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Minimizing the Risk of Reporting False Aromaticity and Antiaromaticity in Inorganic Heterocycles Following Magnetic Criteria

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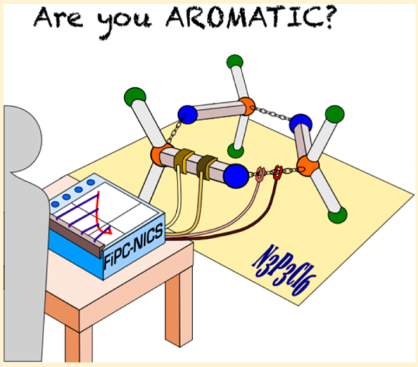
Supporting Information

ABSTRACT: Although aromaticity is a concept in chemistry, in the last years, special efforts have been carried out in order to propose theoretical strategies to quantify it as a property of molecular rings. Among them, perhaps the computation of nucleus independent chemical shifts (NICSs) is the most commonly used, since it is possible to calculate it in an easy and fast way with most used quantum chemistry software. However, contradicting assignments of aromaticity by NICS and other methods have been reported in the literature, especially in studies concerning inorganic chemistry. In this Article is proposed a new and simple strategy to use the NICS information to assess aromaticity, identifying the point along the axis perpendicular to the molecular plane where the in-plane component of NICS becomes zero; it is called free of in-plane component NICS (FiPC-NICS). This spatial point is proposed as secure to consider NICS as an aromaticity descriptor; this simple proposal is evaluated in borazine and cyclotriphosphazenes. The results are compared with carefully examined aromatic stabilization energies and magnetically induced current-density analysis.



INTRODUCTION

Sixteen years ago, Schleyer and collaborators stated "Aromaticity, a concept generally associated with organic compounds, results in exceptional geometric, energetic and magnetic properties. However, the conventional criteria are often difficult to apply to inorganic analogues".[1,2] This statement is just as valid today as it was then. Despite the fact that aromaticity is a concept and not an experimentally measurable quantity, many indices have been suggested to quantify it. Most of these indices have been originally developed within the organic chemistry framework, but with increasing applications in inorganic chemistry.[3−6] In this context, the fundamental question about the existence of delocalized bonding, and its stabilizing effect in some inorganic heterocycles, is a subject of longstanding and ongoing debate.[7−14] The investigation of the aromatic nature of such compounds has increased the number of encouraged researchers, as those compounds seem to satisfy the Hückel $4n + 2$ π-electron rule in the same way as benzene itself. However, due to the difference in electronegativity between heteroatoms, the distribution of electron density, and hence, the chemical bonding patterns in these systems, should be different from that of benzene.[15] Therefore, the extrapolation of the aromaticity notion from the organic to the inorganic world should be done cautiously in order to avoid abuse of this already fuzzy concept. To put it another way, strategies that appropriately describe aromaticity in organic molecules could lead to totally erroneous conclusions about aromaticity in inorganic systems.

Our motivation is to emphasize the risks when popular strategies, which work adequately in organic chemistry, are used to analyze inorganic molecules without the adequate cautions. Such risks have been pointed out several times before,[2,16−19] but just as important as the knowledge about these risks is to propose alternatives to avoid them. In this work, we propose a simple strategy to assess aromaticity using the NICS information. Our proposal is based on identifying a spatial point where the NICS should be cleaned of effects that could conduct to erroneous interpretations about aromaticity. To compare the obtained results by this new strategy, other indices have been calculated using energetic and magnetic criteria.

The studied systems were borazine ($B_3N_3H_6$) and cyclotriphosphazenes $N_3P_3X_6$ with X = F, Cl, Br, and H. Borazine is a planar inorganic ring, which was proposed as an inorganic-benzene analogue based on its symmetrical structure and the number of π electrons (the same as benzene).[20−22] However, the conclusions based on most of the criteria of aromaticity could only point out a nonaromatic behavior,[2] or at least a weak aromatic character.[23−25] In contrast to the abundant literature concerning the aromaticity in borazine, the studies on

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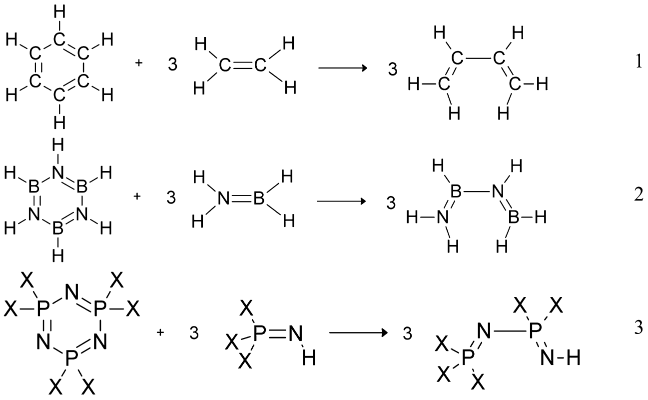
cyclotriphosphazenes are scarcer. The conclusions based on the use of some theoretical descriptors are contradictory, describing them as slightly-, non-, and antiaromatic systems.[26−28] The influence of the substituent (X) on the aromaticity has also been discussed; the electron-withdrawing X-groups have been reported to favor an enhanced aromaticity.[26] Moreover, the presence of out-of-plane-orientated ring ligands makes them interesting benchmark molecules to be analyzed. Many inorganic rings, which are stabilized with ligands oriented in this way, have been reported as aromatic systems following magnetic criteria;[29−32] however, these assignations are not free of controversies and further studies are necessary to conclude about the aromatic character of these molecules.[17−19]

■ METHODOLOGY DESCRIPTION

To evaluate the aromaticity in the previously described systems, different criteria were considered. Although this work is focused in magnetic properties, aromatic stabilization energies are estimated and used to compare with the magnetically obtained quantities.

a. Aromatic Stabilization Energy. Aromatic stabilization energy has been evaluated using different isodesmic (Scheme 1) and homodesmotic (Scheme 2) reactions. Reactions 2 and 3 have been previously proposed as inorganic analogues of reaction 1 for benzene.[2,28] Reactions 5−8 are proposed and evaluated for the first time in this work as inorganic analogues of reaction 4 (see Scheme 2). These reactions have been proposed following the same organic chemistry recommended criteria: to minimize additional effects that could disturb the reaction energies, such as strain, changes of hybridization, unbalanced conjugation, hyperconjugation, and so on.[33]

Scheme 1. Isodesmic Reaction Schemes Used to Estimate the Aromatic Stabilization Energy Shown in Table 1



b. Magnetically Induced Current Density. According to the pioneering ideas of Elvidge and Jackman, an aromatic molecule could be defined "as a compound which will sustain an induced ring current".[34] To understand the concept of aromaticity, studies of the ring current susceptibilities are supported by the visualization of the current densities on a two-dimensional grid. Lazzeretti and Zanasi introduced this idea in 1981.[35,36] On the other hand, by integrating the ring current in a plane perpendicular to the molecular plane, we obtain the net ring current susceptibility (ring current strengths, RCSs), which was suggested as a quantitative indication of aromaticity[37] and also was used for this purpose in this work.

c. Magnetic Field Induced by the Electrons of the Molecule Itself (Induced Magnetic Field, $\mathbf{B}^{\mathrm{ind}}$). $\mathbf{B}^{\mathrm{ind}}$ is the negative of the isotropic shielding constant (σ_{iso}) and equivalent to the popular nucleus independent chemical shift (NICS)[38] index ($\mathbf{B}^{\mathrm{ind}}$ = NICS = $-\sigma_{\mathrm{iso}} = -1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$).[39,40] Because of the increased popularity of NICS,[41] we are going to use this term henceforth instead of the $\mathbf{B}^{\mathrm{ind}}$. Originally, NICS was proposed to be computed in the center of the molecular plane; rings with large negative NICS values are generally classified as aromatic, whereas positive and zero values are associated as a symptom of antiaromaticity or nonaromaticity, respectively.[41] Some variations have been suggested to the NICS index, as to compute it at 1 Å above the center of the molecular plane or even the use of the out-of-plane component ($\mathrm{NICS}_{zz} = -\sigma_{zz}$), which is expected to highlight the specific behavior of the π electrons.[41]

d. Identifying Regions at Which the Local Contributions to NICS Are Minimized. The risks associated with the extrapolation of the whole magnetic behavior of one compound, or even of its aromatic character, from just one "single-value" magnetic property have been pointed out several times.[42] In particular, the use of the NICS computed in the traditional way could lead to completely erroneous interpretations about aromaticity. To avoid these problems, Stanger proposed an alternative NICS-based method based on scanning NICS values over a distance and separating them into in-plane and out-of plane contributions.[43,44] Inspired by these ideas, we propose a simple strategy to assess aromaticity as is described below.

As in the Stanger proposal, isotropic or total NICS could be decomposed into three components, $\mathrm{NICS} = -1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, which could be reorganized as $\mathrm{NICS} = (\mathrm{NICS}_{\text{in-plane}} + \mathrm{NICS}_{\text{out-of-plane}})$, where $\mathrm{NICS}_{\text{in-plane}} = -1/3(\sigma_{xx} + \sigma_{yy})$ and $\mathrm{NICS}_{\text{out-of-plane}} = -1/3(\sigma_{zz})$. The in-plane components are expected to be more sensitive to the local induced fields arising from the core and localized (lone pairs and bonding) electrons. These local magnetic fields should be of short-range, meaning that they should decay in small spatial intervals. On the other hand, the out-of-plane component is expected to highlight the induced fields due to cyclic delocalized electrons, as in the aromatic and antiaromatic systems. It is important to remark that, in our assumption, σ and π electrons are involved indistinctly.

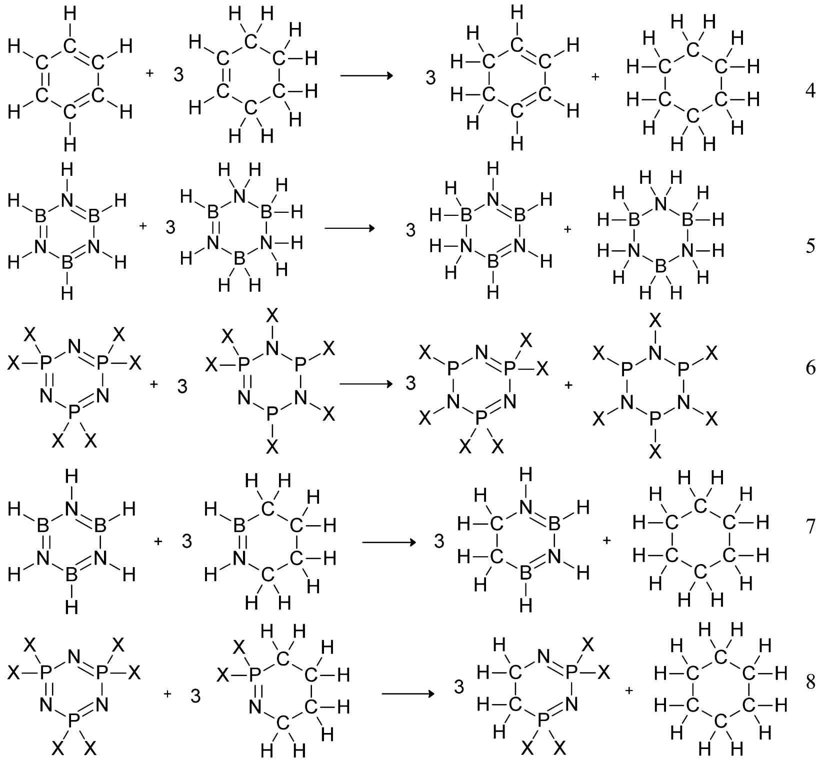
We suggest computing NICS at a point above the molecular plane where the in-plane component decays to zero, giving an indication that the local contributions to the induced magnetic fields at this point are no longer important. We named this NICS, free of in-plane component NICS (FiPC-NICS). A simple way to estimate FiPC-NICS is computing NICS profiles along the axis perpendicular to the molecular plane. In this case and following the traditional way to work with NICS, the molecule is placed in the $x.y$ plane with its geometrical center at the origin of coordinates. Then, by plotting the $\mathrm{NICS}_{\text{in-plane}}$ vs $\mathrm{NICS}_{\text{out-of-plane}}$, we can identify where the in-plane component of NICS becomes zero; it means at the point where NICS = NICS_{zz}. Additionally, we propose using the shape of the curves to compare with prototypical curves obtained from aromatic, nonaromatic, and antiaromatic well-established molecules.

In Figure 1, we have graphically reported how this strategy works in representative molecules: aromatic (benzene; C_6H_6), nonaromatic (1,4-cyclohexadiene and 1,3-cyclohexadiene; C_6H_8), antiaromatic (cyclobutadiene; C_4H_4), and one acyclic olefin (cis-1,3-butadiene, C_4H_6) molecule. As we can observe on the far right in Figure 1, the distance at which the in-plane component becomes zero does not exactly correspond to 1.0 Å for these organic molecules. The FiPC-NICS for the aromatic benzene and the antiaromatic cyclobutadiene is identified at approximately 1.2 Å, validating the recommendation of using $\mathrm{NICS}(1)_{zz}$ in the aromaticity assessment of organic rings. The FiPC-NICS values are in complete agreement with the expectations, according with the aromatic, non-, and antiaromatic nature of the evaluated molecules.

The shapes of the curves are also important to analyze; the main difference between aromatic and antiaromactic rings is that one has negative NICS out-of-plane values and the other positive NICS out-of-plane values. Additionally, observing from the superior part of the figure, the antiaromatic and aromatic curves have concave and convex slopes, respectively. Interestingly, the opposite nature about aromaticity in these two molecules is graphically represented by their curves. On the other hand, for the nonaromatic molecules, the relation between NICS components has a linear shape.

The performance of this strategy when is used in regions closer to chemical bonds was also evaluated computing the NICS profiles starting from the geometrical center of cis-1,3-butadiene. The curve has almost a linear shape, but the FiPC-NICS is slightly negative. It is also important to remark that the distance at which the FiPC-NICS is

Scheme 2. Homodesmotic Reaction Schemes Used to Estimate the Aromatic Stabilization Energy Shown in Table 1



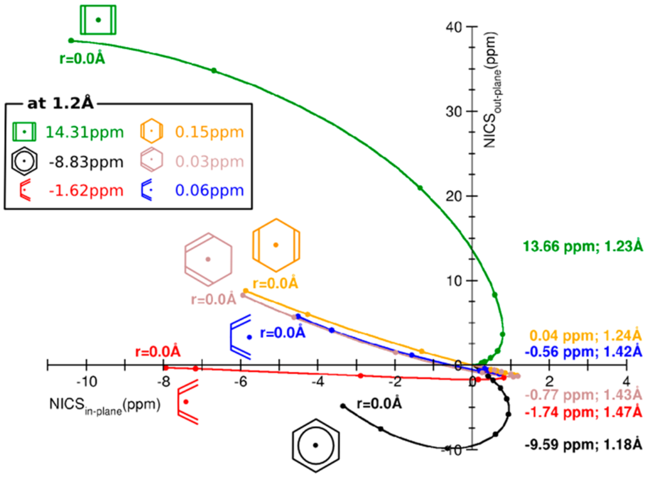


Figure 1. Plots of the NICS$_{in\text{-}plane}$ vs NICS$_{out\text{-}plane}$ to identify the FiPC-NICS for aromatic, nonaromatics, and antiaromatic molecules used to introduce this strategy. The dots over the lines represent increments of 0.5 Å, which correspond to each value of NICS, starting at the molecular center (0.0 Å).

located is dependent on the chemical bonding nature; e.g., in molecules that allow resonance between π bonds (1,3-cyclohexadiene and cis-1,3-butadiene), the FiPC-NICS is identified at approximately 1.4 Å, unlike the other molecules where it is identified at 1.2 Å. However, it is important to highlight that their nonaromatic character is correctly described by this descriptor.

■ COMPUTATIONAL METHODS

The geometry optimizations, the electronic energies and the induced magnetic field ($\mathbf{B}^{ind}$) computations were performed with the PBE0 functional in conjunction with the 6-311++G** basis set employing the Gaussian 09 package of programs.[45] The shielding tensors were computed using the GIAO approach.

The magnetically induced current densities were obtained by using the four-component Dirac−Coulomb Hamiltonian as implemented in the DIRAC code.[46] For the purpose of comparison, we used the same basis set and functional as in the Gaussian calculations. In DIRAC, the small component basis set has been generated using unrestricted kinetic balance (UKB), which provides a flexible basis set for magnetic properties (simple magnetic balance, sMB).[47] The two-dimensional Gauss−Lobatto algorithm[48] was used to integrate the magnetically induced ring-current susceptibilities. We chose an integration plane perpendicular to the molecular plane. This integration plane is a perpendicular bisector of a specific bond and starts approximately at the molecular center and extends 10 atomic units in all directions. For details about strategies used to calculate and analyze magnetically induced current densities in DIRAC, see refs 47, 49, and 50. For the graphical representations of $\mathbf{B}^{ind}$, we employed the Molekel code 5.4.0.8.[51] The magnetically induced current-density plots were obtained by using the PyNGL package.[52]

■ RESULTS AND DISCUSSION

Let us start our discussion by analyzing the aromaticity description of the studied systems by means of aromatic stabilization energy criterion. In Table 1 are shown the aromatic stabilization energies (ASEs), computed using the reactions 1−8 (Schemes 1 and 2), distributed as follows. In the second column of the table, the ASEs calculated by eq 1 for benzene and their analogues (reactions 2 and 3) for the inorganic rings are reported. The same reactions have been used in the past to estimate the ASEs of the inorganic rings analyzed here; however, the results are highly discordant among them[27,28] and also with our present results.

According to these ASEs, borazine presents a 31% of aromaticity compared to benzene, whereas the cyclotriphosphazenes are described as highly aromatic when X = F (70%), moderately aromatic when X = Cl, and weakly aromatic when X = Br, H. This higher aromatic character predicted for some of the cyclotriphosphazenes contradicts the experimental evidence

Table 1. Aromatic Stabilization Energies (in kcal·mol^{-1})

system	I[a]		II-1[b]		II-2[c]		II[d]	
C_6H_6	33.9	(100)	33.6	(100)	33.6	(100)	33.6	(100)
$B_3N_3H_6$	10.7	(31)	13.4	(40)	9.9	(30)	9.9	(30)
$(NPF_2)_3$	24.0	(71)	5.2	(15)	13.7	(41)	5.2	(15)
$(NPCl_2)_3$	6.7	(20)	0.9	(3)	13.4	(40)	0.9	(3)
$(NPBr_2)_3$	3.4	(10)	0.0	(0)	13.3	(40)	0.0	(0)
$(NPH_2)_3$	1.6	(15)	−1.2	(−4)	7.6	(22)	−1.2	(−4)

[a] ASEs calculated with the isodesmic reactions 1−3. [b] ASEs calculated with homodesmotic reactions: 4 (benzene), 5 (borazine), and 6 (cyclotriphosphazenes). [c] ASEs calculated with the homodesmotic reactions: 4 (benzene), 7 (borazine), and 8 (cyclotriphosphazenes). [d] Selected ASEs calculated with the best homodesmotic reactions for each system. Read the text for the details.

of lack of visible and deep UV radiation (up to 220−230 nm) absorbance in these systems.[53,54] To identify the possible sources of error associated with these estimations, we analyzed the structural data of the reactants and products used in the respective reactions (see Figure 1-SI, Supporting Information). As we can see in the figure, the angles and distances of the products change dramatically compared to those of the reactive species when cyclotriphosphazenes are analyzed. These structural rearrangements should be a consequence of the negative hyperconjugation effects, which are maximized in the case of the F (higher distortions) and minimized in the case of the H (lower distortions).

In the third and fourth columns of Table 1 (II-1 and II-2), we can observe the ASEs obtained by the more sophisticated reactions 4−8. Reaction 4 is used to estimate the ASE of benzene, and it is the same in both columns. In reactions 5 and 6, we constructed completely inorganic analogues of the reactants and products as their organic counterpart (reported in the third column, II-1), whereas, in reactions 7 and 8, we used hybrid systems, combining inorganic and organic fragments, where the organic fragment works as a pincer of the inorganic part (reported in the fourth column, II-2). In the last column (II), the most adequate inorganic analogues to the homodesmotic reaction 4 (II-1 and II-2) have been organized. This selection was performed in the light of the following evidence; reaction 5 is discarded due to the fact that boron atoms are forced to sp^3 hybridization, which is expected to generate strain in the B−H bonds. Recently, we have shown that boron avoids classical hybridizations in boron−hydrogen compounds.[55] This strain is minimized when hybrid structures are used (reaction 7, Figure 4-SI, Supporting Information). On the other hand, in the complete inorganic reaction used for cyclotriphosphazenes (reaction 6), there is no presence of strain, and in general, the chemical environments are correctly balanced between reactants and products (see Figure 5-SI, Supporting Information). Nevertheless, when hybrid structures are used to estimate the ASEs of cyclotriphosphazenes (reaction 8), the strain effect is manifested in the shortness of the P−N−P angle in the products (118°) compared to 122° in its reactant counterpart, as it is observed in Figure 6-SI (Supporting Information).

In contrast to the misleading ASEs obtained by isodesmic reactions (column I), the adequate selection of homodesmotic reactions allows us to calculate the ASEs (column II) that agree with other evidence that addresses the aromatic character in these inorganic rings. The borazine molecule presents aromatic character but not comparable to the benzene. The cyclotriphosphazenes are not aromatic with the exception of the $(NPF_2)_3$, which is described as a marginally aromatic system.

In Figure 2, the induced current density and the induced magnetic fields ($\mathbf{B}^{ind}$) plotted in the molecular plane for the borazine and the hexafluorocyclotriphosphazene are shown. As it was previously noted for borazine,[42] three islands of regionally delocalized diatropic current densities appear around the nitrogen atoms. Interestingly, these islands are also present in the hexafluorocyclotriphosphazene. The same patterns also appear in the other analyzed cyclotriphosphazenes (see Figures 7-SI to 11-SI in the Supporting Information). It is important to note that there are some differences when comparing the local islands in borazine and in cyclotriphosphazenes. In the first case, the islands have a triangular shape with rounded corners, whereas, in the cyclotriphosphazenes, these have a circular shape. These differences could be ascribed to the N−H bonds

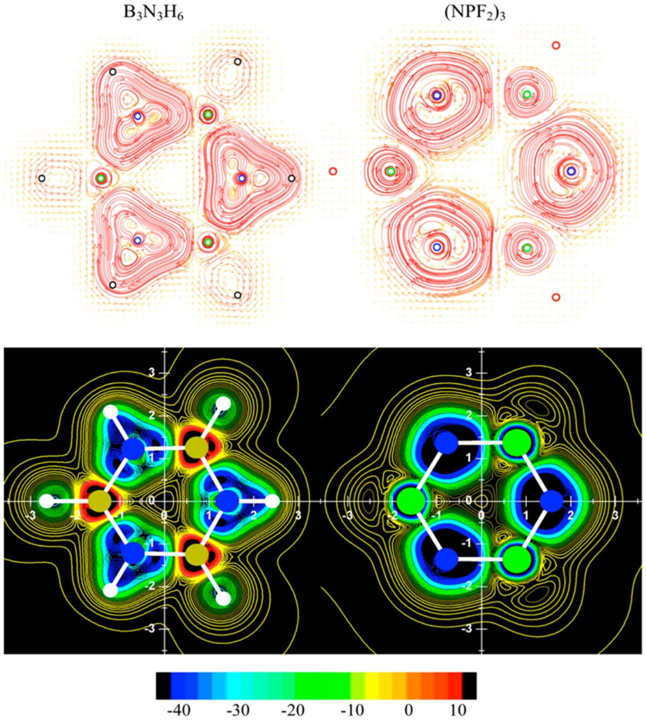


Figure 2. At the top of the figure are shown the current densities of borazine ($B_3N_3H_6$) and the hexafluorocyclotriphosphazene ($(NPF_2)_3$). The magnetic field vector points are toward the reader. At the bottom of the figure are shown the contour lines in the molecular plane of the induced magnetic field ($\mathbf{B}^{ind}$) in the range of 10.0 to −40.0 μT for the borazine ($B_3N_3H_6$) and the hexafluorocyclotriphosphazene $(NPF_2)_3$. Blue and red colors indicate shielding (negative values) and deshielding (positive values), respectively. The scale is given in ppm. Small circles represent the atomic centers, blue for nitrogen in both systems.

Table 2. Magnetic Properties of Benzene, Borazine, and Cyclotriphosphazenes

	NICS[a]				$NICS_{zz}$[a]				FiPC-NICS[a]		RCS[b]	
system	0		1		0		1					
C_6H_6	−8.2	(100)	−10.4	(100)	−14.7	(100)	−29.7	(100)	−9.6	(100)	12	(100)
$N_3B_3H_6$	−1.6	(20)	−2.7	(26)	12.3	(−84)	−5.2	(18)	−2.5	(26)	3.3	(28)
$(NPF_2)_3$	−7.1	(87)	−4.1	(39)	10.3	(−70)	−1.7	(6)	−1.8	(19)	1.9	(16)
$(NPCl_2)_3$	−4.9	(60)	−3.1	(30)	11.3	(−77)	0.8	(−3)	−0.8	(8)	1.5	(13)
$(NPBr_2)_3$	−3.4	(41)	−2.1	(20)	13	(−88)	2.4	(−8)	−0.3	(3)	0.7	(6)
$(NPH_2)_3$	−1.2	(15)	0	(0)	22.4	(−152)	4.4	(−15)	0.2	(−2)	0.9	(8)

[a]Values in ppm. [b]Values in nA T^{-1} (nano-ampere/tesla^{-1}).

in borazine, whereas, in the cyclotriphosphazenes, the nitrogen has a lone pair of electrons in this region.[56] Guided by these results, we would like to highlight the electronic delocalization of the six σ electrons surrounding each nitrogen atom. In our opinion, this electronic delocalization deserves to be analyzed in detail due to its possible implication in important chemical aspects of these inorganic systems. Concerning the aromaticity assessment by magnetic criteria, this phenomenon generates a particular influence on the induced magnetic fields (Figure 1), where the presence of diatropic regions, around the nitrogen atoms, clearly covers a bigger area than the one expected by the induced fields of core electrons, increasing the complexities on the analysis of the magnetic properties.

In Table 2, the single-value properties used to assess aromaticity by magnetic criteria are reported. In the first columns, the popular NICS and their most widely used variants, NICS(1), $NICS_{zz}$, and $NICS_{zz}(1)$ are displayed. In the last two columns, the FiPC-NICS and the RCS are shown. In parentheses, the percentages of aromaticity relative to benzene, according to each descriptor, are shown.

According to the data, there are significant discrepancies among aromaticity assignations from different approximations of NICS. For instance, the $NICS_{zz}(0)$ describes all the inorganic rings as highly antiaromatic, whereas NICS(0) classifies them as highly aromatic ($(NPF_2)_3$), moderately aromatic ($(NPCl_2)_3$ and $(NPBr_2)_3$), and weakly aromatic ($N_3B_3H_6$ and $(NPH_2)_3$) systems. The NICS and $NICS_{zz}$ computed outside the molecular plane are also discordant in their description of aromaticity. NICS(1) classifies borazine and cyclotriphosphazenes, with the exception of $(NPH_2)_3$, as moderately aromatic compounds. On the other hand, $NICS_{zz}(1)$ predicts a weakly aromatic character in borazine, whereas the cyclotriphosphazenes evolve from marginally aromatic when X = F to weakly antiaromatic when X = H. At this point of the discussion, it is important to remark that $NICS_{zz}(1)$ gives, in a general way, a similar description about aromaticity as FiPC-NICS. The small discrepancies are related to small differences in the values, which affect significantly the correlations compared to the higher aromatic character of benzene.

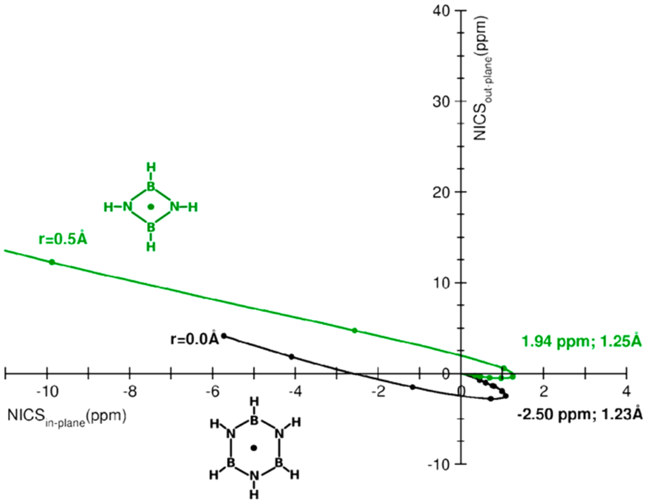


Figure 3. Plots of the in-plane components vs the out-of-plane component of the induced magnetic field for the borazine. The curve intersection with the out-of-plane component is considered as the free of in-plane component NICS (FiPC-NICS) reported in Table 2.

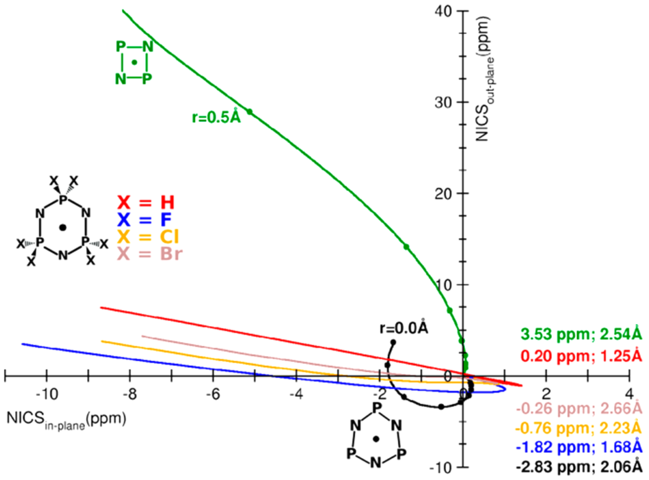


Figure 4. Plots of the in-plane components vs the out-of-plane component of the induced magnetic field for cyclotriphosphazenes. The curve intersection with the out-of-plane component is considered as the free of in-plane component NICS (FiPC-NICS) reported in Table 2

The FiPC-NICS analysis for borazine is shown in Figure 3. The curve shape shows a pattern like an aromatic system and is opposite to their antiaromatic model ($B_2N_2H_4$). According to FiPC-NICS, borazine presents an aromatic character of 30% (relative to benzene), similar to the description obtained by the selected ASEs. For the cyclotriphosphazenes, the FiPC-NICS predicts an appreciable aromatic character only in the case of the $(NPF_2)_3$, whereas the $(NPCl_2)_3$ is marginally aromatic, the $(NPBr_2)_3$ is nonaromatic, and the $(NPH_2)_3$ is described as slightly antiaromatic. The graphical representation of the FiPC-NICS search is shown in Figure 4. To maintain the strategy proposed in the FiPC-NICS analysis for organic molecules and borazine, benzene and cyclobutadiene analogues for P−N rings have been proposed, the P_3N_3 and P_2N_2, respectively. The aromatic and antiaromatic pattern for these models is evidenced in the shape of the curves; however, the magnitudes are different compared with those of their organic counterpart.

It is important to remark that the distance at which FiPC-NICSs are obtained differs greatly between the systems and also to point out that this quantity is highly dependent on the bonding structure of the systems.

Finally, in the last column of Table 2, the RCSs are reported. This descriptor provides similar results as those obtained by the selected ASEs and the FiPC-NICS for all the studied systems, with the exception of the $(NPH_2)_3$. RCS classifies it as marginally aromatic. This result disagrees with the current-density plots, as discussed in the following paragraphs. In the case of the $(NPF_2)_3$, a clear diatropic ring current is observed connecting the three previously described islands surrounding the N atoms (see Figure 2 and Figure 8-SI (Supporting Information)); the same pattern is observed in the plane 1 Bohr above the molecular plane (see Figure 8-SI). Therefore, the aromatic assignation to this molecule obtained by ASE, FiPC-NICS and RCS, is in total agreement with these current-density distributions. In contrast, the same analysis for the $(NPH_2)_3$ allows us to conclude that there is no presence of diatropic ring current around the molecular ring; instead, it is possible to appreciate a slight paratropic current through the periphery of the complete molecular ring (see Figure 11-SI, Supporting Information). As it was previously rigorously discussed by Saue and collaborators,[57] the IRCS values are, to some extent, dependent on the integration plane orientation, for it is difficult to avoid regions of high current density, which could lead to integration instabilities. In effect, this is graphically represented in Figure 5, where it is clearly observed that the integration plane passes through regions with a higher presence of local current densities. Although this is not of critical importance, this could undoubtedly include errors in the quantitative aromaticity interpretations via RCS when similar systems are compared.

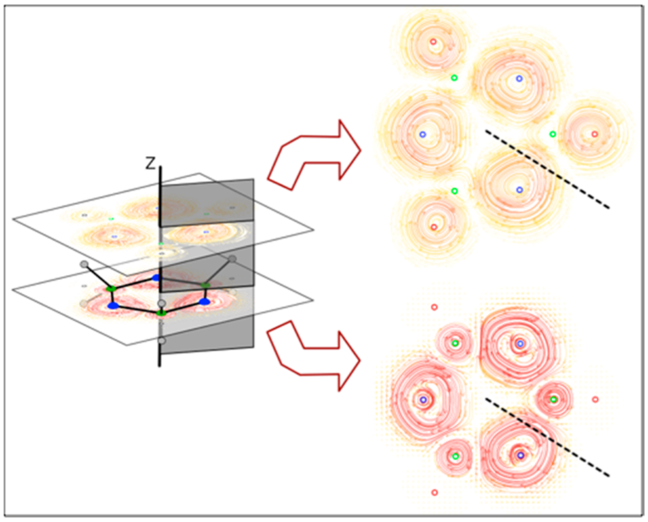


Figure 5. Schematic representation of the plane used to integrate the magnetically induced ring currents to obtain the IRCS descriptor. The plots correspond to magnetically induced current density for $N_3P_3F_6$.

CONCLUSIONS

In this contribution, a new and simple strategy to use the nuclear independent chemical shift (NICS) information in the assessment of aromaticity in inorganic heterocycles is proposed. The strategy is based on identifying a spatial point where the induced magnetic field magnitude should be mainly due to the phenomena of aromaticity or antiaromaticity. We called this NICS the free of in-plane component NICS (FiPC-NICS); it was tested to describe aromaticity of borazine and a series of cyclotriphosphazenes. The FiPC-NICS results are compared with those obtained by other aromaticity criteria, aromatic stabilization energies (ASEs), and ring current strengths (RCSs). FiPC-NICS describes borazine as weakly aromatic and cyclotriphosphazenes as nonaromatics with the exception of hexafluorocyclotriphosphazene, which is diagnosed as marginally aromatic. These results agree with those obtained by the other descriptors, unlike what happens with the traditional analysis of NICS. The FiPC-NICS provides not just single values to be considered as symptoms of aromaticity or antiaromaticity; instead, it allows visualizing the relation between the in-plane and out-of-plane components of NICS. The plots of these correlations provide curves whose shapes seem to be characteristics for aromatic, nonaromatic and antiaromatic systems.

ASSOCIATED CONTENT

Supporting Information

Structures and coordinates of the systems used to evaluate ASEs. Plots of the induced magnetic fields and induced current densities for the studied systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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