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ORIGINAL CONTRIBUTION

Stability, Reactivity, and Aromaticity of Benzene, Borazine, and Hexasilabenzene

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ABSTRACT

Stability, reactivity and aromaticity of benzene and its inorganic analogues, borazine and hexasilabenzene have been analyzed in the light of conceptual density functional theory based global and local reactivity descriptors. Borazine is found to be more stable than benzene whereas hexasilabenzene is the least stable and more reactive. Ligand effect on the stability, reactivity and aromaticity have also been discussed. It has been observed that electron-withdrawing group makes the molecules more reactive. Aromaticity of these molecules calculated by nucleus independent chemical shift method reveals that benzene is more aromatic than the borazine and hexasilabenzene.

KEYWORDS: *Electrophilicity, Aromaticity, Hardness, Dual descriptor, ELF*

1. INTRODUCTION

Density functional theory (DFT)[1] is an alternative way of understanding quantum mechanics where electron density plays an important role rather wavefunction. Nowadays it becomes a powerful tool to explain the stability and reactivity of atoms, molecules, cluster[2,3] and cluster assemblies[4]. When DFT helps to describe popular concepts like chemical potential, electronegativity etc. conceptual DFT emerges. Based on CDFT[5,6,7,8] different global and local descriptors can be achieved which can analyze the stability and reactivity. In this work we have taken three different molecules, benzene[9], borazine[10], hexasilabenzene[11,12] and compare their stability, reactivity, and aromaticity in the light of CDFT based descriptors like hardness[7], electrophilicity[8] and dual descriptors[13]. It is well known that benzene is aromatic in nature because of the presence of 6π electrons which is accordance to Hückel (4n+2)π aromaticity rule[14,15]. Borazine and hexasilabenzene both are the inorganic analogues of benzene and shows aromaticity. To account their aromaticity nucleus independent chemical shift (NICS)[16,17,18] technique has been adopted. For the stability of a particular organic molecules, the aromaticity criterion became highly effective. Further investigation shows that the term aromaticity cannot be used only in organic chemistry; it can also be used for inorganic molecule. Stock and Poland proposed benzene relative inorganic compound borazine [$(B_3N_3H_6)$][10] also known as "inorganic benzene" in 1926. Three nitrogen centers of borazine compound are capable to donate its lone pair to the empty p-orbital of boron to participate cyclic π-electron delocalization process. This total electron delocalization also obeys the Hückel's aromaticity rule. In order to see the substitution effect on stability, reactivity and aromaticity on these systems, we have taken both electron-donating and withdrawing groups in the form of $-CH_3$ and $-NO_2$ respectively. The main aim of this work is to do a comparative study on the properties of the parent systems as well as their substituted analogues. In the next section, we have discussed on the computational details followed by results and discussion.

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2. COMPUTATIONAL DETAILS

Ground state geometry of all studied molecules have been obtained by using B3LYP level of theory with 6-31G (d, p) and 6-311G (d, p) basis sets. Vibrational frequency calculation has been performed to ensure the true minima on the potential energy surface. Different reactivity descriptors have been calculated by using standard techniques. To gain the information about aromaticity, NICS scan[19] calculation has been adopted. Shaded surface map with projection effect of electron localization function (ELF)[20] of all molecule was performed in Multiwfn[21]software. All the calculations are done in Gaussian 09 program[22] .

3. RESULTS AND DISCUSSION

The ground state geometries of benzene(C_6H_6), borazine ($B_3N_3H_6$) and hexasilabenzene (Si_6H_6) are given in Figure 1. From the geometries, it is evident that all the geometries are planer, and they have equal bond distances between C…C (1.39 Å), B…N (1.43 Å) and Si...Si (2.22 Å). The geometries of -CH_3 and -NO_2 substituted benzene(C_6H_6), borazine ($B_3N_3H_6$) and hexasilabenzene (Si_6H_6) are given in Figures 2 and 3. It has been observed that after substitution also they maintain the planer geometries. The graphical plots of electron localization function of benzene(C_6H_6), borazine ($B_3N_3H_6$) and hexasilabenzene (Si_6H_6) are given in Figure 4. From this Figure, it has been observed that the electron density over the constituent atoms of benzene, hexasilabenzene are equal but in borazine system the electron density is unequally distributed. More electron density is situated on N center than the B center. This suggests that in borazine, N is electron rich and B is electron deficient which results the electron delocalization over the ring.

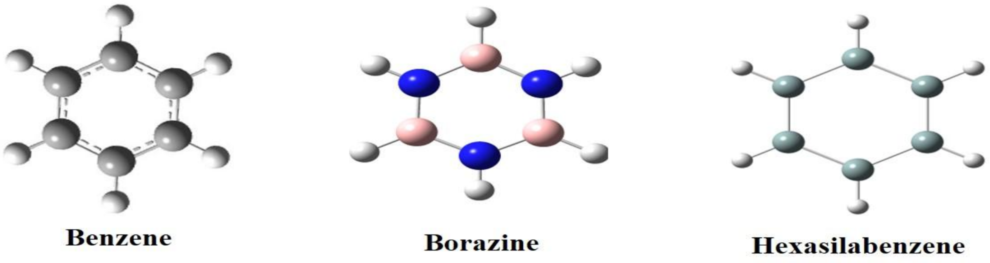


Figure 1: Optimize structures of (A) Benzene (B) Borazine (C) Hexasilabenzene

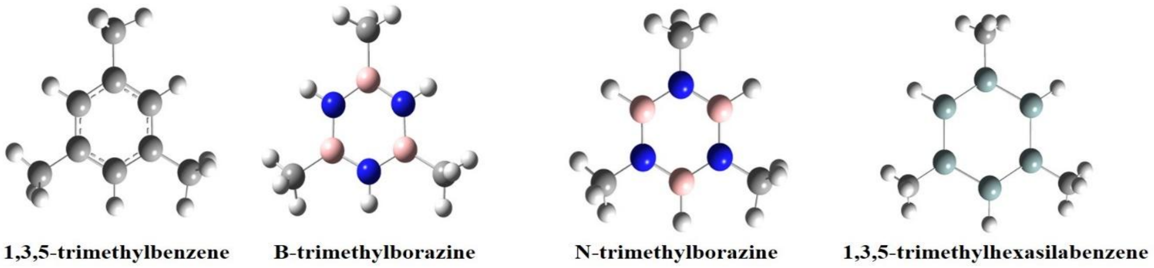
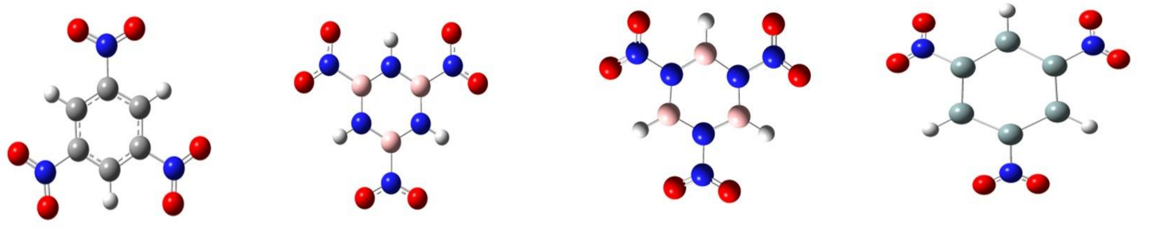
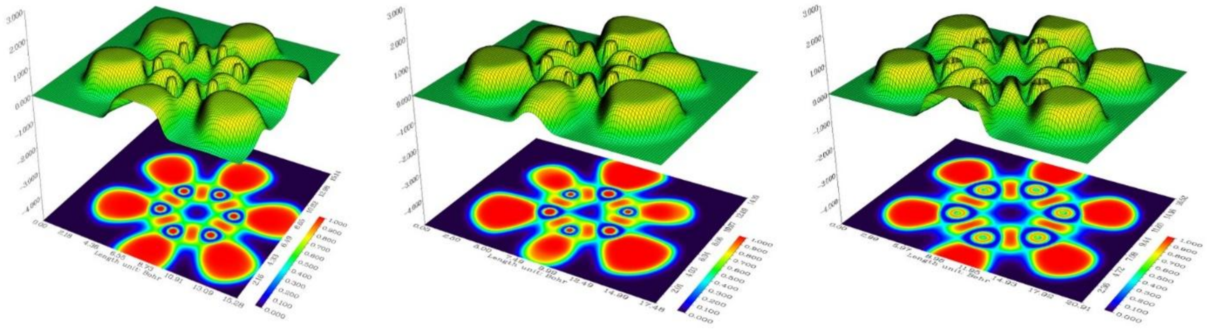


Figure 2: Optimize structures of (D) 1,3,5-trimethylbenzene (E) B-trimethylborazine (F) N-trimethylborazine (G) 1,3,5-trimethylhexasilabenzene



1,3,5-trinitrobenzene **B-trinitroborazine** **N-trinitroborazine** **1,3,5-trinitrohexasilabenzene**

Figure 3: Optimize structures of (H) 1,3,5- trinitrobenzene (I) B-trinitroborazine (J) N-trinitrobrozine (K) 1,3,5-trinitrohexasilabenzene



Benzene **Borazine** **Hexasilabenzene**

Figure 4: ELF (Electron Localization Function) studies of (A) Benzene (B) Borazine (C) Hexasilabenzene.

3.1 Stability:

To analyze the stability of the above mentioned molecules, we have calculated the hardness(η) by using B3LYP hybrid functional with two different basis sets in the form of 6-31G (d, p) and 6-311G (d, p). The corresponding values are tabulated in Table 1. It is well known fact that, larger the LUMO-HOMO gap, greater will be the stability. Here we have calculated the hardness (η) which is a popular CDFT descriptor, from the difference of ionization energy (IE) and electron affinity (EA) of the corresponding molecules. In the self-consistent field approximation, IE and EA can be calculated from the energy difference of cationic, neutral, anionic systems. Looking at the hardness(η) values of benzene (C_6H_6), borazine ($B_3N_3H_6$) and hexasilabenzene (Si_6H_6) it is evident that borazine ($B_3N_3H_6$) is most stable among them and hexasilabenzene (Si_6H_6) is least stable. If we compare the stability among the C_6H_6 and its - CH_3 and -NO_2 substituted analogues, it has been found that hardness (η) value decreases for both -CH_3 and -NO_2. Among the -CH_3 and -NO_2 substituted benzene, 1,3,5-trinitrobenzene is less stable than 1,3,5-trimethyl benzene. So, the stability depends on the nature of ligand. Electron withdrawing like -NO_2 makes less stable molecule than the electron-donating group like -CH_3. A similar trend has been observed for both borazine and hexasilabenzene molecules. Here also, we have observed that 1,3,5-trinitrohexasilabenzene is least stable among all the studied molecules.

Table 1: Ionization energy (IE, eV), electron affinity (EA, eV), hardness (η, eV), electrophilicity (ω, eV) of all the studied molecules in B3LYP level of theory and 6-31G (d, p) [6-311G (d, p)] basis set

Molecule	I.E(eV)	E.A(eV)	η (eV)	ω (eV)
Benzene	9.025 [9.234]	-2.279 [-1.877]	11.305 [11.112]	0.503 [0.609]
1,3,5-trimethylbenzene	8.181 [8.376]	-2.171 [-1.791]	10.353 [10.167]	0.436 [0.533]
1,3,5-trinitrobenzene	10.764 [10.966]	1.861 [2.049]	8.903 [8.918]	2.238 [2.374]
Borazine	9.867 [10.054]	-2.741 [-2.277]	12.609 [12.332]	0.503 [0.613]
B-trimethyl borazine	9.166 [9.375]	-3.045 [-2.224]	12.212 [11.598]	0.384 [0.551]
B-trinitroborazine	10.419 [10.612]	1.623 [1.805]	8.795 [8.807]	2.061 [2.188]
N-trimethylborazine	8.754 [8.911]	-2.352 [-1.867]	11.106 [10.779]	0.461 [0.575]
N-trinitroborazine	10.764 [10.943]	1.137 [1.210]	9.627 [9.732]	1.839 [1.897]
Hexasilabenzene	7.200 [7.271]	0.701 [0.856]	6.498 [6.414]	1.201 [1.287]
1,3,5-trimethylhexasilabenzene	6.694 [6.792]	0.565 [0.742]	6.129 [6.051]	1.075 [1.173]
1,3,5-trinitrohexasilabenzene	8.325 [8.590]	2.328 [2.753]	5.997 [5.837]	2.365 [2.755]

3.2 Reactivity:

It is anticipated that the stable system will be less reactive. So, we can expect that borazine being most stable than benzene and hexasilabenzene, found to be least reactive among them. To find the reactivity pattern among the molecules, we have calculated CDFT based global reactivity descriptor, electrophilicity index(ω). According to the ω values, more the electrophilicity (ω), more will be the reactivity. The corresponding electrophilicity (ω) values are given in table1. The electrophilicity (ω) values of benzene(C_6H_6), borazine ($B_3N_3H_6$) and hexasilabenzene (Si_6H_6) confirms that borazine ($B_3N_3H_6$) is least reactive and hexasilabenzene (Si_6H_6) is most reactive. For the substituted molecules also electrophilicity (ω) values follow the opposite trend of hardness(η) values. To analyze the reactivity in detail we have also generated a local reactivity descriptor, dual descriptor ($\Delta f(r)$). Dual descriptor helps to understand the nucleophilic and electrophilic centers inside the molecule simultaneously. The dual descriptors are depicted in Figure 5. According to $\Delta f(r)$ values, the electrophilic region is determined by $\Delta f(r) > 0$ values which is shown in pink colour whereas in nucleophilic region $\Delta f(r)$ will be less than Zero. The color code is blue for nucleophilic region. From the Figure 5, it is evident that the reactivity pattern is almost similar for all molecules. After getting the reactivity pattern, we wanted to analyze their aromaticity.

3.3 Aromaticity:

Aromaticity is considered to be another criteria to analyze the stability of the molecules. It has been

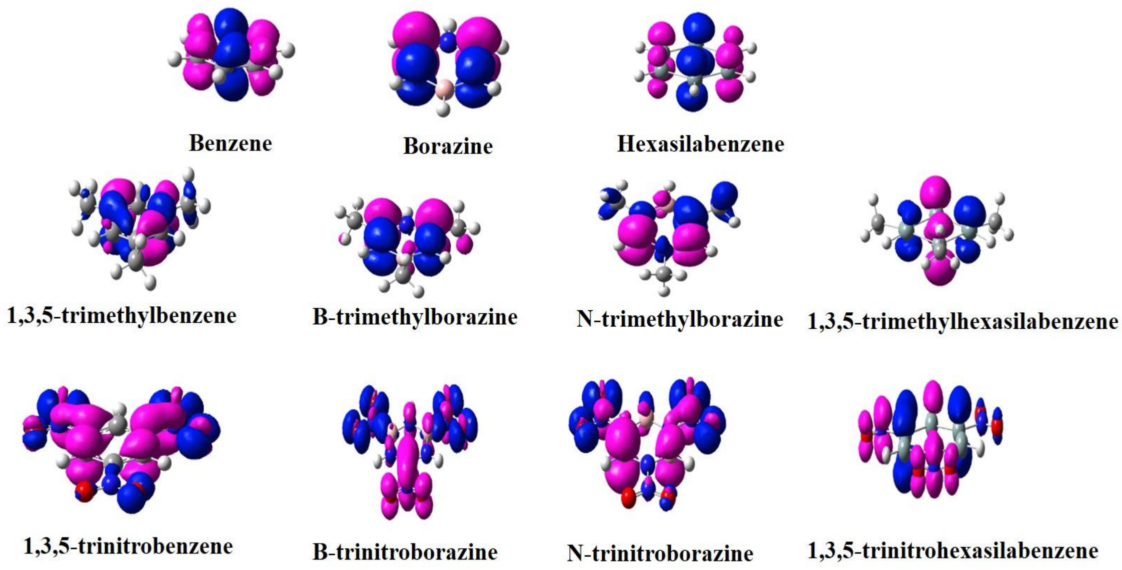


Figure 5**:** Calculated dual descriptor for pink color: Δ*f(r)*> 0; electrophilic/positive region. Blue color: Δ*f(r)*< 0, nucleophilic/negative region

found that aromatic molecules generally has less reactivity in comparison to antiaromatic molecules. Nowadays the aromaticity concept is extended to inorganic system also. Not only π electrons, σ electrons are also playing an important role to determine the aromaticity. It can be computed by using nucleus independent chemical shift (NICS) technique. In the NICS calculation, negative NICS values consider as aromatic and positive values corresponds to antiaromatic molecules. To know the aromatic behavior of our studied molecules, we have adopted NICS calculation at various points starting from center of the ring to 4 Å above the ring. Generally, NICS (0) indicates the σ aromaticity and NICS (1) refers to π aromaticity. The correspond NICS(n) values are depicted in Figures 6 and 7. In the Figure 6, we have given the NICS(n) plot of benzene(C_6H_6), borazine ($B_3N_3H_6$) and hexasilabenzene (Si_6H_6) molecules. In all three cases, we have observed negative NICS values at the center of the ring and 1 Å above the ring. This suggests that all the molecules are aromatic in nature. However, the pattern of NICS(n) is quite different in case of benzene(C_6H_6) and hexasilabenzene (Si_6H_6). We found that benzene has less σ aromaticity than hexasilabenzene. Again, when we move from 0 to 0.5 Å NICS increases for benzene but for Si_6H_6 it decreases. This suggests that π aromaticity is more in benzene than hexasilabenzene.

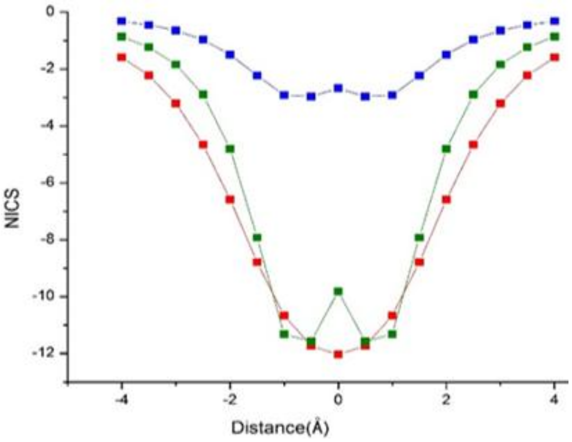
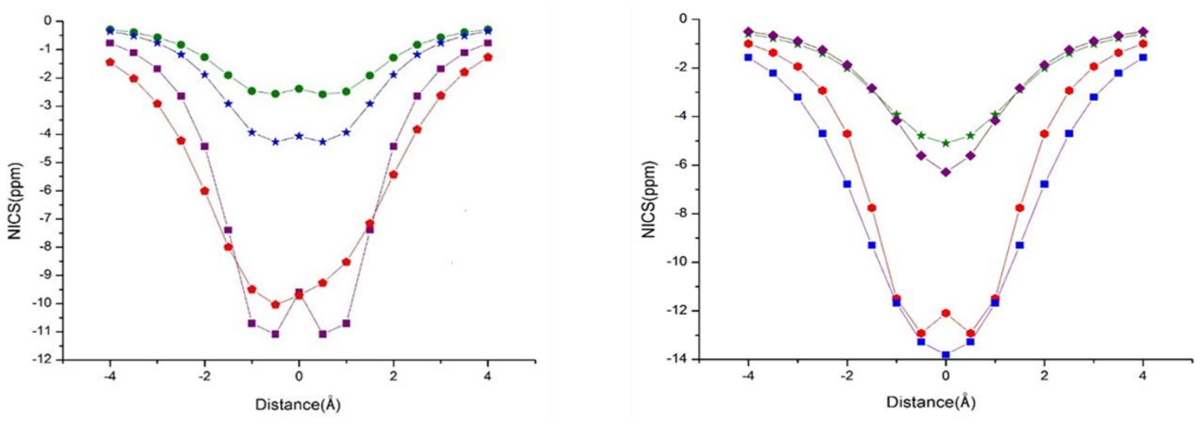


Figure 6: NICS plot of Benzene [Green], Borazine [Blue], hexasilabenzene [Red]



(a) (b)

Figure 7: NICS plots of (a) 1,3,5-trimethylbenzene[Violet], B-trimethylborazine[Green],N-trimethylborazine[Blue], 1,3,5-trimethylhexasilabenzene[Red] and (b) 1,3,5-trinitrobenzene [Red], B-trinitroborazine [Green], N-trinitroborazine [Violet], 1,3,5-trinitrohexasilabenzene [Blue]

Borazine ($B_3N_3H_6$) which is less aromatic than the benzene and hexasilabenzene (Si_6H_6) follows similar NICS(n) like benzene. This trend is same for the substituted molecules as shown in Figure 7. NICS (n) of these substituted molecules suggests that electron withdrawing group makes the molecules more aromatic than electron donating group.

4. CONCLUSIONS:

In conclusion, we have successfully carried out the comparative study of organic benzene and its inorganic form borazine, hexasilabenzene in terms of their stability, reactivity, and aromaticity. Electron donating and withdrawing substituted systems are also studied to see the substituent effect. Global descriptors like chemical hardness(η), electrophilicity(ω) are used to account the stability and reactivity. Nucleus independent chemical shift (NICS) Scan also helps to describe the σ and π-aromaticity of the studies system. Topological exploration of ELF function also supports the pattern of electron density over the molecules.

5. ACKNOWLEDGEMENTS

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