

Substituent effects on cyclic electron delocalization in symmetric *B*- and *N*-trisubstituted borazine derivatives†

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Aromaticity is an important concept in chemistry, useful to rationalize structure, physical properties and chemical behaviour of molecules. Aromaticity of an inorganic relative of benzene, borazine, has been the topic of a number of studies which resulted in its description as weakly aromatic or nonaromatic. However, influence of substituents on its aromatic character is poorly understood. This study shows that an appropriate choice of aromaticity indices can establish a connection between substituent effects and aromaticity of the ring. The changes in cyclic π electron delocalization (aromaticity) were traced by means of the most refined NICS(0) _{π_{zz}} index, the electron delocalization-based index PDI and extra cyclic resonance energy ECRE, computed by using the Natural Bond Orbital (NBO) method. Although various indices often do not correlate well with each other, owing to the multidimensional nature of aromaticity, these three indices agreed quite well. However, the HOMA index failed to give reliable information in this case.

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Introduction

Borazine ($B_3N_3H_6$), an inorganic relative of benzene, was discovered by Stock and Poland in 1926.¹ Being isoelectronic with benzene, planar and with equal bond lengths it was named “inorganic benzene”. Later studies, however, showed that it should be considered as nonaromatic, or at most weakly aromatic,^{2–12} which is a consequence of the large electronegativity difference between boron (2.0) and nitrogen (3.0) placing the six π electrons formally on the nitrogen atoms. A degree of aromatic stabilization will thus depend on the ability of nitrogen to donate its lone pair to the empty p orbital of boron, which is expected to be influenced by electronic effects of substituents attached at the borazine ring. Despite the large number of derivatives that have been synthesized, substituent effects on cyclic π electron delocalization (aromaticity) in borazine ring is poorly understood. Nelson and Pietro¹³ investigated substituent effects in *B*-monosubstituted borazines, using the NBO method, and concluded that the interactions of π -donors with the borazine ring are enhanced with respect to the analogous benzene systems, while interactions involving π -acceptors are diminished. This is the result of the highly polarized nature of the ring π -bonding and π^* -antibonding orbitals which are polarized toward nitrogen and boron, respectively.¹³ The authors intuitively predicted a reversal in the

relative magnitude of substituent–ring interactions for *N*-substituted borazines: π -acceptors should show increased interaction and π -donors decreased. The same authors also showed that the borazine π system is capable of transmitting substituent effects transannularly, but in smaller magnitude relative to benzene.¹³ Parker and Davis¹⁴ studied the aromaticity of a series of fluoroborazines by analyzing geometric parameters and vibrational frequencies, and concluded that fluorination on boron increases aromaticity, while fluorination on nitrogen decreases it. Miao *et al.*¹⁵ re-examined the aromatic character of fluoro derivatives using the energetic criterion (aromatic stabilization energy, ASE), magnetic criteria (magnetic susceptibility exaltation, MSE, and nucleus independent chemical shift, NICS) and topological analysis by using the Quantum Theory of Atoms in Molecules (QTAIM) of Bader.^{16,17} Their study confirmed the decrease in the aromaticity for *N*-fluoroborazines, but revealed that *B*-fluoro derivatives, too, are less aromatic than unsubstituted borazine. By employing the same criteria, Miao *et al.*¹⁸ investigated substituent effects on aromaticity of symmetric *B*-trisubstituted derivatives. A similar study was later done by Phukan *et al.*¹⁹ However, ASE and NICS did not correlate well with each other, in both studies. For some derivatives it is not clear if they are more or less aromatic than borazine itself. This disagreement was explained by the dependence of ASE on the equations and reference molecules used for its evaluation, whereas NICS is an absolute measure and it was found to be a better indicator for cyclic electron delocalization in the studied compounds.^{18,19} Although being an absolute measure,^{20,21} total, isotropic NICS contains contributions from both σ and π electrons, and lone pairs, and is also affected by electron flows perpendicular to the

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ring plane.²² Even NICS(2)_{zz}, corresponding to the out-of-plane component of the shielding tensor at a point located 2 Å above the ring center, which was chosen by Miao *et al.*^{15,18} as a reliable aromaticity indicator for borazine derivatives, still contains a significant contribution from the σ framework, at least for borazine itself.²³ Apart from fluoro derivatives,^{14,15} a study of aromaticity of *N*-substituted borazines does not exist. It appears that further studies are needed to shed more light on electron delocalization in this type of compounds, leading to better understanding of their physical properties and chemical behaviour, and aromaticity in general. From a more applied perspective, this fundamental knowledge should be of value for the design of BN-based materials prepared from borazine and its derivatives.^{24–28}

Herein, we re-evaluated a degree of cyclic π electron delocalization (aromaticity) in symmetric *B*-trisubstituted borazine derivatives by means of magnetic, electronic, structural and energetic criteria, and extended the study to symmetric *N*-trisubstituted borazines. The following substituents have been taken into consideration: electron-accepting groups (Acc), CF₃, CF₃CO, CN and NO₂; electron-donating groups (Don), NH₂, OH, SH, O[−] and S[−]; and halogens, Cl and Br. It should be noted that aromaticity is not a measurable property and its evaluation by theoretical methods is highly dependent on the applied method. Hence, comparison of results obtained with different methods is quite difficult. However, estimates done within the same method can give an information about the relative aromaticity of the investigated molecules.

Methods

As a magnetic criterion we used the most refined NICS(0)_{πzz} index²⁹ which includes only the π electron contribution to the out-of-plane component of the magnetic shielding tensor, at a point located at a ring center. The NICS data were computed on the basis of the localized molecular orbital dissection (LMO-NICS)^{2,30} which separates the total shielding into contributions from bonds, lone pairs and core electrons. It is particularly useful to distinguish the ring π electron contributions from those arising from other π electrons. The NICS values computed for the studied molecules include the contributions from the ring π electrons only (denoted as NICS(0)_{ring(π)zz}), which is relevant to aromaticity. To follow the NMR chemical shift convention, the sign of the computed values is reversed.^{20,21} Thus, significantly negative NICS values (*i.e.*, magnetically shielded) indicate a presence of induced diatropic ring currents (aromaticity), whereas positive values (*i.e.*, deshielded) denote paratropic ring currents (antiaromaticity).

As an electronic criterion we used the *para*-delocalization index (PDI),^{31,32} which is derived from the QTAIM.^{16,17} This index is based on electron delocalization and is defined as a mean of all delocalization indices (DIs) of *para*-related atoms in a given six-membered ring.^{31,32} It proved useful to trace changes in aromaticity due to substituent effects.³³ The higher its value, the more aromatic system is.

The harmonic oscillator model of aromaticity (HOMA) index^{34,35} is a structural type index and is defined as:

$$\text{HOMA} = 1 - \alpha/n \sum (R_{\text{opt}} - R_i)^2$$

where *n* is the number of bonds taken into summation and α is an empirical constant fixed to give HOMA = 0 for structure with alternating single and double bonds and HOMA = 1 for system with all bonds equal to the optimal value, *R*_{opt}.^{34,35}

As an energetic criterion, we used the extra cyclic resonance energy (ECRE) which measures the extra stabilization of the cyclic conjugated system relative to an open chain analogue having the same number and type of conjugations.³⁶ It is obtained as a difference between resonance energies (RE) of cyclic and acyclic molecules, where the RE represents the energy of a localized state minus that of the fully delocalized system. Thus far, the ECREs were estimated on the basis of the block localized wavefunction (BLW) method^{37,38} and were applied to study the (anti)aromaticity of a number of molecules such as benzene,³⁶ cyclobutadiene,³⁶ five-³⁶ and six-membered heterocycles,^{39,40} fluorobenzenes,³⁹ cyclopropane and cyclobutane,⁴¹ different three-membered rings,^{42,43} *N*-heterocyclic silylenes,⁴⁴ and pyrene.⁴⁵ In this work, we used the Natural Bond Orbital (NBO) method^{46,47} to obtain REs and ECREs. Although, it has been pointed out earlier that the NBO method overestimates the resonance and hyperconjugative energies,^{48–50} ECREs are relative quantities and these discrepancies tend to cancel. Positive ECREs indicate extra stabilization associated with aromaticity, negative ECREs denote destabilization due to antiaromaticity.

Results and discussion

We first applied the NBO method to evaluate the ECRE for benzene on the basis of adiabatic resonance energies (ARE), in which a localized state has an optimal geometry. As reference molecules we used all-*trans*-1,3,5,7-octatetraene and *cis*-butadiene and computed the ECRE1 and ECRE2 according to the eqn (1) and (2). Thus, the number of π conjugations is the same in the cyclic system and reference molecules.

$$\text{ECRE1} = \text{ARE}_{\text{benzene}} - \text{ARE}_{\text{all-trans-1,3,5,7-octatetraene}} \quad (1)$$

$$\text{ECRE2} = \text{ARE}_{\text{benzene}} - 3 \times \text{ARE}_{\text{cis-butadiene}} \quad (2)$$

In cyclic conjugated compounds aromaticity is associated with the cyclic delocalization of π electrons. For this reason, the resonance energies were obtained by quenching the π_{C=C} → π_{C=C}^{*} interactions, which was performed by the deletion of the corresponding off-diagonal elements from the NBO Fock matrix.^{46,47} The geometric parameters and AREs are presented in Table 1 and compared with the existing data. The C=C double bond lengths of acyclic structures optimized under the constraints imposed by the NBO method are similar to those obtained by the BLW method, while the lengths of the C–C single bonds are larger, by ~0.04 Å. The optimization of the cyclic, hypothetical 1,3,5-cyclohexatriene under the NBO constraints gave the C=C double bonds shorter by 0.01 Å and C–C single bonds longer by 0.052 Å, in comparison with the BLW method. In general, when the π_{C=C} → π_{C=C}^{*} interactions are disabled, there is a tendency of double bond shortening and

Table 1 Bond lengths, d (Å), of the optimized structures and adiabatic resonance energies, ARE (kcal mol⁻¹).^a Literature data are given in parenthesis

Molecule	$d_{C(1)C(2)}$	$d_{C(2)C(3)}$	$d_{C(3)C(4)}$	$d_{C(4)C(5)}$	ARE
Benzene	1.386	1.386			85.8 (57.5) ^c
1,3,5-Cyclohexatriene ^b	1.304 (1.314) ^c	1.574 (1.522) ^c			
<i>trans</i> -1,3,5,7-Octatetraene	1.325	1.462	1.330	1.459	61.3 (31.8) ^c
<i>trans</i> -1,3,5,7-Octatetraene (localized) ^b	1.313 (1.315) ^c	1.560 (1.517) ^c	1.307 (1.312) ^c	1.558 (1.518) ^c	
<i>cis</i> -Butadiene	1.323	1.480			16.8 (9.1) ^c
<i>cis</i> -Butadiene (localized) ^b	1.313 (1.315) ^c	1.565 (1.529) ^c			

^a Calculations were performed at the HF/6-311+G** level. ^b Optimized with disabled $\pi_{C=C} \rightarrow \pi_{C=C}^*$ interactions, by using the NBO method. ^c From ref. 36 (HF/6-311+G** level; BLW method).

single bond elongation. Although, the AREs computed by the NBO method are larger than those obtained by the BLW method (Table 1), the ECRE1, 24.6 kcal mol⁻¹, and ECRE2, 35.46 kcal mol⁻¹, compare well with the BLW computed values, 25.7 kcal mol⁻¹ (ref. 36) and 29.3 kcal mol⁻¹ (ref. 40) respectively.

The structures of borazine and its symmetric *B*- and *N*-trisubstituted derivatives were optimized at the HF/6-311+G** and B3LYP/6-311+G** levels.^{51,52} In the latter one, the effects of electron correlation are taken into account. The calculated B–N bond lengths, BNB and NBN bond angles are listed in Table 2 and compared with the experimental values,^{53–57} where possible. It appears that both methods, HF and DFT, gave geometries which are in good agreement with the experimental data for borazine and *B*-trihalo derivatives. In general, the B–N bond lengths obtained at the DFT level are slightly longer, and BNB(NBN) bond angles slightly larger(smaller), compared to the HF obtained parameters. For some substituents, two sets of bond lengths/angles were obtained (Table 2).

Substituent effects on molecular geometry⁵⁸ go in the following direction. *Influence on bond lengths*: (1) electron-donating groups (NH₂, OH, S⁻, O⁻) attached at boron atom increase the B–N bond length, the longest being with O⁻ (1.483/1.487 Å at the HF and DFT levels, respectively); (2) electron-accepting groups (CF₃, CN, CF₃CO and NO₂) and halogens attached at boron atom decrease the B–N bond length, the shortest was found for NO₂ (1.406/1.413 Å at the HF and DFT levels, respectively); (3) all substituents (except OH) when attached at nitrogen tend to increase the B–N bond length, more or less; the longest bond is observed for CF₃CO (1.444/1.448 Å mean values at the HF and DFT levels, respectively). *Influence on bond angles*: (1) electronegative substituents (OH, SH, Cl, Br, CF₃, CN, CF₃CO and NO₂) connected to boron atom and electropositive groups (S⁻ and O⁻) attached at nitrogen decrease(increase) the BNB(NBN) bond angles making them closer to ideal values of 120° for sp²-hybridized atoms (the ideal value of 120° was found for borazine-*N*-triolate at the DFT level); (2) the same effect, though less pronounced, show SH, NH₂, CF₃ and COCF₃ when connected to nitrogen; (3) electropositive substituents (S⁻ and O⁻) connected to boron atom and electronegative groups (OH, Cl, Br, CN, and NO₂) attached at nitrogen have the opposite effect, *i.e.* they increase(decrease) the BNB(NBN) bond angles; for example, in borazine-*B*-triolate the bond angles (BNB/NBN 128.7/111.3°, at the DFT level) deviate significantly from optimal values found for borazine

(BNB/NBN 122.9/117.1°, at the DFT level). The changes in bond angles can be explained by the Bent's rule,^{59,60} as was also suggested for fluoroborazines.¹⁴ The Bent's rule states that atomic s character tends to concentrate in orbitals directed toward groups of lowest electronegativity. Thus, in the borazine B–N bond, the more electronegative nitrogen prefers hybrid orbitals with more s character, while the less electronegative boron has orbitals with more p character, resulting in the bond angles alternation (Table 2). When an electronegative group is introduced on boron atom, it becomes more electronegative (relative to boron in borazine) and rehybridizes to include more s character, while nitrogen rehybridizes to include more p character into orbitals forming the ring bonds. This results in an increase in the NBN angles and decrease in the BNB angles. The same occurs when N–H hydrogen is replaced by electropositive groups and a molecule approaches the idealized sp² angle of 120°. Electronegative substituents attached at nitrogen and electropositive groups connected to boron act in opposite direction by placing more s character into the nitrogen orbitals and more p character into the boron orbitals, which results in an increase in BNB bond angles and decrease in NBN bond angles, relative to borazine. Although, electronegative nitrogen withdraws electrons from the B–NH₂ bond in *B*-triaminoborazine, this is canceled by its +*R* effect and bond angles equal those in borazine at the DFT level, or are just slightly altered at the HF level in the same way in which electropositive groups behave. In the case of *N*-SH, *N*-NH₂, *N*-CF₃ and *N*-COCF₃ substituents, some other effects, apart from their electronegativity, obviously come into play making bond angles more or less closer to the idealized sp² angles.

How do substituents affect aromaticity of borazine ring? The ECREs for borazine and its derivatives were computed as a difference in the π electron vertical resonance energies (VRE _{π}) of substituted borazines minus three times VRE _{π} of appropriately substituted BN analogs of *cis*-butadiene, having the same conformational arrangement as it exists in the cyclic compounds (also see the ESI†). The VRE _{π} , in which delocalized and localized structures retain the same geometry, were evaluated by disabling the $\pi_{B=N} \rightarrow \pi_{B=N}^*$ interactions in cyclic and acyclic molecules, using the NBO deletion analysis. When doing this, the HF method has been recommended over the DFT, though it has been shown that HF and DFT values agree reasonably.⁴⁷ We were interested in comparing the results and calculations of ECREs were done at the following

Table 2 Calculated B–N bond lengths (Å), BNB and NBN bond angles (°) (experimental values are given in parenthesis), relative electronic energies of *B*- and *N*-substituted isomers (kcal mol⁻¹), resonance energies of cyclic and acyclic structures (RE_{cyclic} and RE_{acyclic}, kcal mol⁻¹), extra cyclic resonance energies (ECRE, kcal mol⁻¹), NICS (ppm), PDI (electrons) and HOMA values for borazine and its *B*- and *N*-trisubstituted derivatives^a

Molecule	Benzene <i>D</i> _{6h}	Borazine <i>D</i> _{3h}	<i>B</i> -Triamino- borazine <i>D</i> _{3h}	<i>N</i> -Triamino- borazine <i>C</i> _{3h}	<i>B</i> -Trihydroxy- borazine <i>C</i> _{3h}	<i>N</i> -Trihydroxy- borazine <i>C</i> _s
<i>d</i> _{BN} HF/DFT		1.427/1.431 (1.4355 ± 0.0021) ^c (1.429) ^d	1.437/1.442	1.425/1.429 1.431/1.436	1.429/1.434 1.432/1.437	1.426/1.430 1.427/1.430
τ _{BNB} HF/DFT		122.4/122.9 (121.1 ± 1.2) ^c (122.9) ^d	122.8/122.9	122.2/122.7	122.3/122.5	124.5/125.3 124.6
τ _{NBN} HF/DFT		117.6/117.1 (117.7 ± 1.2) ^c (117.1) ^d	117.2/117.1	117.8/117.3	117.7/117.5	115.4/114.6 115.4/114.7
Relative energy HF/DFT			0/0	190.0/180.7	0/0	267.3/248.6
RE _{cyclic} HF/HF2/DFT	162.00/159.44/ 159.52	105.49/104.03/ 108.17	89.42/88.26/88.37	99.99/98.78/103.80	90.21/88.88/89.15	101.60/100.12/104.43
RE _{acyclic} ^b HF/HF2/DFT	19.89/21.06/23.39	29.31/28.38/29.33	27.49/26.89/-	26.26/25.34 ^e /26.00 ^e	27.80/27.25/-	26.37/25.26 ^e /26.42 ^{e,f} 26.85/25.88/26.99 ^g
ECRE ^b HF/HF2/DFT	102.33/96.26/89.35	17.56/18.88/20.18	6.95/7.58/-	21.21/22.75/25.82	6.81/7.13/-	21.54/23.11/24.02 ^h
NICS(0) _{ring(π)zz} HF/DFT	-36.63/-35.77	-4.28/-7.87	-1.52/-3.23	-5.93/-9.67	-2.63/-3.99	-6.28/-10.86
PDI	0.1029	0.0177	0.0076	0.0175	0.0087	0.0181
HOMA	0.991	0.940	0.886	0.933	0.918	0.943
Molecule	<i>B</i> -Trimercapto- borazine <i>C</i> _{3h}	<i>N</i> -Trimercapto- borazine <i>C</i> _s	<i>B</i> -Trichloro- borazine <i>D</i> _{3h}	<i>N</i> -Trichloro- borazine <i>D</i> _{3h}	<i>B</i> -Tribromo- borazine <i>D</i> _{3h}	<i>N</i> -Tribromo- borazine <i>D</i> _{3h}
<i>d</i> _{BN} HF/DFT	1.425/1.431 1.427/1.433	1.436/1.439 1.437/1.439	1.419/1.426 (1.413 ± 0.013) ⁱ	1.432/1.434	1.418/1.425 (1.41) ^j (1.419; 1.423) ^k	1.433/1.435
τ _{BNB} HF/DFT	121.9/122.1	122.0/122.9	121.1/121.4 (120.8 ± 0.9) ⁱ	124.6/125.5	120.8/121.2 (119.5) ^j (120.3; 120.6) ^k	124.1/125.3
τ _{NBN} HF/DFT	118.1/117.9	118.0/117.1	118.9/118.6 (118.5 ± 1.2) ⁱ	115.4/114.5	119.2/118.8 (120) ^j (119.1; 120.7) ^k	115.9/114.7
Relative energy HF/DFT	0/0	131.3/125.9	0/0	215.4/198.9	0/0	190.4/172.6
RE _{cyclic} HF/HF2/DFT	94.95/93.27/93.29	92.59/92.06/96.59	101.23/99.44/99.96	93.33/92.46/98.25	102.16/100.29/100.73	93.02/92.24/98.65
RE _{acyclic} ^b HF/HF2/DFT	-/-	25.75/24.68/25.75 ^f 25.73/24.70/25.70 ^g	29.16/28.38/28.46	25.73/24.62/25.92	29.20/28.42/28.48	25.66/24.51/25.90
ECRE ^b HF/HF2/DFT	-/-	15.39/17.97/19.44 ^h	13.75/14.31/14.58	16.15/18.60/20.48	14.55/15.03/15.29	16.03/18.70/20.95
NICS(0) _{ring(π)zz} HF/DFT	-3.72/-6.59	-4.15/-7.48	-4.16/-7.30	-5.69/-9.90	-4.38/-7.62	-5.44/-9.65
PDI	0.0124	0.0146	0.0137	0.0169	0.0150	0.0168
HOMA	0.934	0.900	0.960	0.927	0.963	0.923
Molecule	<i>B</i> -Tris- (trifluoromethyl)- borazine <i>C</i> _{3v}	<i>N</i> -Tris- (trifluoromethyl)- borazine <i>C</i> _{3h}	<i>B</i> -Tricyano- borazine <i>D</i> _{3h}	<i>N</i> -Tricyano- borazine <i>D</i> _{3h}	<i>B</i> -Tris- (trifluoroacetyl)- borazine <i>C</i> _{3h}	<i>N</i> -Tris- (trifluoroacetyl)- borazine <i>C</i> ₃
<i>d</i> _{BN} HF/DFT	1.418/1.423	1.433/1.436 1.444/1.447	1.419/1.427	1.443/1.447	1.415/1.421 1.421/1.427	1.441/1.444 1.447/1.451
τ _{BNB} HF/DFT	120.8/121.2	122.3/122.7	121.0/121.7	123.4/123.4	121.0/121.6	121.8/122.1
τ _{NBN} HF/DFT	119.2/118.8	117.7/117.3	119.1/118.3	116.6/116.6	119.0/118.4	118.2/117.9
Relative energy HF/DFT	0/0	24.5/36.3	0/0	83.7/83.9	0/0	24.3/28.3
RE _{cyclic} HF/HF2/DFT	110.61/109.25/ 112.76	84.86/83.35/88.39	109.97/107.44/ 110.28	82.14/80.94/ 85.72	107.44/105.47/ 109.00	78.41/77.08/80.16

Table 2 (Contd.)

Molecule	<i>B</i> -Tris-(trifluoromethyl)-borazine C_{3v}	<i>N</i> -Tris-(trifluoromethyl)-borazine C_{3h}	<i>B</i> -Tricyano-borazine D_{3h}	<i>N</i> -Tricyano-borazine D_{3h}	<i>B</i> -Tris-(trifluoroacetyl)-borazine C_{3h}	<i>N</i> -Tris-(trifluoroacetyl)-borazine C_3
RE _{acyclic} ^b	30.93 ^e /30.02 ^e /	25.74/24.37/25.51	30.10/29.02/	24.42/23.46/	29.99/28.49/	26.07/25.44/26.07
HF/HF2/DFT	30.88 ^e		29.55	24.46	29.64	22.34/21.82/22.31
ECRE ^b	17.83/19.19/20.12	7.64/10.24/11.85	19.66/20.39/21.64	8.90/10.55/12.33	17.47/19.99/20.10	2.44/4.67/6.00 ⁱ
HF/HF2/DFT						
NICS(0) _{ring(π)zz}	-4.79/-8.79	-2.79/-5.56	-4.90/-8.92	-3.18/-6.16	-5.41/-9.92	-2.30/-4.11
HF/DFT						
PDI	0.0176	0.0128	0.0164	0.0119	0.0189	0.0107
HOMA	0.969	0.885	0.956	0.851	0.965	0.848

Molecule	<i>B</i> -Trinitro-borazine D_{3h}	<i>N</i> -Trinitro-borazine D_3	Borazine- <i>B</i> -trithiolate D_{3h}	Borazine- <i>N</i> -trithiolate D_{3h}	Borazine- <i>B</i> -triolate D_{3h} ^m	Borazine- <i>N</i> -triolate D_{3h}
d_{BN} HF/DFT	1.406/1.413	1.444/1.441	1.445/1.453	1.435/1.441	1.483/1.487	1.429/1.441
τ_{BNB} HF/DFT	118.5/119.3	125.4/125.6	125.3/125.7	119.5/120.5	128.6/128.7	119.2/120.0
τ_{NBN} HF/DFT	121.5/120.7	114.6/114.4	114.7/114.3	120.5/119.5	111.4/111.3	120.8/120.0
Relative energy HF/DFT	0/0	133.8/129.4	0/0	149.8/135.7	0/0	264.6/238.7
RE _{cyclic}	115.10/112.58/	82.76/84.29/	91.15/89.24/	101.08/99.75/	74.81/-/-	114.25/111.06/
HF/HF2/DFT	115.08	89.83	88.30	104.45		111.68
RE _{acyclic} ^b	31.19 ^e /30.33 ^e /31.23 ^e	24.12/24.75/25.94	-/-	21.72 ^e /20.76 ^e /20.86 ^e	24.45 ^e /-/-	19.65 ^e /18.74 ^e /18.33 ^e
HF/HF2/DFT						
ECRE ^b	21.52/21.59/21.39	10.40/10.05/12.02	-/-	35.91/37.47/41.88	1.46/-/-	55.31/54.84/56.69
HF/HF2/DFT						
NICS(0) _{ring(π)zz}	-5.84/-9.84	-2.58/-5.30	-2.60/-4.90	-8.07/-12.83	-0.88/-	-13.19/-19.39
HF/DFT						
PDI	0.0183	0.0118	0.0115	0.0203	0.0056	0.0290
HOMA	0.991	0.890	0.815	0.892	0.480	0.892

^a Values for geometrical parameters and relative energies denoted as HF and DFT were obtained at the HF/6-311+G** and B3LYP/6-311+G** levels, respectively. RE, ECRE and NICS values denoted as HF were obtained at the HF/6-311+G**//HF/6-311+G** level; values denoted as DFT were obtained at the B3LYP/6-311+G**//B3LYP/6-311+G** level; values denoted as HF2 were obtained at the HF/6-311+G**//B3LYP/6-311+G** level; PDIs were calculated at the B3LYP/6-311+G**//B3LYP/6-311+G** level; HOMA values are based on B3LYP/6-311+G** geometries. ^b In certain cases the REs and ECREs are missing due to the mismatch between the most stable resonance contributors in cyclic and acyclic compounds. ^c From ref. 53 (electron diffraction). ^d From ref. 54 (X-ray data). ^e Reference structures were kept in conformation which is not a minimum on PES. ^f Substituent Hs oriented *syn*. ^g Substituent Hs oriented *anti*. ^h Two *anti* and one *syn* conformations, with respect to the orientation of substituent Hs (see ESI). ⁱ From ref. 55 (X-ray data). ^j From ref. 56 (X-ray data). ^k From ref. 57 (X-ray data). ^l VRE for reference structure is based on relative population of two conformers. ^m At the DFT level, the most stable resonance contributor had nitrogen lone pairs only.

levels: HF/6-311+G**//HF/6-311+G**, HF/6-311+G**//B3LYP/6-311+G** and B3LYP/6-311+G**//B3LYP/6-311+G**. The corresponding values are labeled as HF, HF2 and DFT, respectively (Table 2). The NICS(0)_{ring(π)zz} data (Table 2) were computed at the HF/6-311+G**//HF/6-311+G** level and correlated with the HF/6-311+G**//HF/6-311+G** ECREs, and at the B3LYP/6-311+G**//B3LYP/6-311+G** level and correlated with the HF/6-311+G**//B3LYP/6-311+G** and B3LYP/6-311+G**//B3LYP/6-311+G** ECREs. The correlations are shown in Fig. 1. In all three cases satisfactory linear correlations were found, with the highest correlation coefficient, $R^2 = 0.952$, at the pure HF level. The ECRE values obtained at the HF/6-311+G**//B3LYP/6-311+G** and B3LYP/6-311+G**//B3LYP/6-311+G** level differ by 0.10–4.41 kcal mol⁻¹ and a slightly better agreement between NICS and ECREs was found for HF/6-311+G**//B3LYP/6-311+G** level ($R^2 = 0.944$ versus $R^2 = 0.930$ for B3LYP/6-311+G**//B3LYP/6-311+G**). The PDI data were computed at the B3LYP/6-311+G**//B3LYP/6-311+G** level and correlated

with B3LYP/6-311+G**//B3LYP/6-311+G** NICS and HF/6-311+G**//B3LYP/6-311+G** ECRE values (Fig. 2). In both cases good correlations were obtained. The HOMA values⁶¹ are based on the B3LYP/6-311+G** geometries. The corresponding data for benzene are included in Table 2 for comparison.

We first briefly discuss some structural characteristics of the studied molecules, which are important for the understanding of substituent effects on cyclic electron delocalization. In all *B*-substituted compounds the substituents lie in the plane of the ring (for CF₃, one of the C–F bond is orthogonal to the ring), thus allowing maximal electronic interactions with the borazine π system. This is not the case for the *N*-substituted derivatives in which substituents are tilted from the ring plane (for CF₃CO: $\tau_{BNCO} = 28.1^\circ/26.9^\circ$ at the HF/DFT; for NO₂: $\tau_{BNNO} = 30.7^\circ/28.3^\circ$ at the HF/DFT), or from the ring/C–F bond orthogonality, in the case of CF₃ ($\tau_{BNCF} = 59.5^\circ$ at both HF and DFT). This means reduced $\pi_{\text{ringB=N}}^*/\pi^*(\sigma^*)_{\text{substituent}}$ interactions, or blocked $n_{\text{substituent}}/\pi_{\text{ringB=N}}^*$ interactions for NH₂, OH and SH, since in the

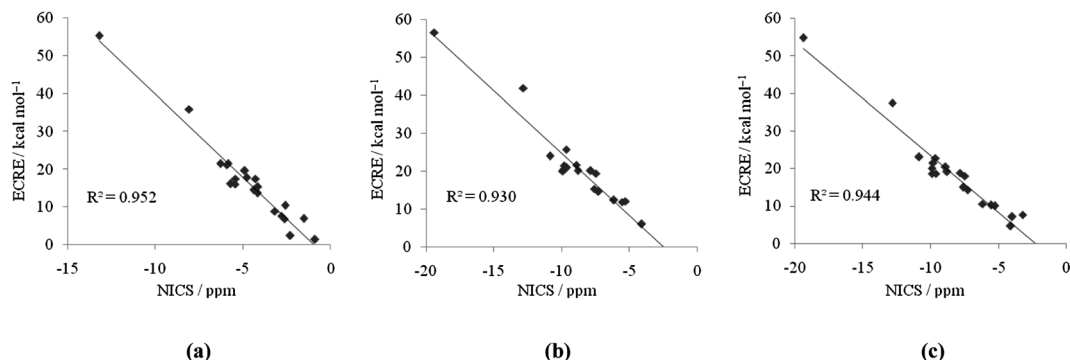


Fig. 1 Correlation of NICS and ECRE values: (a) HF/6-311+G**//HF/6-311+G** NICS and HF/6-311+G**//HF/6-311+G** ECREs; (b) B3LYP/6-311+G**//B3LYP/6-311+G** NICS and B3LYP/6-311+G**//B3LYP/6-311+G** ECREs; (c) B3LYP/6-311+G**//B3LYP/6-311+G** NICS and HF/6-311+G**//B3LYP/6-311+G** ECREs.

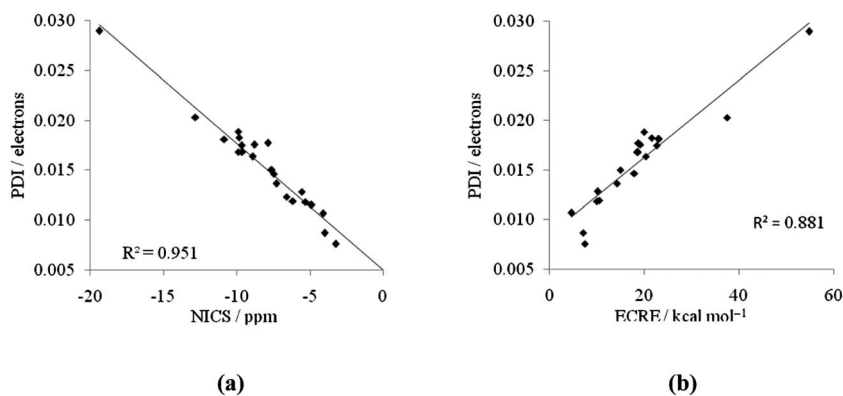


Fig. 2 Correlations of B3LYP/6-311+G**//B3LYP/6-311+G** PDIs with B3LYP/6-311+G**//B3LYP/6-311+G** NICS (a) and HF/6-311+G**//B3LYP/6-311+G** ECREs (b).

latter case substituent p-like lone pairs are in the same plane with the borazine ring.

From an examination of NICS and ECRE data given in Table 2 it is evident that electron-donating groups (O^- , S^- , NH_2 , OH and SH) attached at boron atoms and electron-accepting substituents (CF_3CO , NO_2 , CF_3 and CN) connected to nitrogens decrease the cyclic π electron delocalization relative to unsubstituted borazine. Thus, if we consider borazine as weakly aromatic, all these derivatives are nonaromatic. Due to the mismatch between the most stable resonance structures of cyclic and acyclic molecules⁶² certain ECRE values are missing. In addition, borazine-*B*-triolate had only nitrogen lone pairs at the DFT level. Nevertheless, from the just mentioned facts and the available data it can be inferred that the least cyclic π electron delocalization exists in borazine-*B*-triolate. While NICS and ECRE could not discern the subtle differences in substituents effects, this could be done by using the PDI data and the following order of increasing cyclic π electron delocalization can be established: $B-NH_2 < B-OH < N-COCF_3 < B-S^- < N-NO_2 < N-CF_3 < N-CN < B-SH$. The HOMA values, generally, do not follow the trend given by NICS, ECRE and PDI, thus indicating that the B–N bond lengths are not determined solely by π electron delocalization. In the case of *B*-Don derivatives, the increased electron density on boron atoms, coming from the substituents,

makes the ring π electrons more localized around the nitrogens, resulting in decreased cyclic π electron delocalization. Electron-accepting groups attached at nitrogen act by two effects: (i) by negative inductive ($-I$) effect they increase nitrogen electronegativity which in turn decreases its tendency to share π electrons with boron, and (ii) by negative resonance ($-R$) effect they detract π electrons from the ring ($\pi_{B=N} \rightarrow \sigma_{C-F}^*$ hyperconjugative interaction for CF_3). The strength of the latter effect is reduced, since the interacting orbitals are not in an optimal position (see before).

In the case of *B*-halo derivatives, all indices, except HOMA, agree that these derivatives are less aromatic than borazine. Here, the electron donation from halogen to the borazine π system overcomes the opposing $-I$ effect. This contrasts the situation in halobenzenes, where halogens behave as deactivating groups (toward electrophilic agents), and can be rationalized by the enhanced $n \rightarrow \pi_{B=N}^*$ interaction,¹³ as already discussed in the Introduction. Are *N*-halo derivatives more or less aromatic than borazine? While the ECREs obtained at the HF/6-311+G**//HF/6-311+G** and HF/6-311+G**//B3LYP/6-311+G** levels are slightly lower than the corresponding values for borazine, B3LYP/6-311+G**//B3LYP/6-311+G** ECREs and NICS values are slightly higher. A decision can be made on the basis of PDI values, which are slightly lower than for borazine.

Thus, *N*-haloborazines are less aromatic than borazine, but more aromatic than the *B*-halo isomers.

The data in Table 2 suggest that the electron-accepting groups (CF₃, CN, CF₃CO and NO₂) attached at boron atoms and electron-donors (NH₂, OH, S⁻ and O⁻) connected to nitrogen atoms increase aromaticity of borazine ring. While the *N*-S⁻ and *N*-O⁻ strongly enhance the extent of cyclic π electron delocalization, the effect of other groups is smaller. The influence of donors follows the trend NH₂ < OH < S⁻ < O⁻. Although, the resonance interaction of *B*-connected π acceptors is diminished with respect to benzene,¹³ all the studied groups are suitably positioned (see before) to accomplish a maximal π electron density withdrawal from nitrogen to boron by their $-R$ effect ($\pi_{B=N} \rightarrow \sigma_{C-F}^*$ hyperconjugative interaction in the case of CF₃). If the boron electronegativity enhancement, due to the substituents $-I$ effect, is added to this, it is clear why all these molecules are more aromatic than unsubstituted borazine.

How do *N*-Don substituents act? Having in mind that borazine π electrons are mostly localized around nitrogen atoms, a significant delocalization of substituent lone pairs into the borazine π system is not expected. Indeed, $n_{\text{substituent}} \rightarrow \pi_{B=N}^*$ interaction energies, obtained from the second order perturbative analysis of Fock matrix in the NBO basis, for borazine-*N*-trithiolate (1.94/1.93 kcal mol⁻¹ per substituent, at the HF/DFT level) and borazine-*N*-triolate (7.08/7.66 kcal mol⁻¹ per substituent, at the HF/DFT level) are much lower than for the isomeric borazine-*B*-trithiolate (44.39/30.87 kcal mol⁻¹ per substituent, at the HF/DFT level) and borazine-*B*-triolate (93.80 kcal mol⁻¹ per substituent, at the HF level). In the case of *N*-triamino and *N*-trihydroxyborazine such interactions are absent, since substituent p-like lone pair orbitals are placed in the ring plane (see before).⁶³ Moreover, OH and NH₂ groups attract electrons by their $-I$ effect, which would decrease electron sharing between nitrogen and boron. Hence, in the *N*-Don derivatives, nitrogen lone pairs are actually pushed toward boron atoms due to electrostatic and Pauli repulsion with substituent lone pairs. This is more prominent for OH with two lone pairs than for NH₂ with only one. In the case of S⁻ and O⁻ this is further strengthened by their anionic character (three lone pairs) and p-like lone pair delocalization. In fact, the *N*-borazinetriolate is the most aromatic of all the studied molecules, but still significantly less than the prototypical aromatic molecule, benzene (approximately twice less). It is also important to realize that larger REs do not necessarily mean greater aromatic

stabilization, since the extra stabilization due to the cyclic electron delocalization depends on delocalization energy of an acyclic system. For example, *N*-OH and *N*-S⁻ derivatives have lower REs than all *B*-Acc systems, but are more aromatic. The most aromatic borazine-*N*-triolate has RE which is slightly lower than that of *B*-trinitroborazine (Table 2).

Although, sulfur in SH possesses two lone pairs, *N*-trimercaptoborazine is less aromatic than borazine. In this case, the repulsion between sulfur and nitrogen lone pairs is obviously smaller, since sulfur electrons are farther away. Replacement of hydrogen by sulfur only enhances nitrogen electronegativity, resulting in less cyclic electron delocalization relative to borazine. Here, one may want to ask a question why are then *N*-trichloro and *N*-tribromoborazines more aromatic than the corresponding mercapto derivative, even though they contain more electronegative atoms. The answer comes from an examination of donor-acceptor interaction energies, which reveals larger $n_{Cl/Br} \rightarrow \pi_{B=N}^*$ than $n_{SH} \rightarrow \pi_{B=N}^*$ delocalization. At the DFT level the energies of three such interactions, corresponding to total substituent lone pairs delocalization into the ring π^* orbitals, are: 5.19/3.51 kcal mol⁻¹ for chlorine/bromine versus 0.46 kcal mol⁻¹ for SH, in this latter case arising from lone pair positioned parallel to the π system of borazine. This electron donation from halogens partly compensates their $-I$ effect.

Generally, there was no correlation of HOMA with NICS, PDI and ECRE values (Fig. 3). This finding point to the conclusion that the B-N bond lengths of the studied compounds are not a simple reflection of π electron delocalization, but are also affected by other influences, like inductive effect of substituents and electron repulsion. For example, the chlorine electron withdrawal in *B*-trichloroborazine due to the $-I$ effect obviously shortens the B-N bond length, but its $+R$ effect, which is here more pronounced than in benzene derivatives, does not allow nitrogen lone pairs to delocalize toward boron atoms, thus decreasing the aromaticity (HOMA_{borazine} = 0.940; HOMA_{*B*-trichloroborazine} = 0.960). In the case of *N*-Don derivatives, the B-N bond shortening due to the increased π electron delocalization is counterbalanced or even overcome by electron repulsion arising from the enhanced electron density in the ring. As a consequence, these compounds have HOMA values equal or lower to those of borazine (Table 2).

Aromaticity is usually associated with a special energetic or thermodynamic stability of a cyclic molecule. Among the studied molecules, borazine-*N*-triolate is the most aromatic, but is more than 200 kcal mol⁻¹ higher in energy (Table 2) than the

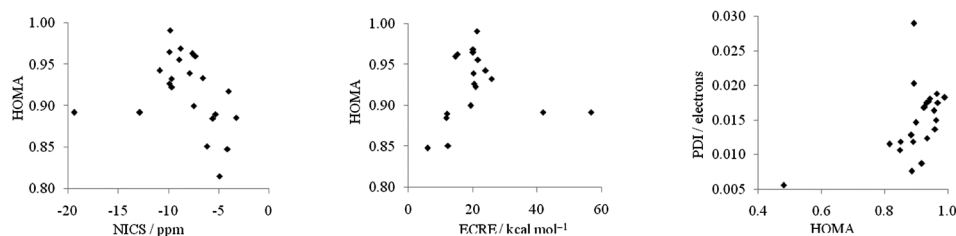


Fig. 3 HOMA against NICS(0)_{ring(π)zzz}, ECRE and PDI, at the B3LYP/6-311+G** level.

isomeric borazine-*B*-triolate, which is the least aromatic (actually nonaromatic, with the smallest degree of cyclic π electron delocalization). Also, *N*-triaminoborazine, *N*-trihydroxyborazine and borazine-*N*-trithiolate exhibit a higher degree of cyclic π electron delocalization (synonym for aromaticity), but are significantly less stable (higher in energy) than the *B*-substituted isomers. Obviously, their aromatic stabilization can not overcome the energy rise due to the repulsion between nitrogen and substituent lone pairs, while the energy of *B*-Don systems is significantly lowered by substituent/ring resonance interactions. But, can the *N*-Don derivatives be regarded as aromatic (relative to *B*-Don isomers)? The IUPAC definition of aromaticity⁶⁴ states that "aromaticity is the concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced thermodynamic stability (relative to acyclic structural analogues) and tendency to retain the structural type in the course of chemical transformations." If we follow the definition and make a comparison with acyclic analogs, the mentioned molecules are partly aromatic (based on ECREs). However, another question arises: can aromaticity be equaled with energetic/thermodynamic stability, as is usually done in the literature? On the basis of the given results, it appears that aromaticity should be considered as a type of stabilizing effect coming from the cyclic electron delocalization, but not as a stabilization of a molecule, on the whole. Several previous studies have also led to the conclusion that the most energetically stable isomer is not necessarily the most aromatic one.^{65–68}

Conclusions

In conclusion, this study established a connection between substituent effects and aromaticity of an inorganic ring, borazine. Unlike its organic counterpart benzene, the aromaticity of which resists substituent influences,³³ that of borazine is significantly affected by the nature of substituents. Substituent influence on decreasing aromaticity, relative to borazine, can be ordered as following: $B-O^- > B-NH_2 > B-OH > N-COCF_3 > B-S^- > N-NO_2 > N-CF_3 > N-CN > B-SH$. The strongest effect on increase in aromaticity show $N-O^-$ followed by $N-S^-$. The influence of $N-OH$, $N-NH_2$, $B-NO_2$ and $B-COCF_3$ is smaller and appears to be slightly more pronounced than that of $B-CF_3$ and $B-CN$. It is important to note that the *N*-Don substituted molecules are much more aromatic than the *B*-Don isomers, but have much higher energy content. This points to the conclusion that aromaticity should not be equaled with energetic/thermodynamic stability, as is often done in the literature, but regarded as a type of stabilizing effect coming from the cyclic electron delocalization.

The aromatic character of the studied systems can be satisfactorily described by three indices, based on different criteria: magnetic (NICS(0)_{ring}), electronic (PDI) and energetic (ECRE). The failure of structural HOMA index to provide a proper information is ascribed to the strong influence of substituents on molecular geometry, resulting in the dependence of the B–N bond lengths on factors other than just the π electron delocalization. Having in mind that aromaticity could be considered as a multidimensional

phenomenon and that various indices often do not correlate well with each other,^{69–74} the observed good correlations between NICS(0)_{ring}, PDI and ECRE, obtained by quenching the $\pi_{B=N} \rightarrow \pi_{B=N}^*$ interactions in cyclic and reference molecules by using the NBO method, is important.

Computational details

All calculations were performed by using the Gaussian 03 and Gaussian 09 program packages.^{75,76} Geometries were fully optimized at the HF/6-311+G** and B3LYP/6-311+G** levels,^{51,52} except for *N*-OH reference systems (*syn* and *anti*; see the ESI†) which were forced into the near-planar geometry to ensure σ – π separation. All cyclic and most of the reference, acyclic structures were confirmed as energy minima by vibrational frequency analyses (no imaginary frequencies). In order to be able to compare the REs of cyclic and acyclic systems, and to ensure the σ – π separation, some reference structures were kept in a conformation which is not a minimum on PES ($B-O^-$, $B-CF_3$, $B-NO_2$, $N-NH_2$, $N-S^-$ and $N-O^-$). The NICS(0)_{ring}(π)_{zz} values, including contributions from ring π electrons only, were computed using the GIAO method^{77,78} at the HF/6-311+G**//HF/6-311+G** and B3LYP/6-311+G**//B3LYP/6-311+G** levels. The dissection of NICS values into orbital contributions was done by employing the natural chemical shielding-natural bond orbital (NCS-NBO) analysis.⁷⁹ The extra cyclic resonance energies, ECREs, were calculated as a difference in the π electron vertical resonance energies (VRE _{π}) of substituted borazines minus three times VRE _{π} of appropriately substituted BN analogs of *cis*-butadiene. The VRE _{π} , in which delocalized and localized structures retain the same geometry, were evaluated by disabling the $\pi_{B=N} \rightarrow \pi_{B=N}^*$ interactions in cyclic and acyclic systems, using the NBO deletion analysis.^{46,47} HOMA values^{34,35,61} are based on B3LYP/6-311+G** geometries. The PDI data were obtained at the B3LYP/6-311+G** level using the AIMAll program package.⁸⁰

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