In silico studies toward the recognition of fluoride ion by substituted borazines

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ABSTRACT

The substituted borazines have been computationally investigated as new type of receptors for the recognition of fluoride ion. Fluorine, methyl and phenyl groups have been selected as electron-withdrawing, electron-releasing and aromatic substituents for the study employing DFT (B3LYP/6-311 + G**) and ab initio (MP2/6-311 + G**) levels of calculations. N-substituted borazines have shown higher fluoride ion affinity than their corresponding B-substituted borazines. In the case of fluorinated borazines, the binding affinity of fluoride is enhanced with the increasing number of substitutions. The F$^-$ and Cl$^-$ ions, generally, prefer to bind with the boron atom of substituted borazine rings, whereas, Br$^-$ ion prefers to bind with NH hydrogens of the borazine receptor units. Phenyl derivatives of borazine also showed analogous behavior with halide anions. The binding affinities of halides with fluorinated and phenyl derivatives of borazine have been found to be much higher than the simple borazine receptor molecule. The NBO analyses performed for the complexation of F$^-$ ion with fluorinated borazines suggest that the Lewis energy contribution in the total SCF energy enhanced with increasing the substitutions. However, in the case of methylated borazines, the delocalization energy is responsible for the stabilization of F$^-$ ion complexes. The N-trifluoroborazine showed much higher fluoride ion affinity (30.9 kcal/mol) in aqueous phase than the simple borazine.

1. Introduction

Fluoride is the smallest anion and due to its tremendous hardness, often displays differing properties to the rest of the halides [1]. This anion is often added to drinking water and toothpaste because of its beneficial effects in dental health. It is also useful in the treatment of osteoporosis [2]. The balance of fluoride in dental health is necessary in forming and preserving the tooth enamel, but too higher concentration of F$^-$ ion can be a source of dental caries. The over-exposure of fluoride is termed as Fluorosis, which can cause kidney failure and severe skeletal defects [3]. Taking into account these adverse effects, researchers are interested to design receptors to detect fluoride ion, especially in water. This field of research has also been stimulated by the potential use of such receptors for the detection of organophosphorus nerve agents such as Sarin. This nerve agent is known to release fluoride ion upon hydrolysis.

The high hydration enthalpy of fluoride ion ($\Delta H = -504$ kJ/mol) is one of the factors providing challenges in the recognition of this anion in aqueous medium [4,5]. To overcome this difficulty, several groups are currently involved in making receptors in which the fluoride binding site is a Lewis acidic element such as boron, aluminum or tin [1,6–12]. Further, boron containing compounds act as good Lewis acid acceptors for fluoride ion as it forms very strong Lewis acid base pairs and induce the changes in structural and physical properties. The tri-substituted boron atom is sp^2 trigonal planar in nature with an empty p orbital perpendicular to the plane of the molecule. This feature dominates the receptor chemistry of boron compounds. Anions are able to interact with or donate into this vacant site, causing a subsequent change in the geometry from planar to tetrahedral as well as change in the hybridization from sp^2 to sp^3. The tetrahedral nature of the phenyl-boronate anion was confirmed by Lorand and Edwards in 1959 [13]. Such changes are reflected in their electronic, fluorescence or chemical shifts in the NMR spectra [14–16]. The complexations of fluoride ion with triarylboranes are also reported [10,17–23]. Fluoride binding capability of PhBMes$_2$ has been reported by spectroscopic and crystallographic methods [24]. Further, it has been observed that gas phase reaction of Ph$_3$B with fluoride ion is exothermic by 342.0 kJ/mol [25]. However, similar calculation for PhBMes$_2$ shows that fluoride ion binding is exothermic by 268.7 kJ/mol, which is considerably lower than Ph$_3$B [26]. These observations indicate the influence of the bulkiness of the substituents toward fluoride ion binding [8]. Further, Lewis acid based bidentate fluoride receptors with B/B and B/Hg as binding sites are also known [27–31]. The fluoride binding constants of bidentate boranes increases 3–4 times than the corresponding monofunctional analogs [9]. Cationic boranes are also reported as a boron based receptors for anion recognition [32,33]. It has been observed that the anion affinity of cationic boranes increases due to favorable Coulombic effects.

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Recently, we have predicted computationally that the simple borazine can act as fluoride ion sensor and confirmed by NMR studies [34]. The interaction of cations with π electrons of borazine has also been reported [35]. In present article, we have examined the effect of substituents on borazine as receptor for their ability to bind the halide anions. Synthesis of many substituted borazines with halogens, alkyl and phenyl groups as a substituents are reported [36,37]. Nöth and co-workers have discussed about the syntheses and structures of trihaloborazines [37]. It has been mentioned that the fluoro-derivative of 2,4,6-trihaloborazine is thermally more stable than its corresponding chloro- and bromo-derivatives [37]. Further, the thermally very stable triphenylborazines are also well known [37]. Therefore, we have performed a study with representative examples of substituted borazine systems to examine the recognition of fluoride ion. We have considered the fluorine substituents to examine the influence of electron-withdrawing groups toward the affinity of fluoride ion in particular and the methyl groups to examine the effect of electron releasing substituents on the binding of anions with borazine receptors. Phenyl rings were also substituted to the borazine unit to investigate the effect of aromatic rings on the receptor unit, which can be considered as a model for the experimental studies with fluorophores and chromophores for the colorimetric/spectroscopic detections of anion binding with such receptor units [38]. The recognitions of chloride and bromide ions with substituted borazines have also been performed for comparative purposes.

2. Computational methodology

All borazine derivatives and its anion complexes were fully optimized with density functional theory (DFT) using Becke3 Lee Yang Parr functional and 6-311 + G** basis set [39–41]. It has been shown that B3LYP method is consistent with experimental values for structural properties and vibrational frequencies of borazine and its fluoro-derivatives [42]. The minima of all the geometries were confirmed by the frequency analysis. Single point calculations were done at the MP2/6-311 + G** level using B3LYP optimized geometries [43]. All MP2 calculations were performed with the frozen-core (FC) approximation. Further, to see the influence of solvent medium, energy calculations were performed in aqueous phase at MP2/6-311 + G**//B3LYP/6-311 + G** level with default Polarizable Continuum Solvation Model (IEF-PCM) [44–48]. The default UFF radii were used for the solvent calculations, which incorporate explicit hydrogen atoms [46]. Natural Bond Orbital (NBO) analyses were carried out with MP2/6-311 + G** method [49]. However, the decomposition of the SCF energy in to the Lewis energy and delocalization energy, using NBO deletion analysis was performed with B3LYP/6-311 + G** level of theory. Gaussian 09 program is not equipped to perform the NBO deletion analysis with MP2 method. The electron densities computed with B3LYP and MP2 are likely to be similar for the systems studied here and no noticeable difference is anticipated [50]. The interaction energy is simply obtained by the energy of the complex subtracted from the sum of the energy of constituents. The anion binding energies are generally higher and the effect of basis set superposition error (BSSE) is relatively small and hence, our calculated interaction energies do not include BSSE corrections [51]. The relative binding energies obtained from the respective receptor units and anions provide valuable insights toward the ability to form stable complexes for such receptors. All calculations were performed with Gaussian 09 program [52].

3. Results and discussions

To examine the influence of substitution on borazine toward the recognition of halide anions, computational studies have been

X = F, Me, Ph
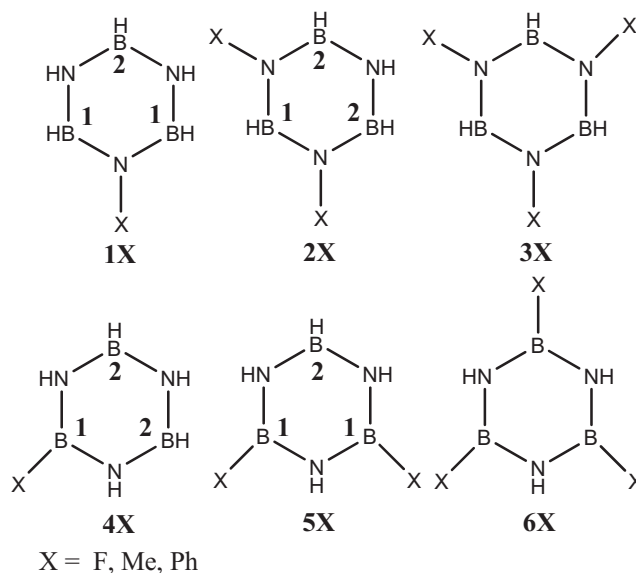
Scheme 1.

performed using various substituted borazines as shown in Scheme 1.

We have considered both B-substituted and N-substituted borazines for the study. Further, mono-, di- and tri-substituted borazines have also been investigated. The studied substituted borazines were tested for the recognition of halide ions (F⁻, Cl⁻ and Br⁻) computationally. Mono- and di-substituted borazines have offered two different boron atoms for interaction with anions (Scheme 1). The other possibility of anion interaction with NH hydrogen atoms has also been examined. We have noticed that the interaction of anions with BH hydrogens is much weaker and hence not considered in the present study [34].

3.1. Fluorine derivatives of borazine

The B-fluorinated borazines are more stable than the corresponding N-fluorinated borazines in agreement with the earlier reports [42]. The B3LYP and MP2 calculated binding energies in the gas phase show that the fluorine substituted borazines bind the F⁻ and Cl⁻ ions more strongly with boron atoms than the NH hydrogens of the same molecule (Figs. S1 and S2 of the supplementary data and Fig. 1).

In the case of N-fluoroborazine (**1F**) both B3LYP and MP2 calculated results suggest that the binding affinity of F⁻ ion toward boron atom adjacent to the N-F group (**1F-F-1**) is ∼2.0 kcal/mol higher than the boron atom opposite to the N-F group (**1F-F-2**). Further, in the case of N-difluoroborazine (**2F**) the F⁻ ion shows more binding affinity for the boron atom located in between the N-F groups (**2F-F-1**) than the other boron atoms of the same molecule (**2F-F-2**) (Fig. 1). The strength of the binding of F⁻ ion with borazine was obtained by evaluating the total charge transfer (CT) from anions to the substituted borazine (q_{CT}), derived from natural population analysis (NPA) at MP2/6-311 + G** level (Table 1). The calculated q_{CT} values suggest more charge transfer in the case of **1F-F-1** and **2F-F-1** compared to **1F-F-2** and **2F-F-2**, respectively, which is in accord to the calculated binding affinities (Table 1).

Further, with increasing the number of fluorine substitutions on nitrogen, enhancement in F⁻ ion affinity is observed. To analyze the origin of such interactions, NBO (Natural Bond Orbital) analysis has been performed for the fluorine derivatives of borazine bound with the F⁻ ion [49]. According to the NBO method, the total SCF energy, E_{tot} can be decomposed into two terms; the Lewis
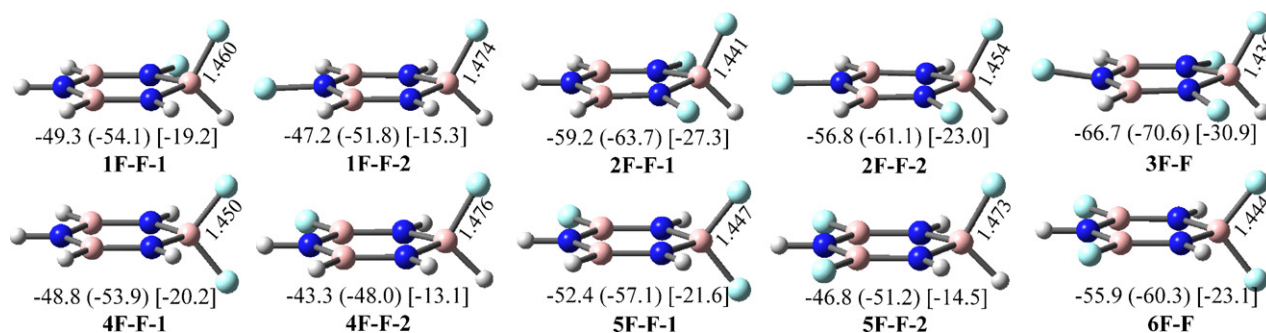
Fig. 1. B3LYP/6-311 + G** optimized geometries, calculated binding energies (kcal/mol) and important bond distances (Å) of F⁻ ion complex of fluorinated borazines calculated in the gas phase. MP2/6-311 + G** calculated energies in the gas and aqueous phases are given in parentheses and square brackets, respectively [blue = nitrogen; pink = boron; cyan = fluorine; white = hydrogen].

energy and the delocalization energy. Lewis energy, E_{Lew}, is associated with the localized B3LYP wave function and is obtained by zeroing all the orbital interactions that is deleting the off-diagonal elements of the Fock matrix. The delocalization energy, E_{del}, corresponding to all the possible interactions between orbitals is calculated as $E_{del} = E_{tot} - E_{Lew}$. E_{Lew} includes all energy contributions apart from delocalization effects. These are, in particular, steric and electrostatic effects which cannot be separated within the NBO method. We have analyzed the binding energy of N-fluorinated borazine with F⁻ ion in terms of Lewis binding energy (ΔE_{Lew}) and delocalization binding energy (ΔE_{del}) (Table 2). The binding energy of F⁻ to N-fluoroborazine (**1F-F-1**) seems to be destabilized by 1.5 kcal/mol in terms of Lewis binding energy, whereas, stabilized by 50.8 kcal/mol via delocalization process. However, (**2F-F-1**) and (**3F-F**) were stabilized by 6.4 kcal/mol and 21.0 kcal/mol, respectively, in Lewis term. These results suggest that the contributions of steric and electrostatic effect are more toward the enhancement in the F⁻ ion affinity with increasing the number of fluorine substitutions on nitrogen atoms (Table 2). The B—F bond lengths also correlate well with the binding affinity of

nitrogen substituted borazines. On moving from N-fluoroborazine to N-trifluoroborazine, the B—F bond length decreases with the enhancement in the binding energies (Fig. 1).

In the case of boron substituted borazine—MP2/6-311 + G** calculated results show that the F⁻ ion has greater binding affinity toward B—F boron atom compared to the B—H boron of the same molecule (Fig. 1). The more electropositive nature of B—F boron atom than the B—H boron atom appears to be one of the factors for higher F⁻ ion affinity in the former case (Fig. 2). Further, NBO analyses suggest that complexes with F⁻ ion at B—F boron are highly stabilized by Lewis energy compared to the B—H boron atom (Table 2). The newly formed B—F bond lengths also correlate well with this observation (Fig. 1). Further, as observed in N-fluorinated borazines, F⁻ ion affinity increases with increasing the number of fluorine substitutions on boron atom (Fig. 1). The calculated Lewis binding energy (ΔE_{Lew}) and delocalization binding energy ΔE_{del} of these systems suggest that steric and electrostatic effects are chiefly responsible for the increase in the F⁻ ion affinity on moving from B-fluoroborazine to B-trifluoroborazine.

N-fluorinated borazines show higher F⁻ ion affinity compared to the corresponding B-fluorinated borazines at both levels of theory. This observation can be rationalized on the basis of aromaticity of fluorinated borazines. Parker and Davis have reported that B-fluorinated borazines are more aromatic in nature compared to the N-fluorinated borazines [42]. Further, Miao et al. have shown that computed aromatic stabilization energy (ASE) for B-fluorinated borazines are higher than N-fluorinated borazines, which also support the greater aromaticity in B-fluorinated borazine [53]. The lower binding energy of F⁻ ion with B-fluorinated borazines seems to arise due to the higher aromaticity compared to the corresponding less aromatic N-fluorinated borazines [42].

The calculated chloride ion affinities of fluorinated borazines follow the similar trend as observed with F⁻ ion (Fig. S2 of the supplementary data). Bromide ion generally prefers to bind with NH hydrogens of fluorinated borazines with much lower binding affinity. However, in N-trifluoroborazine, due to unavailability of NH

Table 1
MP2/6-311 + G** calculated total charge transfer (q_{CT}) (kcal/mol) from the F⁻ ion to fluorine and methyl substituted borazine rings.

	X = F	X = Me
1X-F-1	47.16	42.07
1X-F-2	43.30	41.59
2X-F-1	51.66	44.26
2X-F-2	48.35	41.9
3X-F	52.60	43.63
4X-F-1	51.90	45.36
4X-F-2	42.70	41.76
5X-F-1	52.35	45.08
5X-F-2	44.47	41.57
6X-F	54.12	44.83

Table 2
B3LYP/6-311 + G** calculated total binding energy (ΔE_{tot}), Lewis binding energy (ΔE_{Lew}) and delocalization binding energy (ΔE_{del}) in kcal/mol for F⁻ ion complexes fluorinated of borazine.

	ΔE_{tot}	ΔE_{Lew}	ΔE_{del}
1F-F-1	−49.3	+1.5	−50.8
1F-F-2	−47.2	−7.7	−39.5
2F-F-1	−59.2	−6.4	−52.8
2F-F-2	−56.8	−14.6	−42.2
3F-F	−66.7	−21.0	−45.7
4F-F-1	−48.8	−21.7	−27.1
4F-F-2	−43.3	−11.2	−32.1
5F-F-1	−52.4	−41.8	−10.6
5F-F-2	−46.8	−30.6	−16.2
6F-F	−55.9	−62.0	+6.1
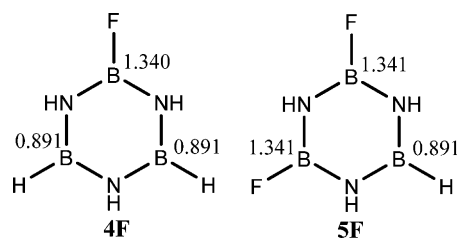
Fig. 2. MP2/6-311 + G** calculated NBO charges on boron atoms of B-fluoroborazine and B-difluoroborazine.

-39.6 (-44.6) [-11.9]

Borazine-F

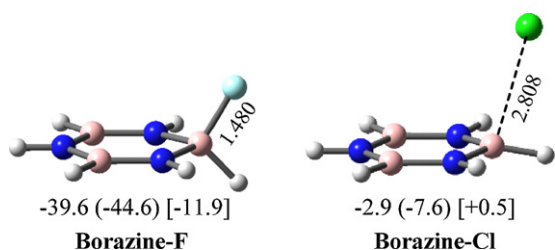-2.9 (-7.6) [+0.5]

Borazine-Cl

Fig. 3. B3LYP/6-311 + G** optimized geometries, calculated binding energies (kcal/mol) and important bond distances (Å) of borazine with F⁻ and Cl⁻ ions calculated in the gas phase. MP2/6-311 + G** calculated energies in the gas and aqueous phases are given in parentheses and square brackets, respectively [blue = nitrogen; pink = boron; cyan = fluorine; green = chlorine; white = hydrogen]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 3
B3LYP/6-311 + G** calculated total binding energy (ΔE_{tot}), Lewis binding energy (ΔE_{Lew}) and delocalization binding energy (ΔE_{del}) in kcal/mol for F⁻ ion complexes of methylated borazines.

	ΔE_{tot}	ΔE_{Lew}	ΔE_{del}
1Me-F-1	−41.6	+79.0	−120.6
1Me-F-2	−39.9	+81.5	−121.4
2Me-F-1	−43.5	+91.1	−134.6
2Me-F-2	−41.8	+93.5	−135.3
3Me-F	−43.7	+91.9	−135.6
4Me-F-1	−38.5	+53.4	−91.9
4Me-F-2	−38.4	+58.9	−97.3
5Me-F-1	−37.4	+45.4	−82.8
5Me-F-2	−37.2	+51.0	−88.2
6Me-F	−36.3	+37.7	−74.0

hydrogen, it prefers to bind with the boron atom of the ring system (Fig. S3 of the supplementary data).

The calculated results suggest that the F⁻ and Cl⁻ ion affinities of fluorine substituted borazines are much higher than the simple borazine molecule (Figs. 1 and 3). Further, the Cl⁻ ion affinities are ~30 kcal/mol lower than the F⁻ ion affinity (Fig. 1 and Fig. S2 of the supplementary data). In the halide series, Br⁻ ion shows the lowest binding affinity with fluorinated borazines.

3.2. Methyl derivatives of borazine

The study has further been extended with methyl substituted borazines. The methyl substitution was considered to examine the influence of alkyl substitution on the binding affinity of borazine toward halide ions. In the case of methyl substituted borazine, both B3LYP and MP2 calculated results suggest that only F⁻ ion has more

binding affinity toward boron atom, whereas, in most of the cases Cl⁻ ion prefers to bind with NH hydrogen instead of boron atom (Fig. 4 and Figs. S4 and S5 of the supplementary data). Only in N-trimethyl borazine, Cl⁻ ion has more affinity toward boron atom compared to the BH proton. The Br⁻ ion fails to form the complex with the boron atoms of methyl substituted borazines. The Br⁻ ion prefers to bind with NH hydrogen of methylated borazines with lower binding affinity than F⁻ and Cl⁻ ions (Fig. S6 of the supplementary data).

The F⁻ ion affinity of methyl substituted borazines is much lower than the corresponding fluorine substituted borazines (Figs. 1 and 4). The calculated binding affinities of methylated borazines are similar to borazine molecule (Figs. 3 and 4). In general, N-methyl derivatives of borazine show slightly higher fluoride ion affinity than borazine (Fig. 4). The NBO analysis suggests that delocalization energies are mainly responsible for the stabilization of these systems compared to Lewis energies (Table 3). Further,
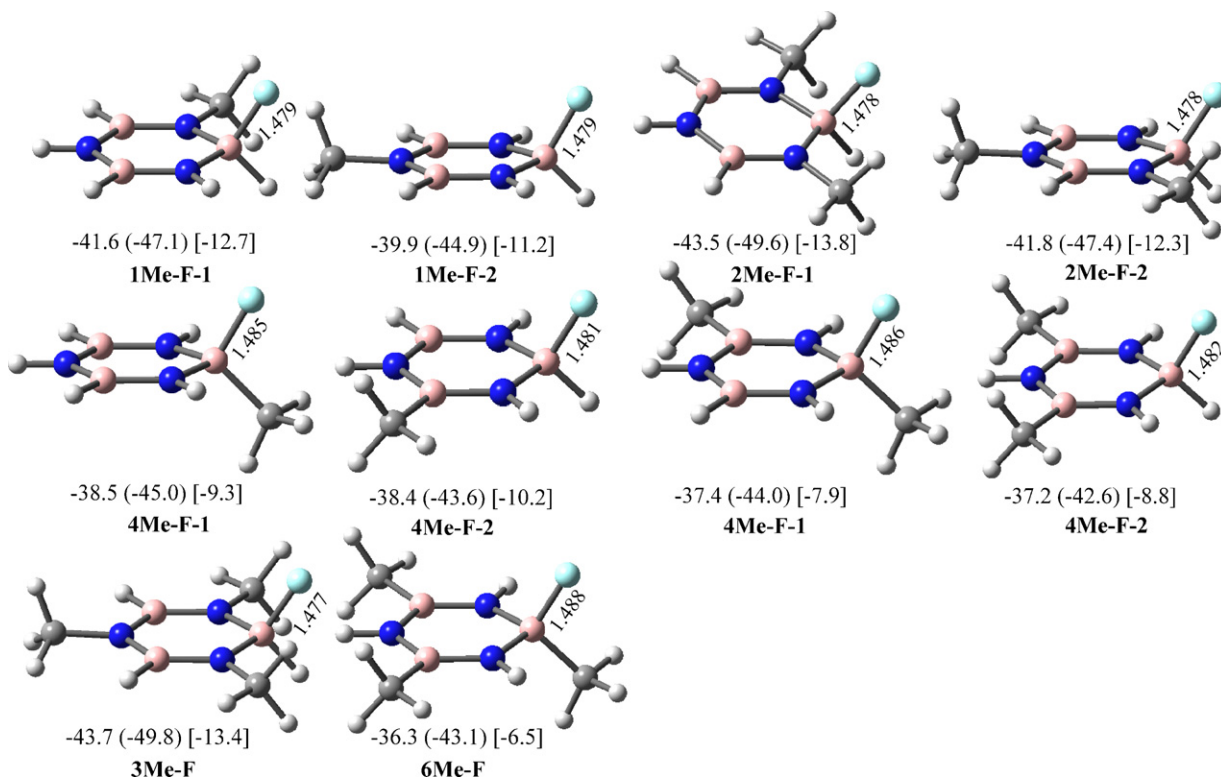

-41.6 (-47.1) [-12.7]

1Me-F-1

-39.9 (-44.9) [-11.2]

1Me-F-2

-43.5 (-49.6) [-13.8]

2Me-F-1

-41.8 (-47.4) [-12.3]

2Me-F-2

-38.5 (-45.0) [-9.3]

4Me-F-1

-38.4 (-43.6) [-10.2]

4Me-F-2

-37.4 (-44.0) [-7.9]

4Me-F-1

-37.2 (-42.6) [-8.8]

4Me-F-2

-43.7 (-49.8) [-13.4]

3Me-F

-36.3 (-43.1) [-6.5]

6Me-F

Fig. 4. B3LYP/6-311 + G** optimized geometries, calculated binding energies (kcal/mol) and B—F bond distances (Å) of methyl derivatives of borazine complexed with F⁻ ions calculated in the gas phase. MP2/6-311 + G** calculated energies in the gas and aqueous phases are given in parentheses and square brackets, respectively [blue = nitrogen; pink = boron; cyan = fluorine; gray = carbon; white = hydrogen]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
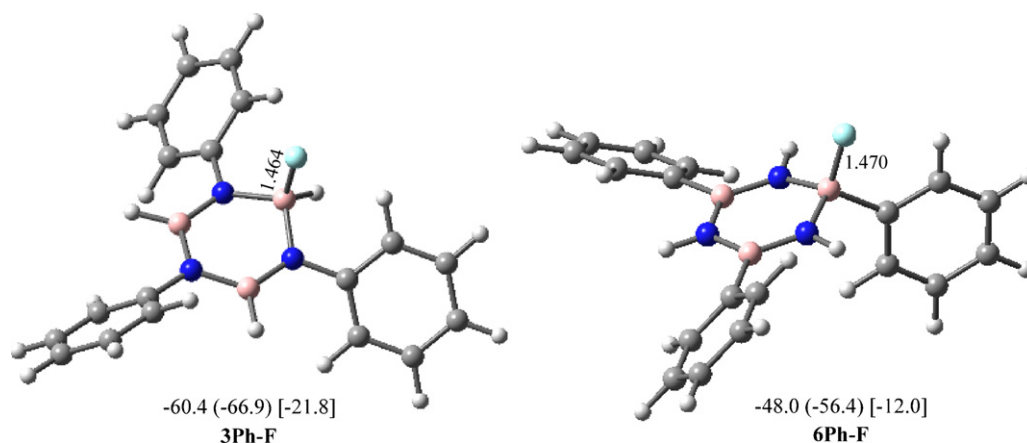
-60.4 (-66.9) [-21.8]
3Ph-F

-48.0 (-56.4) [-12.0]
6Ph-F

Fig. 5. B3LYP/6-311 + G** optimized geometries, calculated binding energies (kcal/mol) and B—F bond distances (Å) of triphenyl derivatives of borazine complexed with F⁻ ion calculated in the gas phase. MP2/6-311 + G** calculated energies in the gas and aqueous phases are given in parentheses and square brackets, respectively [blue = nitrogen; pink = boron; cyan = fluorine; gray = carbon; white = hydrogen]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the calculated charge transfer analysis (q_{CT}) supports the observed binding affinity trend in the respective series (Table 1).

3.3. Phenyl derivatives of borazine

We have explored the effect of phenyl substituents on the binding affinity of halides with borazine receptor. The MP2/6-311 + G** calculated results suggest that F⁻ ion prefers to bind with the boron atom of borazine ring (Fig. 5 and Fig. S7 of the supplementary data). The Cl⁻ ion also prefers to bind with the boron atom of N-phenyl derivatives of borazine (Fig. S8 of the supplementary data), whereas, the NH hydrogens are the preferred site of interaction in B-phenyl derivatives of borazine. The stable complex of Br⁻ ion with the boron atom of B-phenyl derivatives of borazine was not observed at B3LYP/6-311 + G** level, however, the preferred binding was seen with the NH hydrogens of N-phenyl derivatives (Fig. S9 of the supplementary data).

Both B3LYP and MP2 calculated results suggest that phenyl substituted borazines show higher F⁻ ion affinity than the borazine (Figs. 3 and 5 and Fig. S7 of the supplementary data). N-phenyl derivatives of borazine show higher binding affinity toward F⁻ ion than the B-phenyl derivatives. N-triphenyl borazine (**3Ph-F**) showed the best fluoride ion affinity (66.9 kcal/mol) in the phenyl substituted borazines, which is 22.7 kcal/mol higher than borazine at MP2 level of theory (Figs. 3 and 5). As observed in the case of N-fluoro derivatives of borazine, the Cl⁻ ion affinities are much lower than fluoride ion affinity calculated for the same molecule (Figs. S2 and S8 of the supplementary data).

3.4. Influences of solvent on halide ion affinities

To examine the influence of solvent on the affinity of substituted borazines toward anions, continuum solvent calculations (IEF-PCM solvation model) has been employed with MP2/6-311 + G**//B3LYP/6-311 + G** level of theory. Water has been considered as the solvent medium in the study. Similar trends for the binding of halides with the substituted borazines were observed in the aqueous phase as observed in the gas phase calculated results (Figs. 1, 4 and 5). However, the binding affinities in the solvent calculations are lower than the gas phase results [54]. N-trifluoroborazine (**3F-F**) shows the highest F⁻ ion affinity (30.9 kcal/mol) in aqueous medium, which is 19.0 kcal/mol higher than the simple borazine molecule (Figs. 1 and 3). N-triphenyl borazine also showed much higher F⁻ ion affinity than borazine in the aqueous phase (Figs. 3 and 5). These computed results are

encouraging that the binding energies of F⁻ ion with substituted borazine receptors are reasonably higher in the aqueous phase and can be promising candidates for recognizing F⁻ ion in highly polar medium.

4. Conclusions

We have reported DFT and ab initio calculations to examine the influence of substituted borazines toward recognition of halide anions. B- and N-substituted borazines with fluorine, methyl and phenyl substituents have been considered in this study. In general, F⁻ and Cl⁻ ions prefer to bind with the boron atom of substituted borazine rings, however, Br⁻ ion prefers to bind with the NH hydrogens of the same rings. It has been noticed that N-substituted borazines have higher anion affinity compared to the corresponding B-substituted borazines. In the case of fluorine and phenyl substituted borazines, anion affinities increases with increasing the number of substitutions, however, in the case of B-methylated borazines, F⁻ ion affinity get lowered with increasing the number of substitutions. NBO analyses of F⁻ ion complexes of fluorinated borazines suggest that Lewis energy contributes more in total SCF energy with increasing the substitutions. In the case of methylated borazines, the delocalization energy is contributing to stabilize the F⁻ ion complexes. Both B3LYP and MP2 calculated results in the gas phase suggest much higher F⁻ ion affinities for fluorine and phenyl derivatives of borazines than the simple borazine molecule. The F⁻ ion showed reasonably higher binding affinity with N-trifluoroborazine (**3F-F**) and N-triphenylborazine (**3Ph-F**) in the aqueous phase suggests that such receptors can be promising candidates for the recognition of F⁻ ion.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jmgm.2012.06.005.

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