Can Aromaticity be Induced in Borazine? A Theoretical Investigation

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Abstract

Aromaticity is associated with some exceptional structural, energetic and magnetic properties of a compound. The molecules of borazine ($N_3B_3H_6$) and its derivatives ($R^1_3 N_3, R^2_3 B_3$; R^1, R^2= CF_3,H; H,Me; H,^tBu; Me,CF_3; ^tBu, CF_3; F,H; Me,F; F,Me), s-triazine and boroxine ($B_3H_3O_3$) have been investigated for the aromatic character, if any, by computing their optimized geometries, Natural Bond Orbital analysis, ^1H NMR chemical shifts, NICS(0), NICS(1), NICS(1)zz and magnetic susceptibility exaltation (Λ) values at the DFT (B3LYP/6-31+G(d)) level. The results indicate that substitution of the borazine ring by any of the listed substituent groups fails to induce aromaticity in the compound. Likewise, boroxine is also non-aromatic. The calculated indices of s-triazine confirm its aromatic character.

Keywords: Aromaticity, Borazine, DFT Studies, NICS Values, Magnetic Susceptibility Exaltation.

Introduction

The concept of aromaticity continues to attract the attention of the theoretical chemists and in recent times, a number of review articles and monographs have been published dealing with different aspects of this phenomenon (Garatt, 1986; Minkin *et al.,* 1994; Bergmann and Pullman, 1971; Mallion, *et al.,* 1980; Labarre and Crasnier, 1971; Lloyd, 1966; Snyder, 1969; Balaban *et al.,* 1987). Based on particular characteristics, different definitions have been proposed for the aromaticity. In 1931, the most useful criterion for determining aromaticity, that is the theory of the cyclic (4n+2) π systems was postulated by Hückel (Hückel, 1931). In 1936, Pauling postulated the ring current theory, i.e. free electron circulation around the benzene ring (Pauling, 1936). It was followed by the discovery of the diamagnetism-π electron current making contribution to the magnetic susceptibility (London, 1937). In 1956, Pople described the aromaticity in terms of ring current effects on NMR chemical shifts (Pople, 1956). In 1971, Wilson and co-workers reported modern study of diamagnetic susceptibility exaltation (Dauben *et al.,* 1971). In 1974, aromaticity was explained by Flygare and co-workers in terms of magnetic susceptibility anisotropy (Schmalz *et al.,* 1974). In 1980, Kutzelnigg reported IGLO quantum chemical calculations of magnetic properties: chemical shifts and magnetic susceptibility anisotropy (Kutzelnigg, 1980). Schleyer and co-worker (Schleyer and Jiao, 1996) emphasized that on placing an aromatic compound in an external magnetic field, diatropic current is induced

and the NMR chemical shifts experience deshielding effect at the periphery but shielding effect at the centre and diamagnetic susceptibility exaltation is induced.

From time to time, different indicators have been proposed for identifying aromatic character in a particular compound.

Chemical Behaviour – Electrophilic Aromatic Substitution

Although benzene favours electrophilic substitution over addition, many benzenoid hydrocarbons undergo addition reactions rather than substitution. Clearly, the chemical reactivity criterion is not generally applicable to many kinds of systems to which the term "aromaticity" has been applied.

Structural (Geometric) Criterion- Bond Length Equalization

Bond length equalization due to cyclic delocalization is the geometric criterion of aromaticity. The direct determination of bond lengths provides valuable information on the extent of electron delocalization in the molecules.

Singlet states of the antiaromatic compounds are localized and generally have alternating single and double bonds.

Borazine, a non-aromatic compound, is isoelectronic with benzene with six π electrons and has equalized bond lengths. Thus bond length equalization, in the absence of other considerations, cannot be used to characterize aromaticity uniquely.

Magnetic Criteria

A number of proposed criteria for identifying aromaticity are based on the diatropic current induced on placing the aromatic compound in an external magnetic field.

1. ¹H NMR Chemical Shifts

The diatropic current induced on placing the aromatic compound in an external magnetic field causes deshielding effect at the periphery, but a shielding effect at the centre. As a result of this, the peripheral protons in the ¹H NMR spectrum of the aromatic compound shift to the downfield region, whereas protons in the cavity experience upfield shift. For example, the NMR chemical shifts of the outer and inner protons of the aromatic [18]annulene are δ 9.28 and δ -2.99 respectively (Jackman *et al.,* 1962). On the other hand, these values for the antiaromatic [18]annulene dianion are δ -1.13 and δ 28.1 ppm respectively due to a paratropic current (Oth *et al.,* 1973).

Nevertheless, this criterion is not general, since some aromatics like C60 and the oxocarbons do not have hydrogens and ¹³C chemical shifts in the aromatic hydrocarbons are not deshielded. Acidic protons are deshielded. Hence, abnormal chemical shifts may not be taken as the sole criterion of aromaticity.

2. Large Magnetic Anisotropy

The exaltation ($\Delta\chi zz$) of the out of plane magnetic susceptibly anisotropy component, which is the difference between the measured out-of-plane component (χzz) and the increment value, has been proposed as another criterion of aromaticity. However, cyclopentadiene and fulvene have quite small magnetic susceptibility exaltations (-2.4 and -3.3) and are considered to be non-aromatic compounds, but have rather large $\Delta\chi zz$ values of -18.7 and -11.2.

The magnetic susceptibility exaltation (Λ), the difference between the CSGT (continuous set of gauge transformation) computed bulk magnetic susceptibility (χM) of a ring and the hypothetical value ($\chi M'$) obtained by summing the magnetic susceptibilities of the fragments devoid of cyclic electron delocalization, i.e. $\Lambda = \chi M - \chi M'$, is another important criterion of aromaticity. The exaltations (Λ) of the aromatic compounds are negative (diamagnetic), whereas for the antiaromatic systems, they are positive (paramagnetic) (Schleyer *et al.,* 1995). However, magnetic susceptibility exaltations depend on the ring area; it must be appreciated in comparing systems of different rings.

In 1996-97, Schleyer and co-workers proposed Nucleus Independent Chemical shift (NICS) as the criterion of aromaticity (Schleyer *et al.,* 1996; Schleyer *et al.,* 1997).

Thus for identifying aromaticity or antiaromaticity, one criterion cannot be used in isolation; instead, a combination of geometric, energetic and magnetic criteria leads to a more reliable conclusion.

As mentioned earlier, borazine (**2**) is popularly called "Inorganic Benzene". However, unlike benzene, the cyclic delocalization of 6 π-electrons in the borazine ring is reduced due to the large electronegativity difference between boron and nitrogen. Even though, like benzene, borazine has equal B-N bond lengths, the polarity of the B-N bond causes borazine to show reactivity pattern different from that of benzene (Huheey *et al.,* 1993).

Benzene

1

Borazine

2
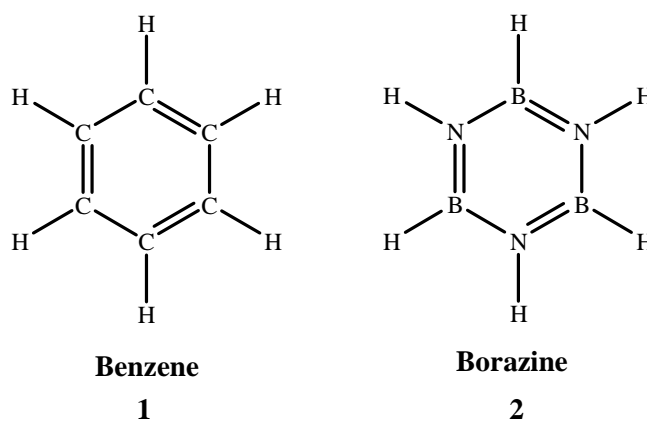
Jemmis and co-worker estimated aromaticity of borazine and other hetero-analogues on the basis of three criteria, namely structural, geometric and magnetic and concluded that the three criteria do not go parallel. While aromatic stabilization energy (ASE) calculations indicated borazine to be aromatic, magnetic susceptibility exaltation and NICS value at the B3LYP/6-31G* level ruled it out (Jemmis and Kiran, 1998). Boyd *et al.,* investigated the structures of benzene, *s*-triazine, borazine and boroxine theoretically and on the basis of Laplacian of the charge density and Mulliken population analysis found that the delocalization of the π electrons decreases and the polarity of the ring bonds increases substantially as the atoms in the ring become more dissimilar. Thus the four compounds show quite different properties in spite of being isoelectronic (Boyd *et al.,*1984). On carrying out the X-ray crystal structure studies of borazine, Maulitz and co-workers found that in contrast to benzene, an unambiguous assignment of symmetry for borazine was not possible. Moreover, the crystal packing of the latter was not comparable to any known phase of benzene and the molecules were not stacked with coplanar rings; instead, they were present in tilted layers (Boese *et al.,* 1994). On mapping the π and total current densities

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induced by a magnetic field in the molecules of benzene, borazine, boroxine, *s*-triazine, the cyclopentadienyl anion and tropylium cation by using a distributed-origin coupled Hartree-Fock method, it was found that in contrast to benzene, *s*-triazine, cyclopentadienyl anion and tropylium cation, which have delocalized π ring currents, the π currents are localized on the nitrogen atoms in borazine and on the oxygen atoms in boroxine (Fowler and Steiner, 1997). On the basis of magnetic properties, namely NICS and magnetic susceptibility exaltation values, Schleyer and co-workers concluded that borazine is not aromatic (Schleyer *et al.*,1997).

The character of the NH···X⁻ (X = H, F, Cl, CN, NC or NCO) interactions of borazine with anions was studied at the B3LYP/6-311++G(d,p) level. The NICS values indicated these compounds to be non-aromatic (Ghiasi, 2009).

Above studies indicate that borazine is not aromatic. The objective of the present studies was to investigate theoretically whether aromaticity could be induced, even partially, by introducing different substituent groups at the nitrogen and boron atoms of the borazine ring. For testing aromaticity in the substituted borazines, we followed two criteria, namely structural (determination of the optimized geometries) and the magnetic, i.e. effects on placing the molecules in the external magnetic field (determination of ¹H NMR chemical shifts, NICS values and magnetic susceptibility exaltations). For the sake of comparison, we computed the structures of two other isoelectronic molecules, namely *s*-triazine (**11**) and boroxine (**12**) also. The results are presented here.

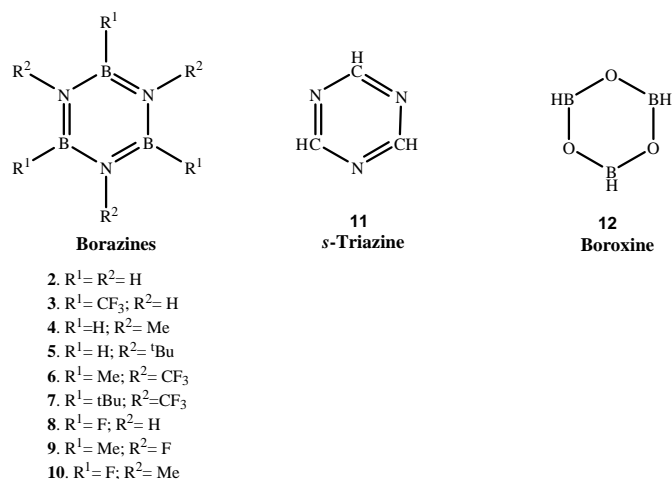## Materials and Methods

Computational Methods

All calculations were carried out using Gaussian 03 suite of programs (Frisch *et al.,* 2003). The geometry optimizations were done in the gas phase at the B3LYP/6-31+G(d) level of theory. Frequency calculations were done at the same level to determine zero-point energies and check the global minimum nature of the species. Natural bond orbital (NBO) calculations were done at the same level to study the occupancy of the natural bond orbitals and determine Wiberg bond indices (WBI) to know the bond order (Reed and Weinhold, 1985).

¹H NMR chemical shifts values were calculated at the GIAO-B3LYP/6-311++G** // B3LYP/6-31+G* level (Ditcheld, 1974). Nucleus Independent Chemical Shift (NICS) values were calculated at the [3,+1] ring critical points (RCP) of the electron density topology as defined by Bader (Bader, 1990) and determined using AIMPAC at the GIAO-B3LYP/6-311++G** // B3LYP/6-31+G* level (AIMPAC Program).

Magnetic susceptibilities were determined at the csgt-B3LYP/6-31+G*//B3LYP/6-31+G* level and exaltation values were calculated by subtracting the sum of the magnetic susceptibilities of the fragments determined at the same level from the values of the respective species.

Results

We computed the following molecules at the B3LYP/6-31+G(d) level (Scheme 1):

Borazines

11
s-Triazine

12
Boroxine

2. R¹= R²= H
3. R¹= CF₃; R²= H
4. R¹=H; R²= Me
5. R¹= H; R²= ᵗBu
6. R¹= Me; R²= CF₃
7. R¹= tBu; R²=CF₃
8. R¹= F; R²= H
9. R¹= Me; R²= F
10. R¹= F; R²= Me

Scheme 1. The molecules investigated at the B3LYP/6-31+G(d) level

Optimized Geometries

Geometries of different molecules optimized at the B3LP/6-31+G* level are shown in Fig. 1.
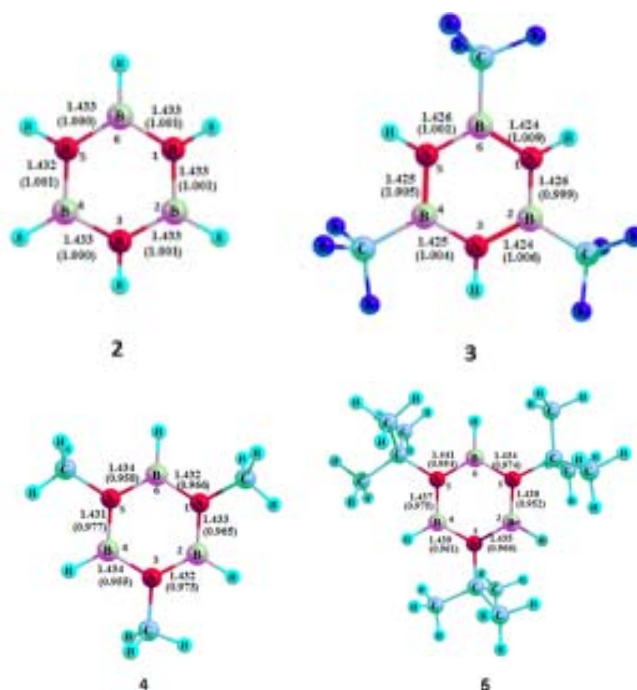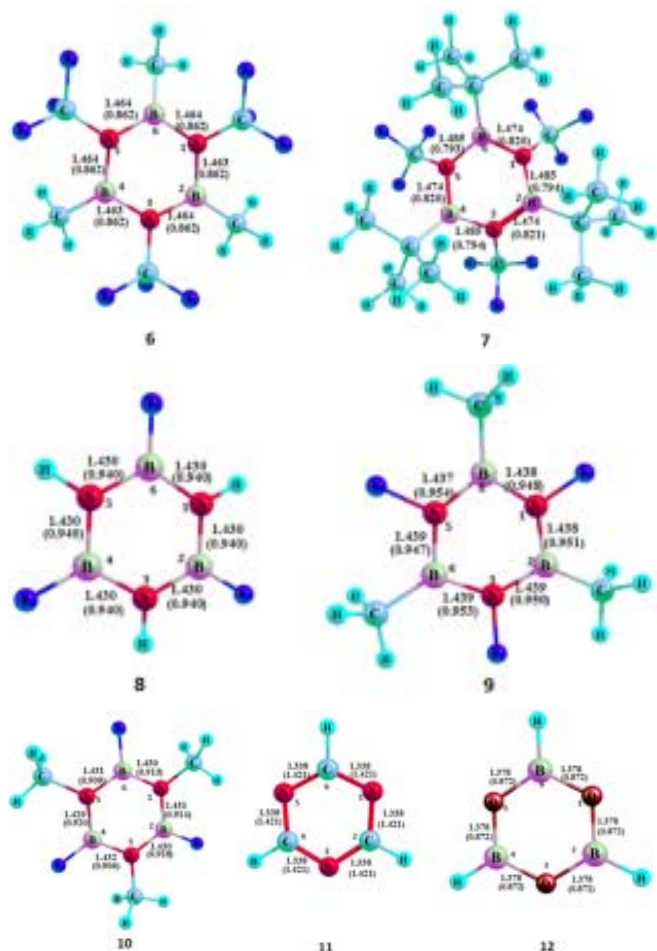
Fig. 1. Optimized Geometries of Compounds 2-12 calculated at the B3LYP/6-31+G(d) Level

Frontier Molecular Orbitals (FMO)

The FMOs of borazine calculated at the B3LYP/6-31+G(d) level are shown in Fig. 2.
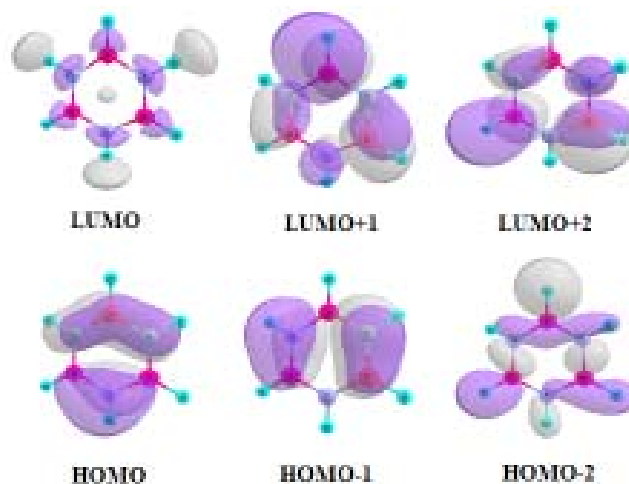

Fig. 2. FMOs of Borazine Calculated at the B3LYP/6-31+G(d) Level

Natural Bond Orbital Analysis

Natural localized molecular orbital (NLMO) occupancies in different molecules are given in Table 1.

Table 1. NLMO Occupancies in Different Borazine Derivatives and Related Molecules

Comp. No.	N1-B2	B2-N3	N3-B4	B4-N5	N5-B6	B6-N1	N1-B6	N3-B2	N5-B4
2	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.83*	*1.83*	*1.83*
3	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.81*	*1.81*	*1.81*
4	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.80*	*1.80*	*1.80*
5	*1.97*	*1.97*	*1.97*	*1.97*	*1.97*	*1.97*	*1.80*	*1.81*	*1.80*
6	*1.96*	*1.96*	*1.96*	*1.96*	*1.98*	*1.96*	*1.80*	*1.79*	-
7	*1.95*	*1.96*	*1.95*	*1.96*	*1.95*	*1.96*	*1.81*	*1.81*	*1.81*
8	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.98*	*1.85*	*1.85*	*1.85*
9	*1.97*	*1.97*	*1.97*	*1.97*	*1.97*	*1.97*	*1.84*	*1.83*	*1.83*
10	*1.97*	*1.97*	*1.97*	*1.97*	*1.97*	*1.97*	*1.82*	*1.82*	*1.82*
11	*1.99* **N1-C2**	*1.99* **C2-N3**	*1.99* **N3-C4**	*1.99* **C4-N5**	*1.99* **N5-C6**	*1.99* **C6-N1**	*1.68* **N1-C2**	*1.68* **N3-C4**	*1.68* **N5-C6**
12	*1.99* **O1-B2**	*1.99* **B2-O3**	*1.99* **O3-B4**	*1.99* **B4-O5**	*1.99* **O5-B6**	*1.99* **B6-O1**	*1.87* **O1-B6**	*1.87* **O3-B2**	*1.87* **O5-B4**

NBO Second Order Perturbation

Major NBO second order perturbation interactions in different molecules are given in Table 2.

Table 2. NBO Second Order Perturbations in Different Molecules

Compound No.	N1-B6→ - *B2-N3	B2-N3→ *B4-N5	B4-N5→ *N1-B6
2	36.47	36.44	36.45
3	38.29	37.76	37.89
4	35.67	35.92	36.01
5	35.18	35.13	34.70
6	28.80	35.79	35.77
7	23.72	23.69	23.48
8	36.63	36.63	36.64
9	34.45	34.51	34.60
10	37.64	37.12	37.46
11	37.98	37.98	37.98
12	34.54	34.53	34.54

Magnetic criteria

^{1}H NMR Chemical Shifts

The NMR chemical shifts of the protons bonded directly to the ring in different borazine derivatives (**2-10**), *s*-triazine (**11**) and boroxine (**12**) are given in Table 3.

Table 3. ^{1}H NMR Chemical Shifts Calculated at the GIAO-B3LYP/6-311++G// B3LYP/6-31+G* Level**

Comp. No.	H1	H2	H3	H4	H5	H6
2	5.44	4.93	5.47	4.96	5.43	4.97
3	6.01	-	6.19	-	5.81	-
4	-	5.24	-	4.89	-	5.02
5	-	5.41	-	5.80	-	5.21
6	-	-	-	-	-	-
7	-	-	-	-	-	-
8	3.64	-	3.65	-	3.63	-
9	-	-	-	-	-	-
10	-	-	-	-	-	-
11	-	9.33	-	9.32	-	9.32
12	-	4.78	-	4.79	-	4.79

NICS values and magnetic susceptibility exaltation

NICS(0), NICS(1) and NICS(1)zz values determined at the (+3,1) centre of the ring, 1 Å above it and the zz tensor of the latter respectively are given in Table 4.

Table 4. NICS(0), NICS(1) and NICS(1)zz and Magnetic Susceptibility Exaltation (Ë) Values of Different Borazine Derivatives and Related Compounds

Compound no.	NICS (0)	NICS (1)	NICS (1)zz	Magnetic susceptibility exaltation ( )
2	-1.56	-2.64	-5.14	-7.15
3	-3.23	-3.39	-5.04	-10.35
4	-3.27	-3.68	-5.83	-5.94
5	-2.81	-3.69	-3.87	-3.96
6	-1.86	-2.96	-1.30	-3.37
7	0.15	1.04	9.69	5.15
8	-4.58	-2.38	-1.92	-4.33
9	-10.63	-5.26	-3.67	-4.58
10	-5.05	-3.12	-1.52	-4.54
11	-4.08	-9.64	-25.43	-17.18
12	-0.42	-1.78	-1.05	-10.87

Discussion

Geometries

It may be noted that except 1,3,5-tri-*t*-butylborazine (**5**) and 1,3,5-tris(trifluoromethyl)-2,4,6-tri-*t*-butylborazine (**7**), all molecules are planar with equalized or nearly equalized bond lengths. The rings of **5** and **7** lose planarity due to steric-hindrance and the bond lengths are no more equal. The presence of the three electron-withdrawing trifluoromethyl groups on the boron atoms in borazine ring (**3**) results in decreasing the B-N bond distances (Δ = -0.009Å) with a corresponding increase in the Wiberg Bond Index (WBI) (Δ = 0.0085). In contrast to **3**, B-N bonds are elongated in **6** (Δ = 0.031Å) having methyl groups on three boron atoms and trifluoromethyl groups on the three nitrogen atoms with a corresponding decrease in WBI (Δ = -0.1388). Nevertheless, in these molecules, the bond distances are nearly equalized. However, the B-N bond lengths remain unaffected by the presence of the three methyl groups on the nitrogen atoms (**4**) of the ring. These results indicate that nature of the substituent groups in the borazine ring influences electron distribution, though marginally.

In *s*-triazine (**11**) and boroxine (**12**), the bond distances are equal.

NBO Analysis

It is obvious that there are strong interactions between the π-orbitals of the ring which remains almost unaffected by the substituent groups. However in compound **7**, second order perturbation interactions between π-orbitals is weakened due to non-planarity.

^{1}H NMR Chemical Shifts

It may be noted that the chemical shifts of the protons bonded directly to the ring atoms in the compounds **2-5,8,12** do not fall in the aromatic region indicating the absence of the diatropic current in the compounds **2-10** and **12**. The chemical shits of the protons of *s*-triazine (**11**), however, fall typically in the aromatic region. Thus on the basis of the ^{1}H NMR chemical shifts, it may be concluded that the compounds **2-5,8,12** are non-aromatic whereas compound **11** is aromatic.

NICS values and magnetic susceptibility exaltation

Schleyer *et al.,* (Schleyer *et al.,* 1996) developed a simple and effective criterion for determining aromaticity of different molecules and transition structures based on the diatropic current induced on placing the system in an external magnetic field. The computed constant, named as the nucleus independent chemical shift (NICS) is the negative of the computed magnetic shielding at the ring centre. A high negative NICS indicates aromaticity of the system, whereas a low negative or a positive NICS reveals non-aromatic or anti-aromatic character respectively. Subsequently, it was suggested that to avoid σ -paratropic influence, NICS value determined above the plane of the molecule is more appropriate for evaluating aromaticity (Schleyer *et al.,* 1997). It was followed by developing various types of Dissected NICS techniques (Chen *et al.,* 2005). It has been found that NICSzz tensor components characterize the π system much better than isotropic NICS parameters, because they are related directly to the induced current density (Steiner *et al.,* 2001). Thus, the best characterization of aromaticity in [n]annulenes was achieved with zz tensor of the NICS π tensor (Corminboeuf *et al.,* 2004). All three types of NICS values of the borazine derivatives (**2-6, 8-10**) and boroxine (**12**) reveal their non-aromatic character. In the case of (**7**), the values are rather unexpected which may be attributed to its non-planar structure. Its NICS[1]zz value falls in the range of anti-aromatic compound, but on the basis of this parameter only, it cannot be construed as the anti-aromatic system.

The NICS(1) and NICS(1)zz values of *s*-triazine (**11**) are in accordance with its aromatic character.

It is reported that magnetic susceptibility exaltation values of all aromatic species are negative (diatropic), whereas those of the antiaromatic systems are positive. The magnetic susceptibility exaltation values calculated for all the compounds are given in Table 4. It may be noted that the values for the compounds **2-6,8-10** and **12** fall in the range -4 to -11 which also support the non-aromatic character irrespective of the nature of the substituent group. The magnetic susceptibility exaltation value of 5

for the compound **7** indicates anti-aromatic character. A value of -18 for the compound **11**is in conformity with its aromatic character.

Conclusions

Structural and magnetic criteria, namely ^{1}H NMR chemical shifts, NICS and magnetic susceptibility exaltation values of borazine and its derivatives reveal that they all are non-aromatic and aromaticity cannot be induced by substitution. In the presence of the bulky substituent groups, the borazine ring acquires non-planarity. The structural and magnetic criteria confirm the aromatic and non-aromatic nature of *s*-triazine and boroxine respectively.

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