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Cyclic π Electron Delocalization in Fluoroborazines

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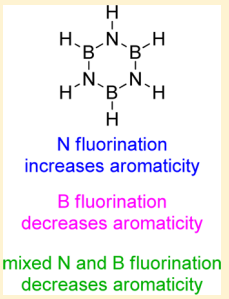
Supporting Information

ABSTRACT: How does the most electronegative atom, fluorine, affect cyclic π electron delocalization (aromaticity) of an inorganic counterpart of benzene, borazine? Previous studies have shown that *N*-fluorination decreases the aromatic character, whereas conclusions about the effect of *B*-fluorination oppose each other (*J. Phys. Chem. A* **1997**, *101*, 9410 and *J. Mol. Struct.: THEOCHEM* **2005**, *715*, 91). The aim of this study is to resolve this discrepancy and also to evaluate a degree of cyclic π electron delocalization in all possible polyfluoroborazines. This was done by employing four aromaticity indices, HOMA, NICS, ECRE, and PDI. NICS, ECRE, and PDI gave a satisfactory description of aromaticity of the studied molecules. It was found that *N*-monofluoroborazine, *N*-difluoroborazine, and *N*-trifluoroborazine are the only fluorinated derivatives that exhibit a higher degree of aromaticity compared to borazine. This result opposes the previous ones regarding the influence of *N*-fluorination.



INTRODUCTION

Borazine ($B_3N_3H_6$) is a boron−nitrogen analogue of benzene, in which the CC units are replaced with an isoelectronic BN pair. Soon after its discovery,[1] it was named inorganic benzene because it has a planar ring with equal BN bond lengths and six π electrons (nitrogen lone pairs). However, the following studies resulted in its description as weakly aromatic or nonaromatic.[2] The reason for this is the large difference in electronegativity between boron (2.0) and nitrogen (3.0), which places the π electrons mostly around the nitrogen atoms. If hydrogen atoms of boron are replaced by an electronegative atom (group), more electron density could be drawn from nitrogen to boron, thereby enhancing cyclic π electron delocalization (aromaticity). Considering the most electronegative atom, fluorine, a question may arise if *B*-mono, *B*-di, and *B*-trifluoroborazine are more aromatic than borazine. In 1997, Parker and Davis[3] tried to answer this question by an analysis of geometric parameters and vibrational frequencies of a series of fluorinated borazines. They concluded that fluorination on boron increases aromaticity, while fluorination on nitrogen decreases it. Some years later, this issue was re-examined by Miao et al.[4] employing an energetic criterion (aromatic stabilization energy, ASE), magnetic criteria (magnetic susceptibilty exaltation, MSE, and nucleus-independent chemical shift, $NICS(2)_{zz}$), and topological analysis by the atoms in molecules (AIM) method. Their study confirmed the decrease in the aromaticity for *N*-fluoroborazines, but revealed that *B*-fluoro derivatives, too, are less aromatic than unsubstituted borazine. To resolve this discrepancy, the aromatic character of fluorinated borazines is re-evaluted using the harmonic oscillator model of aromaticity (HOMA) index,[5] the most refined $NICS(0)_{\pi zz}$ index,[6] the para-delocalization index (PDI),[7] and the natural bond orbital (NBO) method[8] to characterize the extra stabilization arising from cyclic electron delocalization.

METHODS

The HOMA is a geometry-based index and is defined by Kruszewski and Krygowski according to eq 1[5]

$$\mathrm{HOMA} = 1 - \alpha/n \sum (R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \qquad (1)$$

Here, n is the number of bonds taken into consideration and α is an empirical constant chosen to give HOMA = 0 for a nonaromatic system and HOMA = 1 for a system with all bonds equal to the optimal value, R_{opt}, assumed to exist in a fully aromatic system. R_{i} stands for an individual bond length of a system considered. For the B−N bond, α = 72.03 and R_{opt} = 1.402 Å.[9] For the C−C bond, α = 257.7 and R_{opt} = 1.388 Å.[5b]

NICS, introduced by Schleyer and co-workers,[10] belongs to magnetic indices of aromaticity. It is based on an induced π electron ring current when a molecule is exposed to an external magnetic field. NICS is defined as the negative of the magnetic shielding computed at the ring center, NICS(0), or some other points in the vicinity of molecules (usually 1 or 2 Å above the ring center, NICS(1) and NICS(2), respectively). Significantly negative (shielded) NICS values indicate a diatropic ring current and aromaticity, while positive (deshielded) values denote a paratropic ring current and antiaromaticity. In this work, the most refined $NICS(0)_{\pi zz}$ index[6] has been employed. It includes only the π electron contribution to the out-of-plane component of the magnetic shielding tensor (zz). This is the only component of the shielding tensor biased by ring currents because a ring current can be induced only when a magnetic field acts at right angles to the ring plane. To extract the π electron contribution from total NICS, the localized molecular orbital dissection (LMO-NICS)[2a,11] was used. It separates the total shielding into contributions from bonds, lone pairs, and

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Table 1. Calculated Resonance Energies of Cyclic and Acyclic Structures (RE_{cyclic} and $RE_{acyclic}$, kcal/mol), ECRE (kcal/mol), $NICS(0)_{\pi zz}$ (ppm), PDI (electrons), and HOMA Values for the Studied Molecules

molecule		RE_{cyclic}	reference molecules	$RE_{acyclic}$	ECRE	$NICS(0)_{\pi zz}$	PDI	HOMA
borazine	**1**	108.17	3 $NH_2BHNHBH_2$	29.33	20.18	−7.87	0.0177	0.940
2-fluoroborazine	**2**	104.65	$NH_2BHNHBH_2$	29.33	17.28	−6.90	0.0151	0.945
			$NH_2BHNHBHF$	30.89				
			$NH_2BFNHBH_2$	27.15				
2,4-difluoroborazine	**3**	101.01	$NH_2BFNHBHF$	28.29	14.68	−6.21	0.0128	0.951
			$NH_2BHNHBHF$	30.89				
			$NH_2BFNHBH_2$	27.15				
2,4,6-trifluoroborazine	**4**	97.27	3 $NH_2BFNHBHF$	28.29	12.41	−5.77	0.0107	0.955
1-fluoroborazine	**5**	106.89	$NH_2BHNHBH_2$	29.33	20.53	−9.01	0.0181	0.945
			$NHFBHNHBH_2$	30.01				
			$NH_2BHNFBH_2$	27.01				
1,3-difluoroborazine	**6**	105.78	$NHFBHNFBH_2$	27.76	20.99	−10.14	0.0186	0.950
			$NHFBHNHBH_2$	30.01				
			$NH_2BHNFBH_2$	27.01				
1,3,5-trifluoroborazine	**7**	104.97	$NHFBHNFBH_2$	27.76	21.68	−11.21	0.0191	0.954
1,2,6-trifluoroborazine	**8**	98.82	$NH_2BHNHBHF$	30.89	14.74	−7.21	0.0129	0.941
			$NHFBFNHBH_2$[a]	27.41				
			$NH_2BFNFBHF$	25.78				
1,2,4-trifluoroborazine	**9**	100.36	$NH_2BHNFBHF$	29.48	15.08	−7.20	0.0129	0.948
			$NH_2BFNHBH_2$	27.15				
			$NHFBFNHBHF$[a]	28.65				
1,2,4,6-tetrafluoroborazine	**10**	95.24	$NH_2BFNHBHF$	28.29	12.53	−6.67	0.0108	0.945
			$NHFBFNHBHF$[a]	28.65				
			$NH_2BFNFBHF$	25.78				
1,2,3,4,6-pentafluoroborazine	**11**	93.42	$NH_2BFNFBHF$	25.78	12.79	−7.58	0.0109	0.935
			$NHFBFNHBHF$[a]	28.65				
			$NHFBFNFBHF$[a]	26.21				
1,2-difluoroborazine	**12**	103.83	$NHFBFNHBH_2$[a]	27.41	17.61	−7.99	0.0154	0.944
			$NH_2BHNHBH_2$	29.33				
			$NH_2BHNFBHF$	29.48				
1,4-difluoroborazine	**13**	103.55	$NH_2BFNHBH_2$	27.15	17.75	−7.97	0.0155	0.950
			$NHFBHNHBHF$	31.65				
			$NH_2BHNFBH_2$	27.01				
1,2,3,4-tetrafluoroborazine	**14**	98.50	$NH_2BHNFBHF$	29.48	15.40	−8.20	0.0132	0.938
			$NHFBFNHBH_2$[a]	27.41				
			$NHFBFNFBHF$[a]	26.21				
1,2,4,5-tetrafluoroborazine	**15**	98.15	$NHFBFNHBHF$[a]	28.65	15.26	−8.21	0.0132	0.945
			$NHFBHNFBHF$	30.34				
			$NH_2BFNFBH_2$	23.90				
1,2,3,4,5,6-hexafluoroborazine	**16**	91.80	3 $NHFBFNFBHF$[a]	26.21	13.18	−8.48	0.0111	0.922
1,2,3-trifluoroborazine	**17**	101.48	$NH_2BHNFBHF$	29.48	17.69	−9.05	0.0157	0.941
			$NHFBHNHBH_2$	30.01				
			$NHFBFNFBH_2$[a]	24.30				
1,2,5-trifluoroborazine	**18**	101.12	$NHFBHNHBHF$	31.65	17.81	−9.06	0.0157	0.948
			$NHFBHNFBH_2$	27.76				
			$NH_2BFNFBH_2$	23.90				
1,2,3,5-tetrafluoroborazine	**19**	100.78	$NHFBHNFBHF$	30.34	18.37	−10.10	0.0162	0.944
			$NHFBHNFBH_2$	27.76				
			$NHFBFNFBH_2$[a]	24.30				
1,2,3,4,5-pentafluoroborazine	**20**	96.41	$NHFBFNFBHF$[a]	26.21	15.55	−9.19	0.0135	0.934
			$NHFBHNFBHF$	30.34				
			$NHFBFNFBH_2$[a]	24.30				
benzene		159.52	$CH_2{=}CHCH{=}CH_2$	23.39	89.35	−35.77	0.1029	0.990

[a]Not a minimum on the PES.

core electrons and is useful to distinguish the ring π electron contributions from those arising from the fluorine lone pairs.

The PDI, proposed by Poater et al.,[7a] is based on electron delocalization. It is derived from the Bader's AIM theory[12] and is defined as an average of all delocalization indices (DIs) of para-related atoms in a given six-membered ring. This index proved useful to estimate substituent effects on aromaticity of monosubstituted benzene derivatives.[13]

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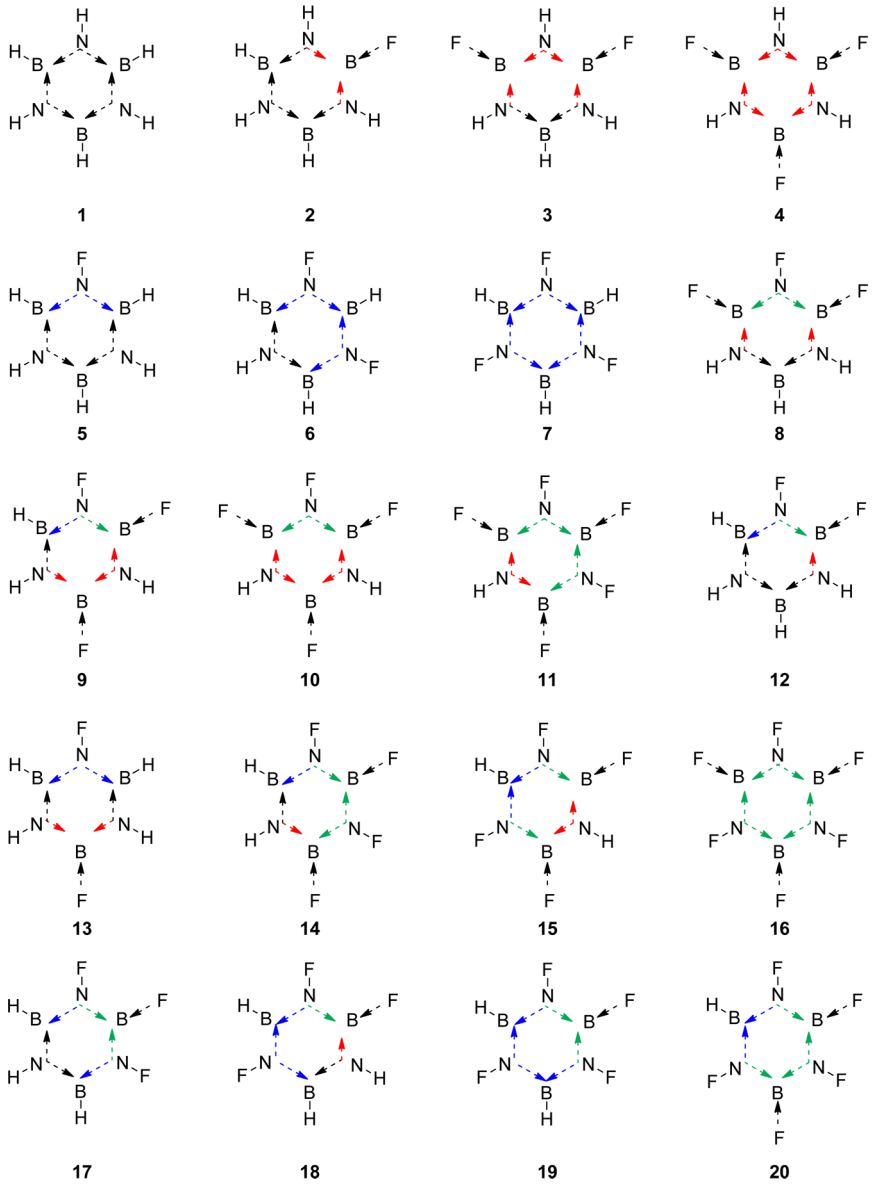

Figure 1. Structural formulas of borazine (**1**) and its fluorinated derivatives **2**−**20**. Dotted black arrows going from N to B show N to B π electron donation. Dotted green arrows indicate a slightly decreased N to B π electron donation, relative to borazine. Dotted red arrows indicate a decreased N to B π electron donation, relative to borazine. Dotted blue arrows denote an increased N to B π electron donation, relative to borazine. Dotted black arrows going from F to B show F to B electron donation due to the fluorine +R effect.

The extra cyclic resonance energy (ECRE), proposed by Mo and Schleyer,[14] is the resonance energy (RE) difference between a cyclic conjugated system and an appropriate acyclic reference, having either the same number of π electrons or the same number of π conjugations (ECRE1 and ECRE2, respectively, in ref 14). For example, the ECRE1 for benzene involved hexatriene as a reference (six π electrons but two conjugated diene moieties), and ECRE2 was based on octatetraene with three diene conjugations, as in the cyclic molecule. The authors found this second reference to be better than the first one.[14] *cis*-Butadiene was also found as a good reference to estimate ECRE as the RE difference between benzene and three butadienes, corresponding to three diene conjugations.[15] ECRE is an energetic measure associated with extra (de)stabilization arising from cyclic electron delocalization. Thus, positive ECREs denote aromatic stabilization, while negative ECREs indicate antiaromatic destabilization. RE is defined as an energy difference between a localized state and a fully delocalized system. If RE is evaluated at an optimal geometry of a delocalized molecule, it is called the vertical resonance energy (VRE). If it measures the energy difference between an optimal delocalized system and an optimal localized state, it is reffered to as the adiabatic resonance energy (ARE).[14] The ECREs for the studied compounds were estimated as a difference in the π electron vertical resonance energies (VRE_π) between a fluorinated borazine and appropriately substituted BN analogue of *cis*-butadiene, the conformation of which matches that in a cyclic molecule. For example, ECRE for hexafluoroborazine was obtained as a difference in VRE_π of the cyclic molecule minus three times the VRE_π of *cis*-$B_2N_2H_2F_4$ (see Table 1 and the Supporting Information). In this case, the number of π conjugations is the same in the cyclic compound and reference molecules. For all derivatives that do not have D_{3h} symmetry, three different reference structures

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were necessary, and their corresponding REs are separately listed in Table 1. VRE_{π} were computed by switching off the $\pi_{B=N} \rightarrow \pi^*_{B=N}$ interactions employing the NBO deletion analysis.[8]

COMPUTATIONAL DETAILS

Geometries were fully optimized at the B3LYP/6-311+G** level[16] using the Gaussian 09 program package.[17] In the case of *B*-trifluoroborazine, for which experimental data exist,[3,18] the obtained structural parameters compare well with the experimental values, d_{B-N} = 1.427 Å (exp.: electron diffraction[3]/X-ray data[18] 1.432 Å/1.418 Å), d_{B-F} = 1.347 Å (1.361 Å/1.338), τ_{BNB} = 121.7° (121°/121°), and τ_{NBN} = 118.7° (119°/119°). The $NICS(0)_{\pi zz}$ values were computed employing the GIAO method[19] at the same theory level and were partitioned into the contributions from LMOs using the natural chemical shielding-natural bond orbital (NCS-NBO) analysis.[20] The PDI data were obtained at the B3LYP/6-311+G** level[21] with the use of the AIMAll program package.[22] The same theory level was employed for the computation of REs. All cyclic structures were minima on the potential energy surface (PES), as verified by frequency calculations (no imaginary frequencies). In order to compare the REs of cyclic and acyclic molecules and to ensure $\sigma-\pi$ separation, only planar reference structures were considered, which in some cases were not energy minima (see the Supporting Information and Table 1). HOMA values are based on B3LYP/6-311+G** geometries. The B−N bond lengths used for calculations of HOMA are listed in Table S1 in the Supporting Information.

RESULTS AND DISCUSSION

At the beginning, the resonance interaction of fluorine lone pairs with the borazine π system should be discussed as it is expected to influence nitrogen to boron electron donation. It was shown earlier that π donors, including fluorine, attached at a boron atom show enhanced interaction with respect to the analogous benzene systems[23] (at the B3LYP/6-311+G** level, employed in this study, the energies of the corresponding interactions obtained from the second-order perturbation analysis of the Fock matrix in the NBO basis[8] amount to *B*-fluoroborazine 31.32 kcal/mol, fluorobenzene 17.87 kcal/mol). The larger energy found for *B*-fluoroborazine stems from the greater off-diagonal Fock matrix element $F(i,j)$ showing the overlap between mixed orbitals,[8] $F(i,j)$ = 0.111 au for *B*-fluoroborazine and $F(i,j)$ = 0.085 au for fluorobenzene. This stronger interaction was considered by Nelson and Pietro[23] to be a consequence of the polarization of the $\pi^*_{B=N}$ orbitals toward boron atoms, which enhances resonance donation from fluorine to boron. The $\pi_{B=N}$ orbitals are oppositely polarized toward nitrogen.[23] Hence, it can be expected that the fluorine ring interaction of the *N*-fluoro derivative would be decreased. Indeed, the energy value of the $n_F \rightarrow \pi^*_{B=N}$ interaction in *N*-fluoroborazine is only 2.65 kcal/mol at the above-mentioned theory level, with the corresponding $F(i,j)$ = 0.032 au.

The computed $NICS(0)_{\pi zz}$, ECREs, PDIs, and HOMA for borazine and its fluorinated derivatives are listed in Table 1. The corresponding data for benzene are also included, for comparison. The negative NICS value for borazine (**1**) (−7.87 ppm) and positive ECRE (20.18 kcal/mol) point to a certain degree of nitrogen to boron π electron donation (dotted black arrows in Figure 1), though significantly less than that in benzene (NICS: −35.77; ECRE: 89.35 kcal). A gradual decrease in both ECRE and absolute values of NICS along the series borazine, *B*-monofluoroborazine (**2**) (17.28 kcal/mol; −6.90 ppm), *B*-difluoroborazine (**3**) (14.68 kcal/mol; −6.22 ppm), and *B*-trifluoroborazine (**4**) (12.41 kcal/mol; −5.77 ppm) indicates a drop in the degree of cyclic π electron delocalization. Obviously, the very strong negative inductive effect (−I) of fluorine is overcome by its positive resonance (+R) effect due to the lone pair donation to the vacant p orbital of the boron atom. The fluorine substituent is known to have a stabilizing effect on carbocations by its +R effect.[24] The increased electron density at the boron atoms, in turn, reduces nitrogen to boron π electron donation and aromaticity (dotted red arrows in Figure 1; fluorine electron donation by the +R effect is denoted as dotted black arrows). These results concur with the conclusion of Miao et al.[4] In a similar manner, an increase in ECRE and absolute NICS values along the series borazine (20.18 kcal/mol; −7.87 ppm), *N*-monofluoroborazine (**5**) (20.53 kcal/mol; −9.03 ppm), *N*-difluoroborazine (**6**) (20.99 kcal/mol; −10.13 ppm), and *N*-trifluoroborazine (**7**) (21.68 kcal/mol; −11.21 ppm) points to an enhancement of aromaticity. This finding opposes the results of Parker and Davis[3] and Miao et al.[4] and may come as a surprise. Recalling that fluorine lone pair donation to the borazine π system is very weak and taking into account the strong fluorine electron-withdrawing ability, which increases nitrogen electronegativity and decreases its electron sharing with boron atoms, these derivatives should actually show a diminished electron delocalization. However, due to the fluorine and nitrogen lone pair repulsion, the nitrogen lone pairs are pushed toward boron atoms, thus increasing the aromaticity (blue arrows in Figure 1). This effect, along with the weak $n_F \rightarrow \pi^*_{BN}$ interaction, obviously overcomes the strong fluorine electron withdrawal. The lone pair repulsion elongates the N−F bonds, the lengths of which amount to 1.405, 1.402, and 1.400 Å for **5**, **6**, and **7**, respectively. The B−F bond lengths in **2**, **3**, and **4** are 1.353, 1.350, and 1.348 Å, shortened by the $n_F \rightarrow \pi^*_{BN}$ interaction, as evidenced by the great second-order perturbation energy of 31.32 kcal/mol, as discussed before. The C−F bond in fluorobenzene is 1.356 Å. The lone pair electron repulsion was also mentioned by Parker and Davis and was recognized as one of the factors responsible for the decreased overall stability of *N*-fluoro versus *B*-fluoro derivatives.[3] In fact, **5**, **6**, and **7** are the only fluoroborazines that are more aromatic than borazine itself. The PDI values are in good agreement with NICS and ECRE data (Table 1). While HOMA values for *N*-fluorinated borazines confirm increased aromatic character, those for *B*-fluorinated derivatives disagree with NICS, ECREs, and PDIs and show the opposite trend. Apparently, the B−N bond lengths in *B*-fluoroborazines are not a simple reflection of π electron delocalization. Here, the fluorine electron withdrawal causes the B−N bonds to become shorter, but its +R effect, which is now more pronounced than that in benzene derivatives, increases the electron density on boron atoms, resulting in diminished π electron delocalization, that is, aromaticity. Although the NICS and ECRE values show exactly the same qualitative trend for compounds **2**−**7**, their quantitative trend differs; while the ECREs indicate that *B*-fluorination decreases aromaticity more than *N*-fluorination increases it, NICS data show the opposite, that is, *N*-fluorination increases aromaticity more than *B*-fluorination decreases it. Thus, the differences in ECREs between borazine (**1**) and its monofluoro derivative **2** (2.9 kcal/mol), between *B*-

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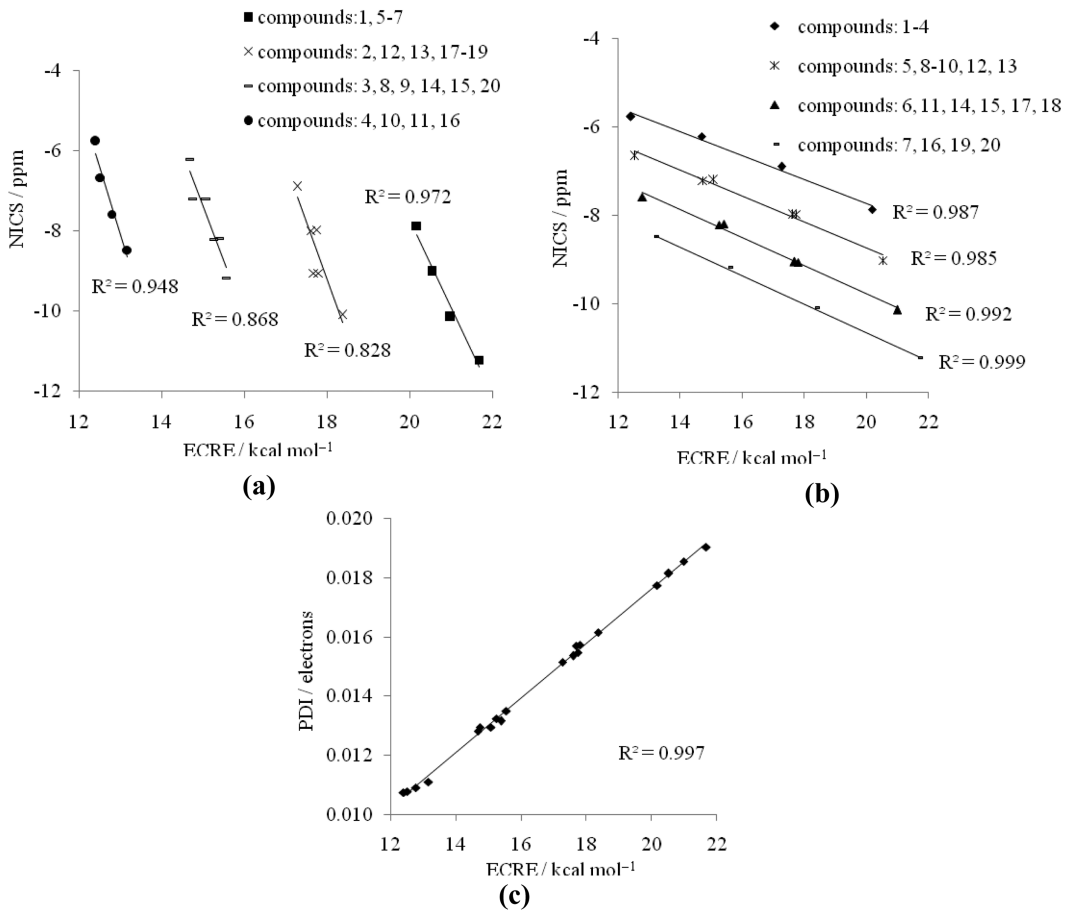

Figure 2. NICS(0)$_{\pi zz}$ versus ECRE for **1**−**20** (a), NICS(0)$_{\pi zz}$ versus ECRE for structurally similar compounds (b) and (c), PDI versus ECRE for **1**−**20** (d), and HOMA versus ECRE for **1**−**20** (e).

fluorinated borazines **2** and **3** (2.6 kcal/mol), and between **3** and **4** (2.27 kcal/mol) are larger than differences for *N*-fluorinated derivatives of 0.35 kcal/mol (**1** and **5**), 0.46 kcal/mol (**5** and **6**), and 0.69 kcal/mol (**6** and **7**). The opposite is seen for NICS values, which differ less for the series of *B*-fluoroborazines than for *N*-fluoro isomers. Thus, NICS values differ by 0.97 ppm (**1** and **2**), 0.69 ppm (**2** and **3**), and 0.44 ppm (**3** and **4**) but by 1.14 ppm for **1** and **5**, 1.13 ppm for **5** and **6**, and 1.07 ppm for **6** and **7**. Further discussion will show that ECREs are more reliable in predicting a degree of aromaticity in the studied compounds **1**−**20**; thus, the effect of *B*-F substitution appears to be stronger than that of *N*-F substitution.

All NICS, ECRE, and PDI data agree on classifying the 1,2,6-trifluoroborazine (**8**), 1,2,4-trifluoroborazine (**9**), 1,2,4,6-tetrafluoroborazine (**10**), and 1,2,3,4,6-pentafluoroborazine (**11**) as being less aromatic than borazine. The first two molecules can be viewed as *B*-difluoroborazines having an additional NF group between the two BF groups, compound **8**, or next to the one B−F group, compound **9**. If we recall that the *B*-F substitution has a stronger effect on decreasing π electron donation from nitrogen to boron than the *N*-F substitution on increasing donation, it follows that the extent of π electron delocalization within the NF−BF fragment would be lower than that within the NH−BH fragment (dotted green arrows in Figure 1). Hence, compared to borazine, cyclic π electron delocalization in **8** and **9** is weaker. The lower aromaticity of **10** and **11**, possessing three BF groups and one and two NF groups, respectively, can be rationalized in the same way.

The ECRE values for 1,2-difluoroborazine (**12**) and 1,4-difluoroborazine (**13**) indicate a drop in the cyclic π electron delocalization with respect to the unsubstituted borazine. However, the NICS data, which are just slightly more negative (Table 1), point to a comparable/slightly enhanced degree of aromatic character. Furthermore, for the rest of the molecules, having either an equal number of BF and NF groups (structures **14**−**16**) or the number of NF exceeding that of BF (structures **17**−**20**), the ECRE and NICS do not agree with each other. In these cases, it is not possible to decide whether a molecule is more or less aromatic than borazine. In fact, the NICS and ECRE data for all compounds **1**−**20** do not correlate well with each other (Figure S1a in the Supporting Information). However, this changes if structurally similar compounds are compared. Thus, NICS and ECRE values for borazine (**1**) and derivatives **5**−**7**, with increasing number of NF groups show linear correlation with R^2 = 0.972 (Figure 2a). Similarly, good linear correlations between NICS and ECREs were observed for *B*-monofluoroborazine (**2**) and its derivatives with an increasing number of NF groups, **12**, **13**, **17**−**19**, *B*-difluoroborazine (**3**) and its derivatives with an increasing number of NF groups, **8**, **9**, **14**, **15**, and **20**, and *B*-trifluoroborazine (**4**) and its derivatives with an increasing number of NF groups, **10**, **11**, and **16**, (Figure 2a). Excellent linear correlations with R^2 > 0.985 can also be obtained starting from borazine (**1**), *N*-monofluoroborazine (**5**), *N*-difluorobor-

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azine (**6**), and *N*-trifluoroborazine (**7**) and increasing the number of BF groups (Figure 2b).

Nevertheless, an examination of NICS and ECRE values only does not provide a clear picture about relative aromaticity of borazine and its fluoro derivatives **12**−**20**. By applying the same reasoning as before, it could be anticipated that the cyclic π electron delocalization in **12**−**20** would actually be diminished and disrupted relative to borazine in regions marked by dotted red and green arrows in Figure 1. Thus, it seems that ECREs give a more reliable estimation of aromatic character of the studied fluoroborazines. This is further corroborated by an excellent agreement of ECREs and the electronic index PDI, for all studied compounds (Figure 2c). It has been shown by Cyrański et al.[25] that aromaticity should be considered as a multidimensional phenomenon and that different aromaticity indices often do not correlate well with each other because they are based on different manifestations of aromaticity. On the other hand, if a good correlation between different indices is found, they can be said to be reliable in predicting this property. Hence, the same results obtained from ECREs and PDIs point to their reliability to assess aromaticity of the studied compounds. Furthermore, both indices showed good correlations with NICS values for structurally similar systems, as shown in Figure 2a and b and in Figures S1c and S1d in the Supporting Information.

However, a question arises, why does the most refined $NICS(0)_{\pi zz}$ index not describe aromaticity of all of the examined molecules correctly? NICS is a measure of the amount of magnetic shielding at a certain point (here, the center of the ring), and in the cases of structures **12**−**20**, the more negative values possibly reflect higher electron density in the ring, arising from fluorine and nitrogen lone pair repulsion, though π electrons are mostly localized to specific regions (black and blue dotted arrows, Figure 1), or are less delocalized compared to borazine (green dotted arrows). This artificial increase in the aromatic character given by the NICS data is present in all NF-substituted molecules but is more prominent when the number of NF groups equals or exceeds that of BF groups. As a result, unsatisfactory correlations of NICS with ECREs and PDIs were obtained for all **1**−**20** (Figures S1a and S1b in the Supporting Information). However, as discussed before, correlations involving structurally similar compounds are very good (Figures 2a and b and S1c and S1d in the Supporting Information).

The HOMA values did not show any correlation with ECREs and PDIs (Figures S1e and S1f in the Supporting Information). The failure of HOMA to give proper information about the extent of aromaticity in fluorinated borazines results from the dependence of B−N bond lengths also on factors other than the π electron delocalization. The main such contribution comes from the strong electron-withdrawing ability of fluorine, which, when attached at boron atoms, increases the σ bond order of the B−N bond and shortens it. Such an argument was also used by Miao et al.[4] to explain an increase in the total bond strength of *B*-trifluoroborazine relative to borazine, deduced from the topological analysis at the bond critical point. As a consequence, the majority of fluorinated borazines have HOMA values higher than borazine. In the case of monosubstituted benzenes,[13] HOMA values did not show satisfactory agreement with substituent constants, which was ascribed to the nature of substituent constants in addition to possible influences of other subtle effects, not further discussed.

The results presented in this paper oppose conclusions of Parker and Davis[3] regarding the influence of *B*-fluorination but concur with those of Miao et al.[4] As for the effect of *N*-fluorination on the aromatic character of borazine, the present study opposes both previous ones. Possible reasons for these discrepancies can be as follows. Parker and Davis[3] based their conclusions on structural changes occurring upon *B*- or *N*-fluorination of borazine and on vibrational frequency analysis. Fluorination on either nitrogen(s) or boron(s) tends to decrease the B−N bond lengths, which was observed by Parker and Davis[3] and in this work (see Table S1 in the Supporting Information). This change could point to an increased π electron delocalization. However, the influence of fluorination on bond angles depends on the fluorine position;[3] introduction of fluorine on boron atom(s) decreases the BNB angles and increases the NBN angles, thus reducing the bond angle alternation existing in borazine (values for borazine are τ_{BNB} = 122.9° and τ_{NBN} = 117.1°, and values for 2,4,6-trifluoroborazine are τ_{BNB} = 121.3° and τ_{NBN} = 118.7° at the theory level employed in this work). In contrast, *N*-fluorination increases the BNB angles and decreases the NBN angles, leading to substantial deviation from an optimal value of 120° for an sp^2-hybridized atom (values for 1,3,5-trifluoroborazine are τ_{BNB} = 128.3° and τ_{NBN} = 111.7° at the theory level employed in this work). An approach to the more ideal geometry in the case of *B*-fluorinated isomers was taken as an indicator of enhanced aromatic character in ref 3. According to the results presented in this paper, it appears that the bond angles do not affect the π electron delocalization significantly as it is mostly determined by spatial orientation of overlapping orbitals (in-plane for maximal overlap). Vibrational frequency analysis done in ref 3 agreed with conclusions drawn from geometry changes. As already pointed out by Miao et al.,[4] vibrational frequencies reflect the total bond strength and do not separate between σ and π components. However, for aromaticity studies, it is necessary to isolate only π component because aromaticity is related to the cyclic π electron delocalization. Miao et al.[4] used ASE as the major criterion of aromaticity. ASEs, however, may vary significantly because they are dependent on reference systems and equations chosen for their evaluation.[13,26] Effects that are not related to aromaticity are sometimes not canceled in equations used for assessment of ASEs. The ECREs used in this work evaluate just the energy lowering arising from the cyclic π electron delocalization, that is, aromaticity. The authors of ref 4 already found that the isotropic NICS values that they computed at ring centers, 0.5 and 1 Å above it, did not correctly describe aromaticity of fluorinated borazines. The reason for this was that isotropic values also include effects arising from electron flows perpendicular to the molecular plane.[4] However, the out-of-plane component of the magnetic shielding tensor computed 2 Å above the ring center ($NICS(2)_{zz}$), chosen as a better aromaticity criterion by Miao et al.,[4] still contains significant contribution from the σ framework, at least for borazine.[27] Thus, an extraction of just the π electron contribution to the out-of-plane component of the shielding tensor, as done for fluoroborazines **1**−**20**, would be a better aromaticity measure.[6] Although, it can also overestimate the aromatic character, as already discussed. Hence, a careful analysis of indices based on different manifestations of aromaticity is necessary. The same comment as the previous one on contributions of both σ and π electrons to the NICS values could be applied to MSE and χ_{anis},

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also considered in ref 4, for these systems that are not very delocalized.

CONCLUSIONS

A degree of cyclic π electron delocalization (aromaticity) of all possible mono- and polyfluoroborazines has been examined by means of four aromaticity indices, HOMA, ECRE, $NICS(0)_{\pi zz}$, and PDI. It was found that only ECRE and PDI can describe aromaticity of all examined structures correctly. The reason why the HOMA index failed to provide compatible information lies in the fact that the length of the B−N bonds depends not only on the extent of the π electron delocalization but on other factors too. The main such influence is the strong electron-withdrawing ability of fluorine, which decreases the B−N bond length, when it is connected to boron atoms. As a result, most of the derivatives have HOMA values higher than those of borazine. This study also shows that the $NICS(0)_{\pi zz}$ index should be taken with caution. The more negative NICS values do not necessarily mean higher aromatic character. In the case of compounds having NF group(s), NICS values also reflect an enhanced π electron density in the ring, which is a consequence of fluorine and nitrogen lone pair repulsion. However, for **8**−**20**, these electrons are still localized to specific regions, and the degree of cyclic π electron delocalization is reduced relative to that of unsubstituted borazine.

Among the examined compounds, only *N*-monofluoroborazine, *N*-difluoroborazine, and *N*-trifluoroborazine show slightly increased aromatic character with respect to borazine (overestimated by NICS). This finding contrasts the previous studies, which showed that *N*-fluorinated borazines are less aromatic than borazine. An enhanced cyclic π electron delocalization in these derivatives is mainly ascribed to the repulsion of fluorine and nitrogen lone pairs, which pushes the π electron density toward boron atoms. A minor contribution comes from the $n_F \rightarrow \pi^*_{BN}$ delocalization. These effects together overcome the strong electron-withdrawing property of fluorine. All other fluorinated derivatives show a decreased cyclic π electron delocalization compared to borazine.

As a comparison, hexafluorobenzene is equally as aromatic as benzene,[2b,28] as are other fluorinated benzenes except 1,3-difluoro and 1,3,5-trifluoro derivatives, which are less aromatic due to the ring charge alternation.[28]

ASSOCIATED CONTENT

Supporting Information

Calculated B−N bond lengths used for calculations of HOMA values, $NICS(0)_{\pi zz}$ versus ECRE and PDI for **1**−**20**, PDI versus $NICS(0)_{\pi zz}$ for structurally similar compounds, HOMA versus ECRE and PDI for **1**−**20**, absolute energies, and *x*, *y*, and *z* coordinates of the optimized structures. 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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