_N to the vector position where the NICS is calculated, and L_N to the angular momentum vector.[9] The first term in the equation corresponds to the diamagnetic contribution and the second one is the paramagnetic contribution to the net magnetic shielding tensors. The nonsymmetric diamagnetic and paramagnetic shielding tensor matrices obtained are then diagonalized to get the in-plane (σ_{xx} and σ_{zz}) and out-of-plane (σ_{yy}) components. The homodesmotic[15,16] and the protonation reactions (used for estimating the ASE)[14] of these systems have also been calculated in order to justify the results obtained in the NICS scans. It is important to notice that in this paper we have presented the NICS scan curves of the B3LYP/6-311++G(d,p) method and scanning curves obtained from the other methods are given in the Supporting Information.

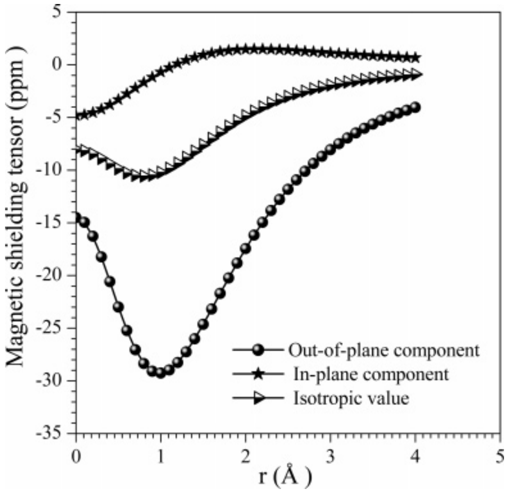


Figure 1. Variation of the magnetic shielding tensor of benzene (C_6H_6) against distance, r, from the ring center.

3.1. Nucleus-Independent Chemical Shift (NICS) Scanning of Benzene and Some of Its Planar Heteroatomic Inorganic Analogues. Figure 1 depicts the NICS scans of benzene where the out-of-plane component and isotropic values pass through minima. The minimum value for the out-of-plane component is observed at $r = 1.0$ Å while the isotropic value has its minimum located at 0.8 Å from the ring center. The scan shape justifies the presence of strong diamagnetic ring current in benzene, which is again the manifestation of cyclic delocalizations of electrons in it. To get a better insight of this cyclic electron delocalization in benzene, the in-plane and out-of-plane shielding tensors have been separated into their diamagnetic and paramagnetic contributions. Parts a and b of Figure 2 represent the diamagnetic and paramagnetic contributions for the in-plane and out-of-plane components, respectively. In the in-plane component, a net diamagnetic contribution is observed only up to a certain distance ($r = 1.4$ Å) and beyond that paramagnetic contribution is more than that of the diamagnetic one. On the other hand, the diamagnetic contribution is more pronounced than the paramagnetic one over the whole scanned distance for the out-of-plane component of benzene. This further supports the trend observed in the NICS values (the out-of-plane component passes through a minimum) given in Figure 1.

Among the various heteroatomic inorganic analogues of benzene, borazine (also referred to as inorganic benzene) is the most well-known compound of paramount interest. Aromaticity in borazine has long been a debated issue. Several investigations have been carried out to offer an explanation of whether it is aromatic or antiaromatic in nature. In their paper, Madura et al.[20] observed that borazine and its derivatives are less aromatic than its benzene analogues but they are not nonaromatic. However, the magnetic criteria such as the diamagnetic susceptibility exaltation, single NICS values which are employed to understand the nature of ring current indicate that it is not aromatic. Kiran et al.[14] in their work highlighted the reactivity criteria to be more significant than the magnetic ones for more polar heteroatomic systems like B–N. They also reported the

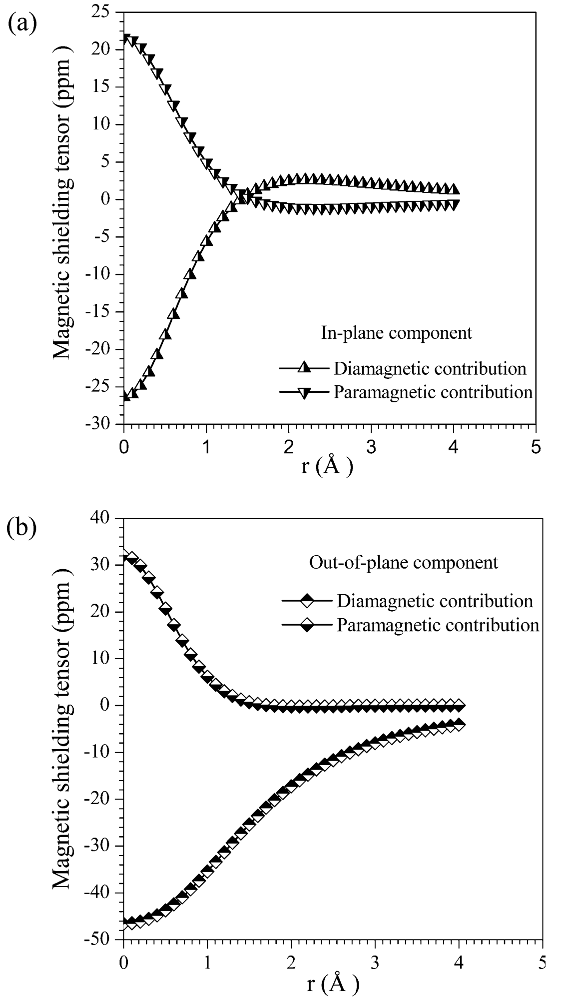


Figure 2. Variation of the diamagnetic and paramagnetic contributions to the (a) in-plane component and (b) out-of-plane component of benzene (C_6H_6) against distance, *r*, from the ring center.

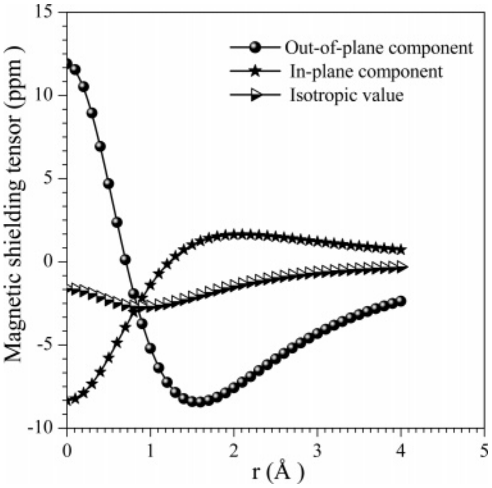


Figure 3. Variation of the magnetic shielding tensor of planar borazine ($B_3N_3H_6$) against distance, *r*, from the ring center.

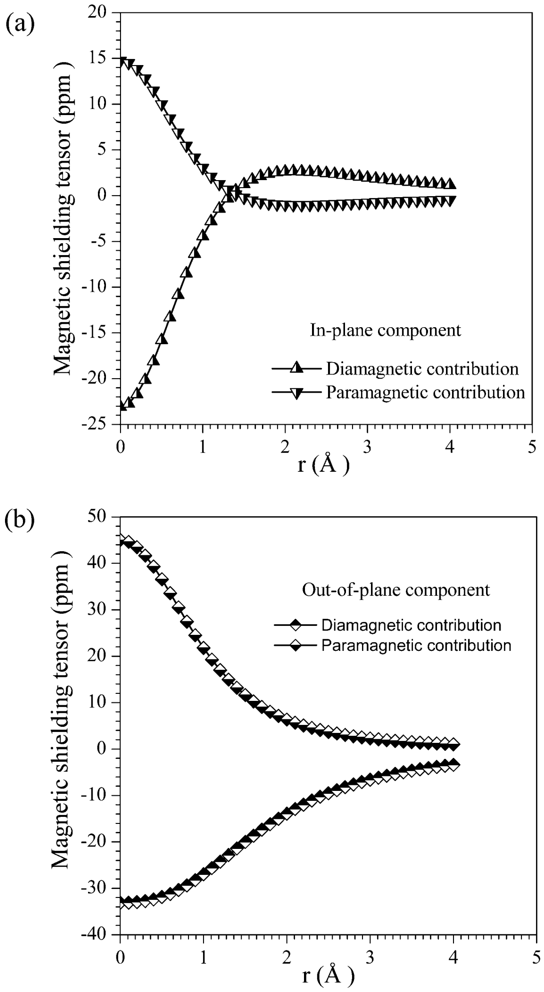


Figure 4. Variation of the diamagnetic and paramagnetic contributions to the (a) in-plane component and (b) out-of-plane component of planar borazine ($B_3N_3H_6$) against distance, *r*, from the ring center.

protonation and methylation energies of several systems including that of borazine and on the basis of the stability of the σ-complex obtained from the above two schemes, they predicted $B_3N_3H_6$ to be aromatic but to a lesser extent relative to benzene. A recent work by Rehaman et al.[21] also predicted an aromatic behavior in borazine.

In the present study, we have employed the NICS scanning procedure rather than the single NICS value to see whether planar borazine ($B_3N_3H_6$) is really aromatic or not. The NICS values are plotted in Figure 3. The scan shape looks almost similar to that of benzene with the out-of-plane component and isotropic values passing through minima. The difference, however, lies in the range of shielding tensor values. Moreover, it has also been observed that the minimum value of the out-of-plane component shifts slightly right to a larger distance (r = 1.6 Å) compared to that of benzene (r = 1.0 Å) and is much shallower than that obtained for its hydrocarbon analogue, benzene. The NICS scan shape in Figure 3 therefore suggests the presence of diamagnetic ring current in borazine. This is further supported by parts a and b of Figure 4 where the diamagnetic and paramagnetic contributions to the in-plane and out-of-plane components respectively are plotted against the scanned distance, *r*, from the ring center. In the in-plane component curve (see Figure 4a) the rate of decrease in the diamagnetic contribution is much more than the paramagnetic one. It has been observed that up to a certain distance (r = 1.3 Å), a net diamagnetic contribution is observed and beyond that the paramagnetic contribution outweighs the diamagnetic counterpart. On the contrary, although near 0.0 Å, the paramagnetic contribution dominates over the diamagnetic counterpart in the out-of-plane component (Figure 4b); however, as we increase the distance, *r*, the rate of decrease of the paramagnetic contribution is much larger than that of the diamagnetic one.

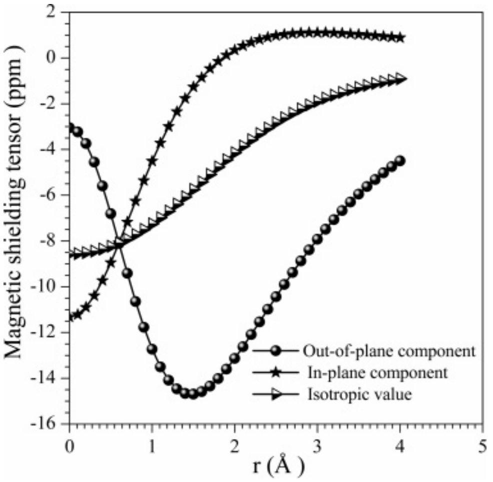


Figure 5. Variation of the magnetic shielding tensor of planar boraphosphabenzene ($B_3P_3H_6$) against distance, *r*, from the ring center.

Hence we get a net diamagnetic contribution at higher distance (beyond 0.7 Å).

Just like borazine, the six-membered $(B-P)_3$ ring systems are the boron−phosphorus analogues of benzene. The planar structure of >BPB< and >PBP< arrays and their allylic nature indicate the possibility of obtaining several delocalized ring systems. Power et al.[15] reported the existence of various such complexes where the bonds between boron and phosphorus are found to be purely σ-type and delocalizations are observed in those systems. The NICS scan shape of the simplest six-membered planar $(B-P)_3$ ring system, i.e., boraphosphabenzene ($B_3P_3H_6$), given in Figure 5 (the out-of-plane component passes through a minimum) predicts the presence of strong diamagnetic ring current and hence cyclic delocalization of electrons in this system. To justify the above situation, we have separated the diamagnetic and paramagnetic contributions of the in-plane (Figure 6a) and out-of-plane components (Figure 6b). In the out-of-plane component, a net diamagnetic contribution is observed over the whole scanned distance whereas the net diamagnetic contribution is observed only up to a certain distance ($r = 1.7$ Å) in the in-plane component.

The six-membered alumazenes ($Al_3N_3H_6$) are the aluminum−nitrogen analogues of benzene. The delocalization in this ring system is very negligible owing to the greater polarity of Al−N bonds compared to either the B−P or B−N bonds. The NICS scan curve represented in Figure 7 reflects this behavior. None of the components of planar $Al_3N_3H_6$ except the out-of-plane component pass through a minimum. However, the minimum observed is very shallow compared to those of the other six-membered heteroatomic systems studied, which reveals that there is diamagnetic ring current in alumazene, but not to the extent observed for other systems studied. Parts a and b of Figure 8 depict the diamagnetic and paramagnetic contribution curves of the in-plane and out-of-plane components, respectively. The in-plane component shows a net diamagnetic contribution but only up to a certain distance ($r = 1.3$ Å) (see Figure 8a) as observed for all the other six-membered systems studied. However, for the out-of-plane component of $Al_3N_3H_6$, although a very shallow minimum is observed in the NICS scan in Figure 7, interestingly Figure 8b clearly shows a net paramagnetic contribution throughout the scanned distance.

To elucidate the role of basis sets and methods on the trends of NICS results for each of these systems, we have carried out the NICS scanning using three basis sets (6-311++G(d,p), 6-311G(d,p), and 6-31G) at three different levels of theory, viz., DFT, HF, and MP2. A vivid description of the trends observed in the NICS scan shapes for all the systems studied is illustrated in the Supporting Information. The figures provide a clear indication of the qualitative similarity in the trends of NICS scans by changing either basis sets or methods. However, slight changes in the NICS values and distances at which minima

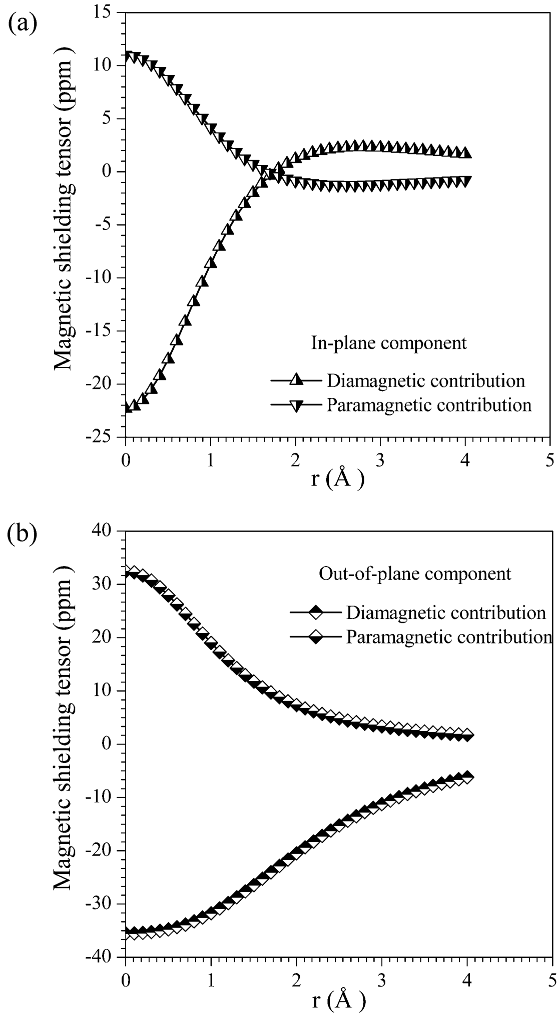


Figure 6. Variation of the diamagnetic and paramagnetic contributions to the (a) in-plane component and (b) out-of-plane component of planar boraphosphabenzene ($B_3P_3H_6$) against distance, *r*, from the ring center.

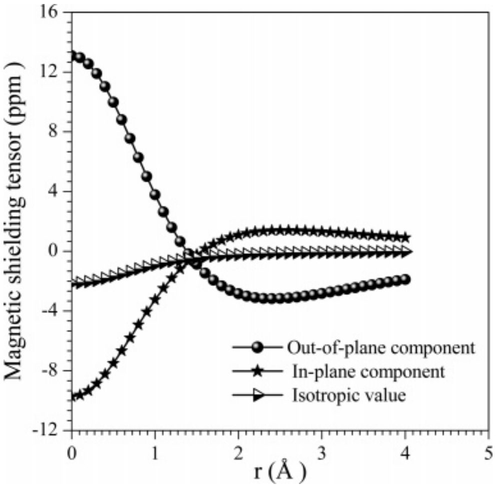


Figure 7. Variation of the magnetic shielding tensor of planar alumazene ($Al_3N_3H_6$) against distance, *r*, from the ring center.

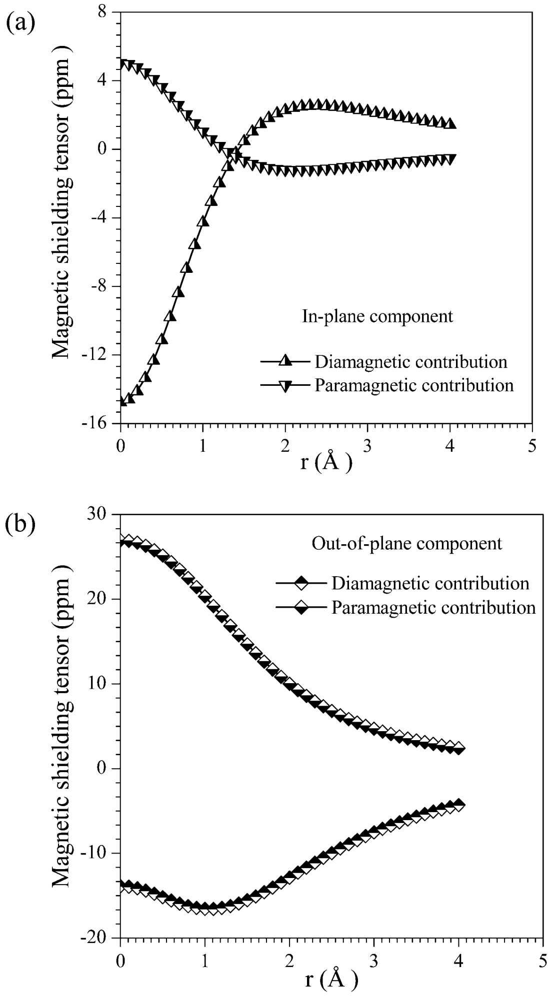
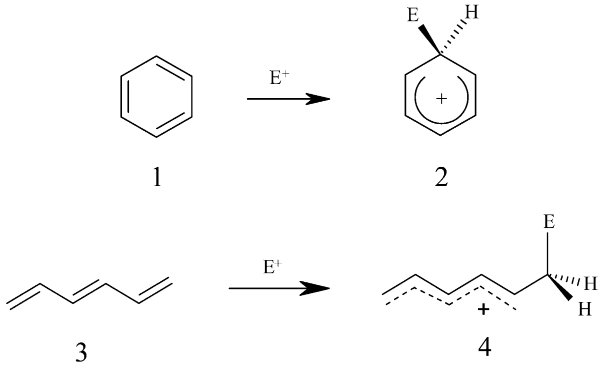


Figure 8. Variation of the diamagnetic and paramagnetic contributions to the (a) in-plane component and (b) out-of-plane component of planar alumazene ($Al_3N_3H_6$) against distance, *r*, from the ring center.

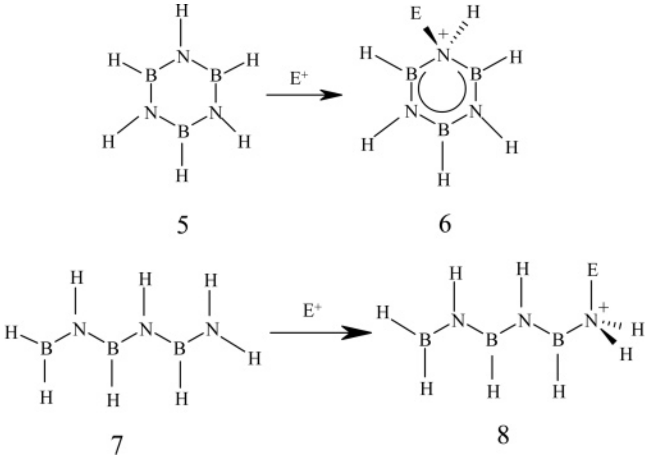
TABLE 1: ZPE-Corrected ΔE_{rxn} (kcal) Values for Homodesmotic Reactions of Benzene, Borazine, Boraphosphabenzene, and Alumazene, Using the B3LYP/6-311++G(d,p) Method

reaction	ΔE_{rxn}
$C_6H_6 + 3C_2H_4 \rightarrow 3C_4H_6$	23.21
$B_3N_3H_6 + 3H_2BNH_2 \rightarrow 3B_2N_2H_6$	10.22
$B_3P_3H_6 + 3H_2BPH_2 \rightarrow 3B_2P_2H_6$	11.48
$Al_3N_3H_6 + 3H_2AlNH_2 \rightarrow 3Al_2N_2H_6$	1.63

SCHEME 1: Protonation Reactions Used for the Estimation of ASE in Benzene (C_6H_6)



SCHEME 2: Protonation Reactions Used for the Estimation of ASE in Planar Borazine ($B_3N_3H_6$)



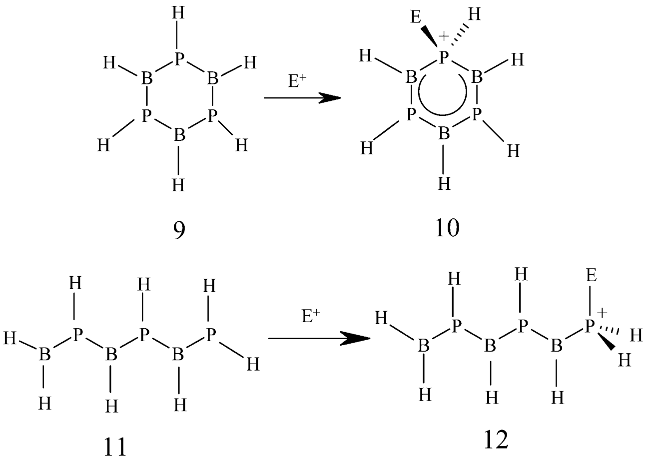
appeared in the scan shape are found with the change in both basis sets and methods.

3.2. Homodesmotic and Protonation Reactions. In this work, we have not only confined our discussion to the NICS scans and its separation into diamagnetic and paramagnetic contributions but also calculated the energies of each of the above-mentioned systems from homodesmotic and protonation reactions. This is done to predict whether the NICS scanning procedure can really provide satisfactory results in assessing aromaticity or antiaromaticity in these systems of interest. The homodesmotic and protonation reactions are very significant and are used by several researchers[14−16] to predict any aromatic or antiaromatic behavior in a system.

The degree of aromaticity in each of these six-membered-ring systems is calculated from the homodesmotic reactions where the number and types of bonds remain the same on both sides of the equations given in Table 1. The difference in energy, i.e., ZPE-corrected ΔE_{rxn}, is the stabilization induced due to delocalization of π-electrons. Table 1 quite clearly reveals the fact that the stabilization due to π-electron delocalization is maximum in the case of benzene (23.21 kcal/mol) and is reduced to more than half the value for borazine (10.22 kcal/mol), while boraphosphabenzene (11.48 kcal/mol) is slightly more stable than borazine. The least stabilization energy for alumazene (1.63 kcal/mol) may be attributed to the more polar Al−N bonds in these systems. This corroborates well with the NICS scan shapes and their results.

The ZPE-corrected aromatic stabilization energy, ASE, of benzene and the six-membered heteroatomic systems studied is determined with the help of protonation reactions. The stabilization energies are evaluated by using the pair of equations given in Schemes 1 to 4 for benzene, borazine, boraphosphabenzene, and alumazene, respectively. The ASE of benzene is taken to be the difference in the protonation energy between **2** + **3** and **1** + **4** (26.91 kcal/mol). The energies for the other systems are calculated by using the same procedure as that of benzene. A detailed analysis for the homodesmotic reactions and aromatic stabilization energies is given in the Supporting Information. Table 2 depicts the ASE values obtained for the systems under investigation. From the table, it is quite evident that as the polarity between two atoms in a bond increases, cyclic delocalization of electrons decreases. The ASE of benzene is the highest while alumazene has the lowest ASE, or in other words it has antiaromatic destabilization energy (ADE). This is also reflected in the homodesmotic reaction and also in the diamagnetic and paramagnetic contributions (Figure 8b). It is interesting to observe that in $B_3P_3H_6$, the ASE value is too small for it to be considered an aromatic species but the NICS scans, diamagnetic and paramagnetic contributions, and the ΔE_{rxn} value

SCHEME 3: Protonation Reactions Used for the Estimation of ASE in Planar Boraphosphabenzene ($B_3P_3H_6$)



SCHEME 4: Protonation Reactions Used for the Estimation of ASE in Planar Alumazene ($Al_3N_3H_6$)

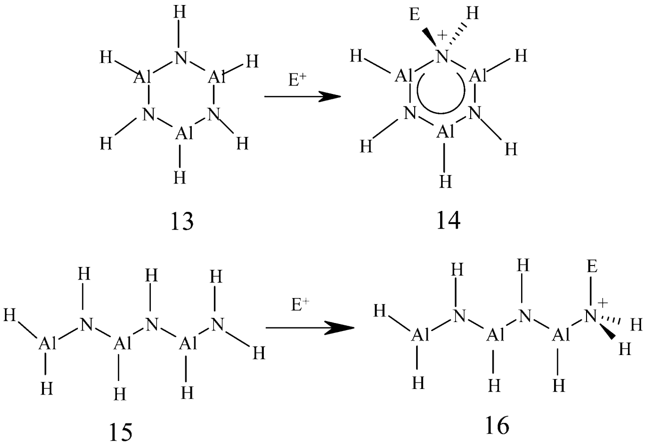


TABLE 2: ZPE-Corrected ASE (kcal/mol) Values for Benzene, Borazine, Boraphosphabenzene, and Alumazene, Using the B3LYP/6-311++G(d,p) Method

six-membered-ring systems	ASE
benzene (C_6H_6)	26.91
borazine ($B_3N_3H_6$)	8.03
boraphosphabenzene ($B_3P_3H_6$)	4.58
alumazene ($Al_3N_3H_6$)	−0.31

predict the presence of strong diamagnetic ring current in $B_3P_3H_6$, which in turn suggests cyclic electron delocalization. Thus the reliability of the NICS scans in the case of $B_3P_3H_6$ is really questionable.

4. Conclusions

The NICS scans performed on benzene and some of its planar heteroatomic inorganic analogues suggest the presence of strong diamagnetic ring current and hence cyclic electron delocalization in all the systems studied except that of alumazene. This is reflected in their NICS scan shape where at least one of the components for benzene, borazine, and boraphosphabenzene passes through a minimum, while the minimum is very shallow in the case of alumazene. Moreover the diamagnetic and paramagnetic contributions to the in-plane and out-of-plane components of each system studied support the NICS scans. In the case of $Al_3N_3H_6$, however, a net paramagnetic contribution is observed for the out-of-plane component while the NICS scan shape suggests the presence of a very weak diamagnetic ring current. The homodesmotic reactions and aromatic stabilization energies performed in each of the systems agree quite well with the NICS scans. The stabilization energy (induced due to delocalization of π-electrons) obtained from the homodesmotic reactions for alumazene is found to be a minimum, which may be attributed to more polar Al−N bonds, and it is also reflected in the NICS scanning and the diamagnetic and paramagnetic contribution curves. The ASE values determined for these systems are well in accordance with the results obtained from the magnetic shielding tensors with the only exception being boraphosphabenzene ($B_3P_3H_6$). In $B_3P_3H_6$ the ASE is found to be too small for it to be considered an aromatic species. However, the NICS scan shape and diamagnetic and paramagnetic contributions predict the opposite trend. The whole investigation suggests that apart from the single NICS value, NICS scans also cannot predict the aromatic/antiaromatic behavior of planar six-membered heteroatomic systems.

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Supporting Information Available: Optimized coordinates of benzene, borazine, boraphosphabenzene, and alumazene along with their optimized structures and ZPE-corrected energy, molecular orbitals of benzene, borazine, boraphosphabenzene, and alumazene, the NICS scan curves obtained for benzene and its planar heteroatomic analogues using B3LYP, HF, and MP2 level of theory using 6-311++G(d,p), 6-311G(d,p), and 6-31G basis sets, ZPE-corrected energies obtained for the homodesmotic reactions and aromatic stabilization energies for benzene and the heteroatomic six-membered systems, borazine, boraphosphabenzene, and alumazene, and the complete reference of Gaussian 03. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Lloyd, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 442. (b) Special Issue on Aromaticity: *Phys. Chem. Chem. Phys.* **2004**, *2*. (c) Rzepa, H. S. *Chem. Rev.* **2005**, *105*, 3697. (d) Kertesz, M.; Choi, C. H.; Yang, S. *Chem. Rev.* **2005**, *105*, 3448. (e) Katritzky, A. R.; Karelson, M.; Sild, S.; Krygowski, T. M.; Jug, K. *J. Org. Chem.* **1998**, *63*, 5228.

(2) (a) Takanashi, K.; Lee, V. Y.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2005**, *127*, 5768. (b) Mesbah, W.; Prasang, C.; Hofmann, M.; Geiseler, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1717.

(3) (a) Li, X.; Kuznetsov, A.; Zhang, H.-F.; Boldyrev, A. I.; Wang, L. *Science* **2001**, *291*, 859. (b) Li, X.; Zhang, H.-F.; Wang, L.-S.; Kuznetsov, A. E.; Cannon, N. A.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 1867. (c) Kuznetsov, A.; Boldyrev, A. I.; Li, X.; Wang, L.-S. *J. Am. Chem. Soc.* **2001**, *123*, 8825.

(4) (a) Kuznetsov, A. E.; Birch, K.; Boldyrev, A. I.; Li, X.; Zhai, H.; Wang, L. *Science* **2003**, *300*, 622. (b) Chen, Z.; Corminboeuf, C.; Heine, T.; Bohmann, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 13930. (c) Santos, J. C.; Tiznado, W.; Contreras, R.; Fuentealba, P. *J. Chem. Phys.* **2004**, *120*, 1670. (d) Santos, J. C.; Andres, J.; Aizman, A.; Fuentealba, P. *J. Chem. Theory Comput.* **2005**, *1*, 83.

(5) (a) Jutzi, P.; Mix, A.; Rummel, B.; Schoeller, W. W.; Neumann, B.; Stammler, H.-G. *Science* **2004**, *305*, 849. (b) Datta, A.; Pati, S. K. *J. Am. Chem. Soc.* **2005**, *127*, 3496.

(6) (a) Rio, D. D.; Galindo, A.; Resa, I.; Carmona, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 1244. (b) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136. (c) Xie, Y.; Schaefer, H. F., III; King, R. B. *J. Am. Chem. Soc.* **2005**, *127*, 2818.

(7) (a) Krygowski, T. M.; Cyrański, M. K. *Chem. Rev.* **2001**, *101*, 1385. (b) Jug, K.; Hiberty, P. C.; Shaik, S. *Chem. Rev.* **2001**, *101*, 1477. (c) Steiner, E.; Fowler, P. W. *J. Phys. Chem. A* **2001**, *105*, 9553. (d) Santos, J. C.; Tiznado, W.; Contreras, R.; Fuentalba, P. *J. Chem. Phys.* **2004**, *120*, 1670. (e) Geunich, D.; Hess, K.; Köhler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758.

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

(9) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.

(10) Stanger, A. *J. Org. Chem.* **2006**, *71*, 883.

(11) Seal. P; Chakrabarti. S. *J. Phys. Chem. A* **2007**, *111*, 715.

(12) Wodrich, M. D.; Corminboeuf, C.; Park, S. S.; Schleyer, P. v. R. *Chem. Eur. J.* **2007**, *13*, 4582.

(13) Stanger, A. *Chem. Eur. J.* **2006**, *12*, 2745.

(14) Kiran, B.; Kumar, A.; Jemmis, E. D. *Inorg. Chem.* **2001**, *40*, 3615.

(15) Power, P. P.; Moezzi, A.; Pestana, D. C.; Petrie, M. A.; Shoner, S. C.; Waggoner, K. M. *Pure Appl. Chem.* **1991**, *63*, 859.

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

(17) Chattaraj, P. K.; Roy, D. R. *J. Phys. Chem. A* **2007**, *111*, 4684.

(18) Frisch, M. J.; et al. *Gaussian 03*, Revision B.03; Gaussian Inc.: Pittsburgh, PA, 2003. (See the Supporting Information for the complete reference.)

(19) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) Lee, C.; Yang W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(20) Madura, I.; Krygowski, T. M.; Cyrański, M. K. *Tetrahedron* **1998**, *54*, 14913.

(21) Rehaman, A.; Datta, A.; Mallajosyula, S. S.; Pati, S. K. *J. Chem. Theory Comput.* **2006**, *2*, 30.