



## Organic and inorganic benzene transform to superalkalis: An *in silico* study

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Organic molecules, benzene, and its inorganic version, borazine are stable due to their aromaticity. The high ionization energies of these molecules suggest that they are reluctant to release the electron. Based on first principle calculation, we have shown the possibility of having superalkali molecules where benzene and borazine are acting as a core. Two different ligands, imidazole (IMD) and imidazole-based N-heterocyclic carbene (NHC) have been used to get the superalkali molecules. It has been found that both benzene and borazine can form superalkali with these ligands and the ionization energy decreases to ~3.0 eV in tri-substituted complexes. We have observed that benzene can make better superalkali than borazine with suitable ligands like imidazole and NHC.

Keywords: Superalkali, NLO property, DFT, aromaticity.

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### Introduction

Benzene<sup>1,2</sup>, and its six-membered inorganic analogue-borazine, also called “inorganic benzene<sup>2</sup>” are already established as the basic units of building larger aromatic organic and inorganic compounds respectively. An aromatic species is generally described by its high stability which is attributed to the presence of profuse  $\pi$ -electron delocalization in the planar rings and following the Hückel's  $(4n+2)\pi$ -electron rule. Consequently, they have a less tendency towards chemical reactions in comparison with the anti-aromatic and non-aromatic systems. Consequently, the aromatic compounds exhibit a high ionization energy (IE). About three decades back, Gutsev and Boldyrev have shown that a large class of hypervalent atomic clusters with the parent formula  $M_{k+1}L$  (where M is an alkali atom and L is an electronegative atom with valence k) possess ionization energy values lower than that of alkali metal atoms. They termed these species as superalkalis<sup>3-5</sup>. Typical examples of superalkalis are  $Li_2F$ ,  $Li_3O$ , and  $Li_4N$ <sup>6</sup>. Apart from this traditional superalkalis, there are different types of dinuclear, polynuclear, non-metallic, zintl and aromatic superalkalis reported in the literature<sup>7-10</sup>. Superalkalis play an important role in chemistry, and by virtue of their lower IE values, act as efficient reducing agents. Studies in the past couple of years have greatly expanded

the scope of superalkalis towards designing large polynuclear clusters. It has been shown that non-metallic as well as various polynuclear superalkalis with different functional groups as the central core can be synthesized, the stability of which depend on the properties of the central core. As the aromatic compounds possess high ionization potential values, it seems quite evident that designing a superalkali compound with an aromatic group can be a challenging task. Nevertheless, some literature do show the existence of aromatic superalkalis. In a recent publication, Reddy *et al.*<sup>11</sup> have shown the existence of aromatic heterocyclic superalkali clusters. Parida *et al.*<sup>12</sup> showed that it is also possible to make superalkali compounds from aromatic organometallic compounds. The superalkali behavior of borazine by ligating a large number of Li atoms is reported by Srivastava *et al.*<sup>13</sup>. In this work, we have used two different aromatic molecules, benzene and borazine as cores. Borazine consists of 3 nitrogen atoms, each of which donates a lone pair of electrons to participate in the delocalization process throughout the six-membered planar B-N-B framework. Thus a total of six electrons delocalized throughout the borazine ring is also at par with the Hückel's aromaticity rule<sup>14</sup>. Being a stable aromatic system, the first ionization energy of both benzene and borazine will be high and therefore they will show reluctance

towards losing an electron upon chemical attack. In this context, we have taken two ligands such as IMD and NHC whose ionization energy values are 8.722 eV and 8.168 eV respectively. These values suggest that they are not superalkali in nature as their IE is higher than that of Li. So we have made an attempt to design the plausible superalkali clusters by coupling the electron-donating organic ligands like NHC and IMD with the aromatic organic/inorganic benzene/borazine cores. It is anticipated that having electron donating nature of IMD and NHC, the electron density over the aromatic benzene and borazine ring will be high. So to maintain the aromaticity the whole system will try to eject electron resulting in lower ionisation energy.

### Computational details

To establish our prediction, we first optimized all the studied molecules to obtain their ground state geometry. All the geometries of the molecules were optimized in the B3LYP<sup>15,16</sup> level of theory with the basis set, 6-31+G(d,p)<sup>17,18</sup>. A long-range corrected functional, CAM-B3LYP<sup>19</sup> is also used in the optimization process to see the effect of basis sets. To obtain more accurate energy values, MP2<sup>20,21</sup> single point calculations were performed on B3LYP/6-31+G(d,p) optimized geometries. Vibrational frequency analysis have also been carried out to ensure the true minima on the potential energy surface in each case by using the same basis set and level of theory. Optimization of cations have been done for all studied systems to calculate the ionization energy. To get insight into the bonding pattern we have calculated 2c-2e bond and partial density of state to get the percentage contribution of ligand and core towards the total molecular orbital. 2c-2e bond has been calculated by AdNDP<sup>22</sup> technique embedded in multiwfn. A Nucleus-Independent Chemical Shifts (NICS)<sup>23</sup> calculations have also been performed to predict the aromatic behavior of the molecules. To get non-linear optical property we have used CAM-B3LYP/6-31+G(d,p) level of theory to calculate the dipole moment and static first-order hyperpolarizability using the following expression.

The expressions involve some common parameters like dipole moment ( $\mu$ ), polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta$ ). First, hyperpolarizability is a third rank tensor which can be described by a 3×3×3 matrix. The Gaussian 09 output provides 10 components<sup>24,25</sup> of this matrix as  $\beta_{xxx}$ ,  $\beta_{xxy}$ ,  $\beta_{xyy}$ ,  $\beta_{yyy}$ ,  $\beta_{xxz}$ ,  $\beta_{xyz}$ ,  $\beta_{yyz}$ ,  $\beta_{xzz}$ ,  $\beta_{yzz}$ ,  $\beta_{zzz}$  respectively. But the theoretical chemists are concerned with  $\beta_{||}$  which is

the component parallel to the ground state charge transfer direction and the other is the total hyperpolarizability  $\beta_{tot}$ . Using the x, y and z components, and the magnitude of the total static dipole moment ( $\mu$ ) and isotropic polarizability ( $\alpha$ ), first-order hyperpolarizability  $\beta_{tot}$  can be calculated by the following equations.

$$\text{Dipole moment} = \mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)$$

$$\text{Static polarizability} = \alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

$$\text{First order hyperpolarizability} = \beta = (\beta_x + \beta_y + \beta_z)^{1/2}$$

The complete equation for calculating the magnitude of the first hyperpolarizability ( $\beta$ ) from Gaussian 09 output is given below:

$$\beta_{tot} = \left[ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2}$$

All the calculations have been carried out by G09W<sup>26</sup>, Gausssum<sup>27</sup> and multiwfn<sup>28</sup> Software.

### Results and discussion

As discussed earlier, our main aim is to design superalkali complexes from organic/inorganic systems, we have taken stable benzene and borazine which are aromatic in nature to design more reactive superalkali molecules by coupling with two well known ligands imidazole and N-heterocyclic carbene (NHC). The Fig. 1 represents the primary components of our study.

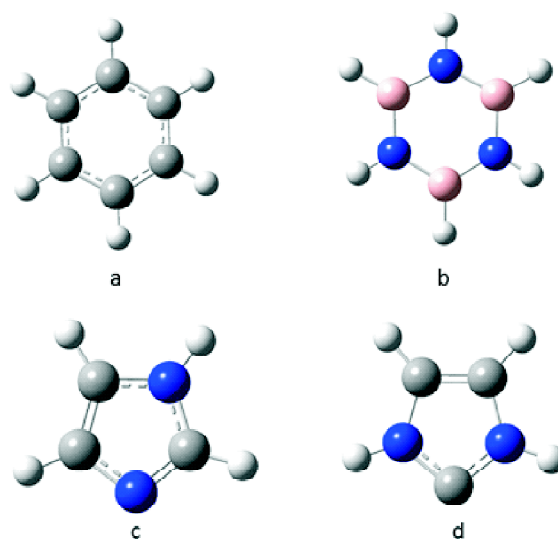
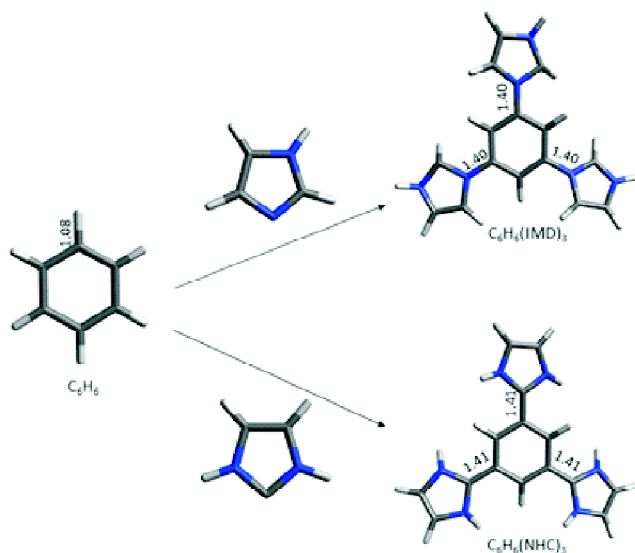


Fig. 1. The optimized geometries of (a) benzene, (b) borazine, (c) imidazole and (d) N-heterocyclic carbene.

**Benzene based superalkalis:** The optimized geometries of NHC, IMD coupled benzene complexes are depicted in Fig. 2 and the ionization energy along with NICS(0) and NICS(1) values of such complexes are given in Tables 1 and 2 respectively.



**Fig. 2.** Pictorial representation of formation of  $C_6H_3(IMD)_3$  and  $C_6H_3(NHC)_3$  from benzene and IMD, NHC with some important bond lengths in Å.

From the values of Tables 1 and 2, it is evident that benzene is having a high ionization energy with an aromaticity value of  $-10.22$  ppm (NICS(1)). The results suggest that benzene is reluctant to release an electron to form a cationic state which is anti aromatic in nature (26.27 ppm). But this situation is reversed when we substitute imidazole (IMD) moieties in benzene. It is evident that ionization energy decreases drastically from 9.065 eV to 3.916 eV. The trend is same for all level of theory calculations. In MP2 level of theory, the IE values of the complexes are even further decreased

**Table 1.** Adiabatic ionisation energy of benzene and tri substituted benzene calculated by using three different level of theories.

Systems	Adiabatic ionisation energy (AIE)		
	B3LYP/ 6-31+G(d,p) (eV)	CAM-B3LYP/ 6-31+G(d,p) (eV)	MP2/def2-tzvpp// B3LYP-631+G(d,p) (eV)
$C_6H_6$	9.065	9.114	9.568
$C_6H_3(IMD)_3$	3.916	4.364	2.123
$C_6H_3(NHC)_3$	3.359	3.080	2.737

to 2.123 eV. These values suggests that the complexes are superalkali in nature. This is due to the fact that imidazole being an electron donating group, donates electron resulting in the increase in electron density on benzene core and decrease on ligand. Thus the aromaticity is disturbed on both benzene and ligand moiety. To maintain the aromaticity the  $C_6H_3(IMD)_3$  complex will eject the electron and becomes stable as cation like alkali metals. To proof that, we have calculated the NICS values. We have noticed that the aromaticity of benzene is also decreased upon the formation of complex. The NICS(1) which generally tells about the  $\pi$ -aromaticity is also decreased from  $-10.23$  to  $-5.71$  ppm in neutral state. Whereas both NICS(0) and NICS(1) become positive (anti aromatic) for benzene in cation geometry. This findings are not in accordance with the lowering of IE value of the complex. But if we see the aromaticity values of ligand, it is evident that they gain in both  $\sigma$ - and  $\pi$ -aromaticity in the cationic state which is the possible reason behind the lower IE of  $C_6H_3(IMD)_3$  complex. It can be further noted that the benzene becomes aromatic in nature for  $[C_6H_3(IMD)_3]^{3+}$  complex.

Similar trend has been found in case of NHC carbene as a ligand. Here also benzene loses its aromaticity while ligand retains in its cationic form. This implies that ligands are sharing their electron during the formation of the complex.

**Table 2.** NICS(0)/[NICS(1)] values of ligands, IMD/NHC and benzene inside the complex

Systems	IMD/NHC (Individual)		Benzene (Individual)		Benzene (In complex)		IMD/NHC (In complex)	
	Neutral	Cation	Neutral	Cation	Neutral	Cation	Neutral	Cation
$C_6H_3(IMD)_3$	-13.23	1.60	-8.16	26.01	-5.96	6.71	-5.39	-10.88
	[-10.57]	[-3.18]	[-10.22]	[26.27]	[-5.71]	[4.29]	[-2.64]	[-7.34]
$C_6H_3(NHC)_3$	-13.04	-15.97			16.06	36.67	-5.44	-11.15
	[-10.13]	[-9.86]			[12.24]	[27.36]	[-2.75]	[-6.93]

To investigate that, we have calculated 2c-2e bond and density of state along with the partial density of states. From Fig. 3 it can be seen that there exist 2c-2e bond with occupation number 1.99 |e| which is close to 2. This suggests that ligands are sharing their electron with benzene to form a covalent bond.

To further investigate on the contribution pattern of ligand and core towards the frontier molecular orbitals of complexes, we have calculated DOS and PDOS of all the studied complexes. Fig. 4 and 5 depict the PDOS of  $C_6H_3(IMD)_3$  and  $C_6H_3(NHC)_3$  complexes.

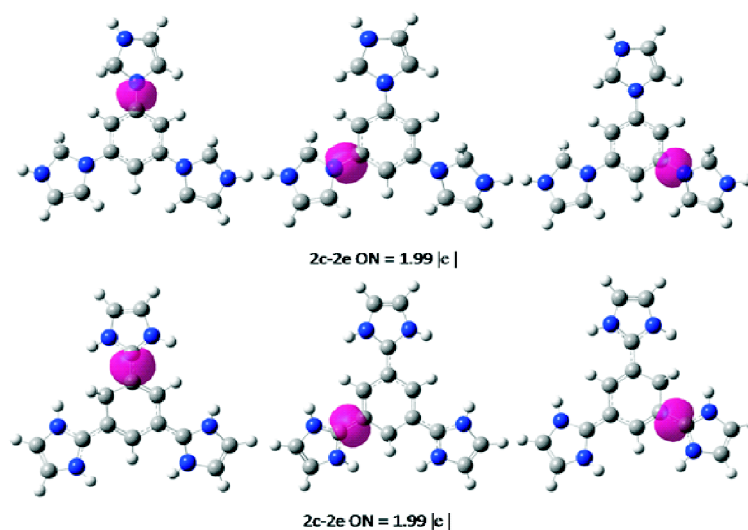


Fig. 3. 2c-2e bond of  $C_6H_3(IMD)_3$  and  $C_6H_3(NHC)_3$  with occupation number.

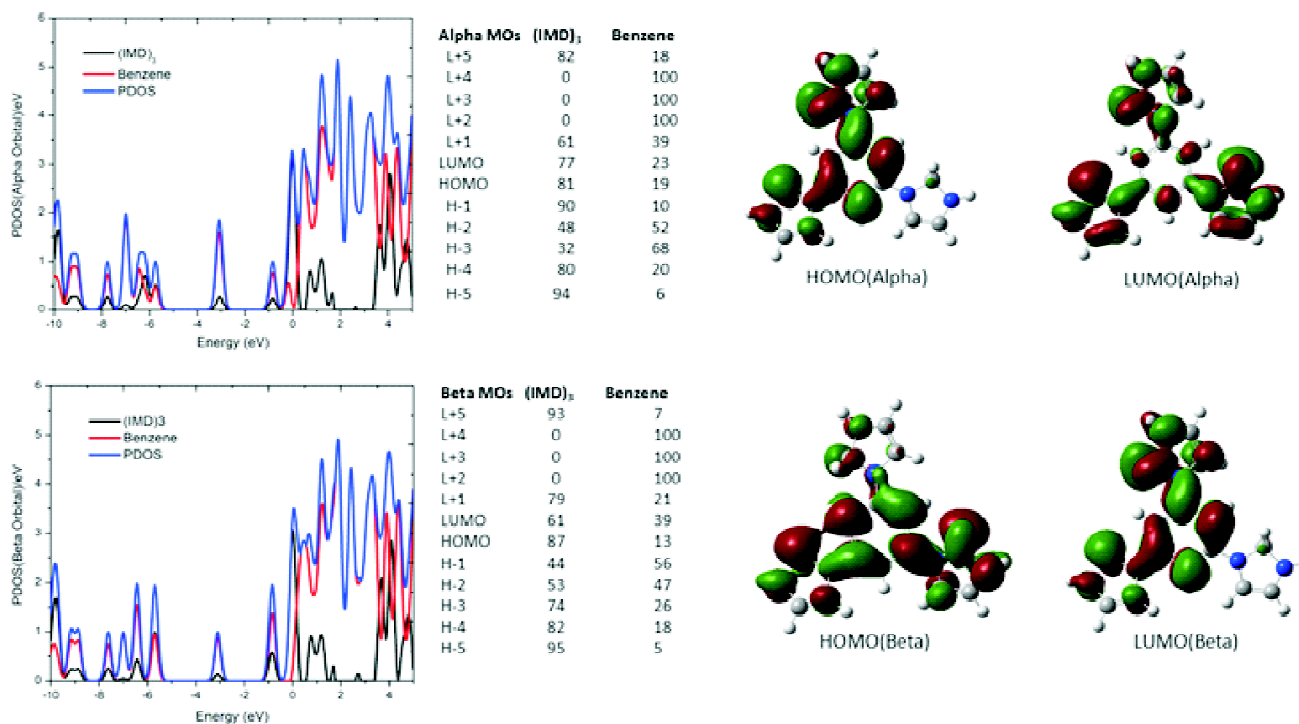


Fig. 4. PDOS with the orbital contribution of  $C_6H_3(IMD)_3$  along with HOMO, LUMO molecular orbital.

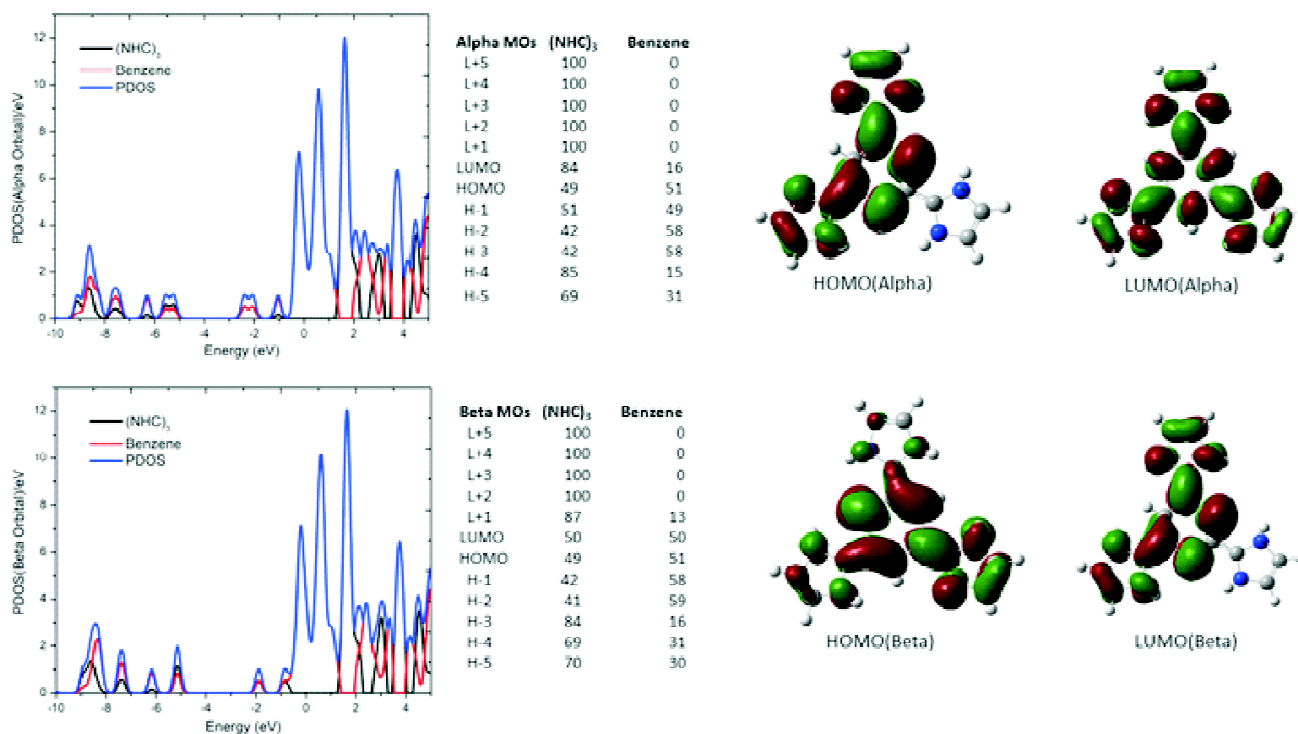


Fig. 5. PDOS with the orbital contribution of  $C_6H_3(NHC)_3$  along with HOMO, LUMO molecular orbital.

From Fig. 4 and 5 it is evident that HOMO and LUMO of the complexes are formed from the contribution from both core and ligands. However the ligand contributes more than the core.

**Borazine based superalkalis:** After successfully designing the superalkali from the stable aromatic benzene we further proceed to design the superalkali from its inorganic analog borazine. The optimized geometries of borazine and some important bond lengths have been given in Fig. 6 and the ionization energy (IE) of such complexes and NICS(0,1) values are given in Tables 3 and 4. From Tables 3 and 4, it is evident that, borazine has higher ionization energy (9.838 eV) and lower aromaticity value (NICS(0) = -2.03) compare to benzene. So, it is expected that it will be more easy to disturb the aromaticity upon substitution. In the case of borazine, we observe that when borazine is substituted by ligands, there is a decrease in the IE value, and all the compounds exhibit the properties of superalkali.

Unlike benzene substituted complexes, borazine also exhibits similar trends in terms of ionization energy. Here

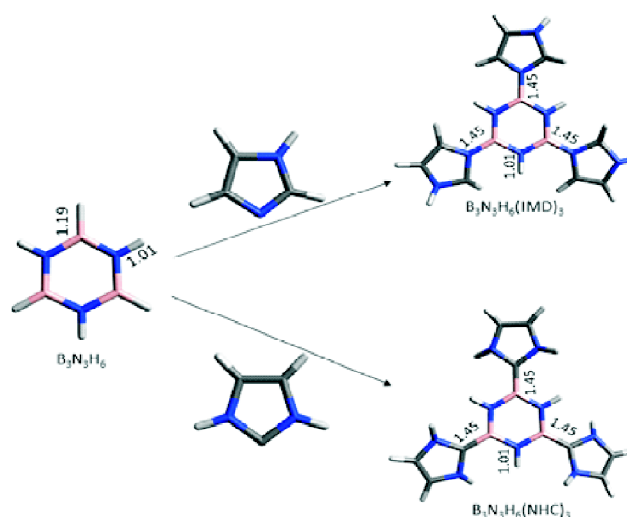


Fig. 6. Pictorial representation of formation of  $B_3N_3H_6(IND)_3$  and  $B_3N_3H_6(NHC)_3$  from borazine and IND, NHC with some important bond lengths in Å.

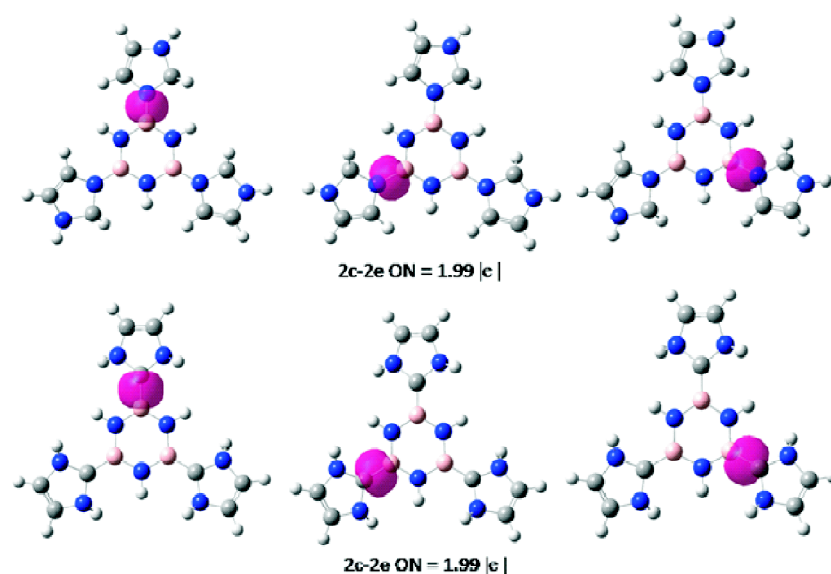
also, we found that tri-substituted borazine has less ionization energy than normal borazine. For the aromaticity, NHC ligand shows similar behavior like benzene. The tri-substi-

**Table 3.** Adiabatic ionisation energy of borazine and tri-substituted borazine calculated by using three different level of theories

Systems	Adiabatic ionisation energy (AIE)		
	B3LYP/ 6-31+G(d,p) (eV)	Cam-b3lyp/ 6-31+G(d,p) (eV)	MP2/def2-tzvpp// B3LYP-631+G(d,p) (eV)
B <sub>3</sub> N <sub>3</sub> H <sub>6</sub>	9.838	9.966	10.38
B <sub>3</sub> N <sub>3</sub> H <sub>3</sub> (IMD) <sub>3</sub>	4.640	2.740	4.421
B <sub>3</sub> N <sub>3</sub> H <sub>3</sub> (NHC) <sub>3</sub>	3.811	4.500	2.880

of states information. The corresponding pictures are given in Fig. 7 and 8. It has been found that like benzene, there exist 2c-2e bond between borazine and ligand IMD, NHC.

Unlike benzene complexes, for borazine complexes also, Ligand contributes more towards the formation of frontier molecular orbitals like HOMO and LUMO. However, core contributions can be observed in both higher and lower molecular orbitals.

**Fig. 7.** 2c-2e bond of B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>(IMD)<sub>3</sub> and B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>(NHC)<sub>3</sub> with occupation number.

tuted borazine shows anti aromatic behavior inside the borazine but aromatic in ligand. So, the system seems to gain aromatic behavior in its cationic form. This is the possible reason for having very lower IE values for tri-substituted borazine complex. We also wanted to study the bonding pattern in terms of the 2c-2e bond and projected density

### Non-linear optical (NLO) property of benzene and borazine based superalkalis

The non-linear optical property describes the behavior of light in nonlinear media, that is, media in which the dielectric polarization responds nonlinearly to the electric field of light. It has vast applications in Information technology and indus-

**Table 4.** NICS(0)/[NICS(1)] values of IMD/NHC, borazine inside the complex

Systems	IMD/NHC (Individual)		Borazine (Individual)		Borazine (Inside the complex)		IMD/NHC (Inside the complex)	
	Neutral	Cation	Neutral	Cation	Neutral	Cation	Neutral	Cation
B <sub>3</sub> N <sub>3</sub> H <sub>3</sub> (IMD) <sub>3</sub>	-13.23	1.60	-2.03	13.83	-1.73	-0.93	-4.47	-3.54
	[-10.57]	[-3.18]	[-2.78]	[9.63]	[-21.18]	[-16.94]	[-1.82]	[-4.66]
B <sub>3</sub> N <sub>3</sub> H <sub>3</sub> (NHC) <sub>3</sub>	-13.04	-15.97			0.71	0.78	-3.19	-11.04
	[-10.13]	[-9.86]			[62.91]	[51.12]	[-0.98]	[-7.98]

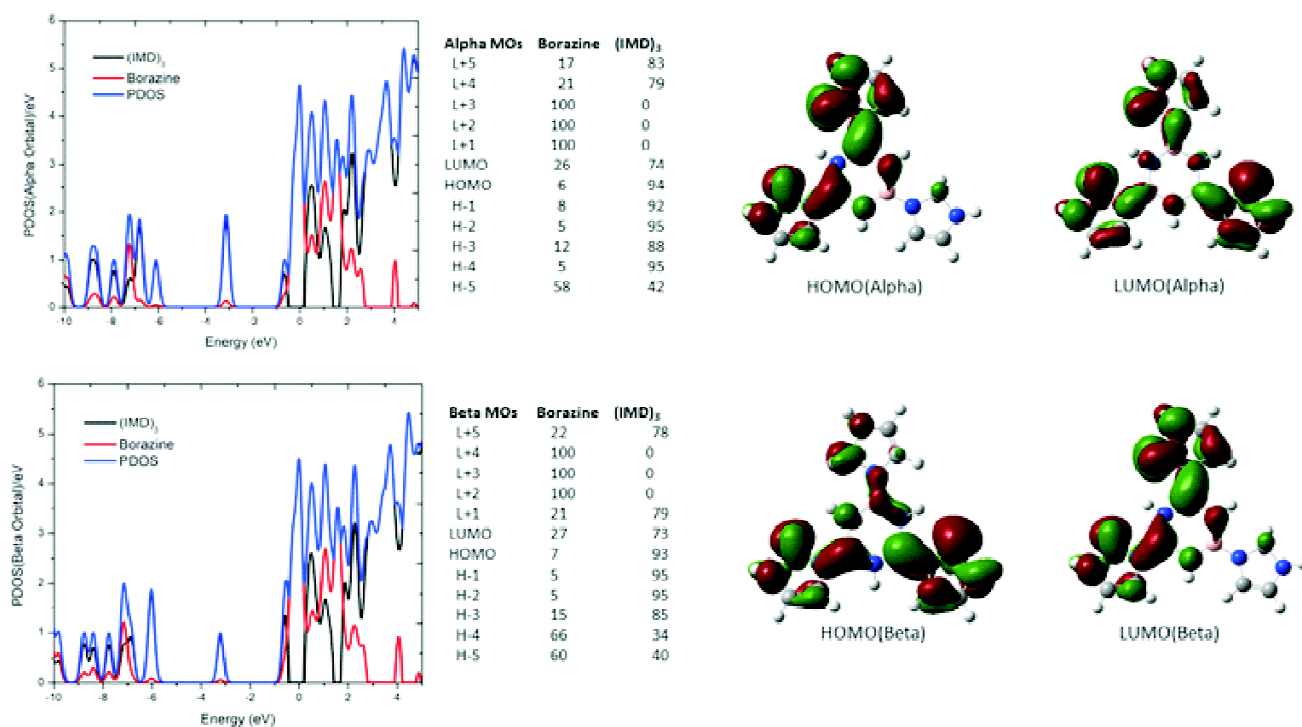


Fig. 8. PDOS with the orbital contribution of  $B_3N_3H_3(IMD)_3$  along with HOMO, LUMO molecular orbital.

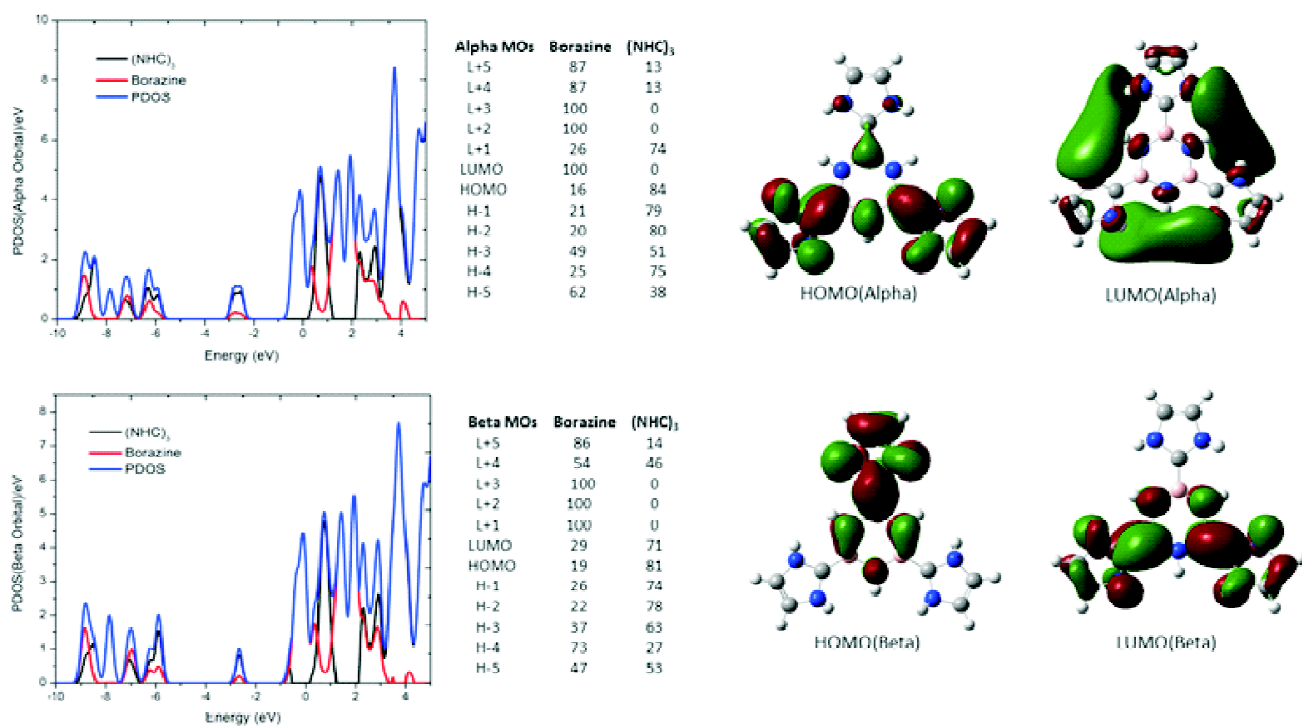


Fig. 9. PDOS with the orbital contribution of  $B_3N_3H_3(NHC)_3$  along with HOMO, LUMO molecular orbital.

**Table 5.** Dipole moment and static first-order hyperpolarizability values of benzene and borazine based superalkalis

Systems	Dipole moment (Debye)	Static first order hyperpolarizability (esu)	Systems	Dipole moment (Debye)	Static first order hyperpolarizability (esu)
C <sub>6</sub> H <sub>6</sub>	0.00	0.00	B <sub>3</sub> N <sub>3</sub> H <sub>6</sub>	0.00	0.00
C <sub>6</sub> H <sub>6</sub> (IMD) <sub>3</sub>	0.721	4.05×10 <sup>-30</sup>	B <sub>3</sub> N <sub>3</sub> H <sub>6</sub> (IMD) <sub>3</sub>	1.044	4.53×10 <sup>-30</sup>
C <sub>6</sub> H <sub>6</sub> (NHC) <sub>3</sub>	6.381	389.28×10 <sup>-30</sup>	B <sub>3</sub> N <sub>3</sub> H <sub>6</sub> (NHC) <sub>3</sub>	0.079	3.96×10 <sup>-30</sup>

try. It has been found that the superalkalis are showing a very good non-linear optical property. In order to get this property, we have calculated the dipole moment and static first-order hyperpolarizability values of all studied systems. The associated values are given in Table 5.

From the calculated non-linear optical property of all the systems, it has been found that all of them show good non-linear optical behavior as all their values were much greater than that of urea, i.e. 0.37×10<sup>-30</sup> esu. Amongst all the molecules, benzene substituted with three NHC ligands exhibits the highest value.

### Conclusions

Based on first-principles calculations, we have successfully designed stable superalkali complexes upon substitution of the aromatic benzene and borazine cores with IMD and NHC ligands. NICS and static first-order hyperpolarizability values show that almost all the complexes are aromatic and exhibit good nonlinear optical properties. These findings will help to synthesize several aromatic based organic/inorganic superalkali complexes having a wide range of applications.

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### References

1. E. Huckel, *Z. Phys.*, 1931, **70**, 204.
2. H. F. Bettinger and T. Kar, *J. Phys. Chem. A*, 2009, **113**, 3353.
3. G. L. Gutsev and A. I. Boldyrev, *Chem. Phys. Lett.*, 1982, **92**, 262.
4. G. L. Gutsev and A. I. Boldyrev, *Adv. Chem. Phys.*, 1985, **61**, 169.
5. G. L. Gutsev and A. I. Boldyrev, *Russ. Chem. Rev.*, 1987, **56**, 519.
6. E. Rehm, A. I. Boldyrev and P. v. R. Schleyer, *Inorg. Chem.*, 1992, **31**, 834.
7. J. Tong, Y. Li, D. Wu, Z.-R. Li and X.-R. Huang, *J. Phys. Chem. A*, 2011, **115**, 2041.
8. J. Tong, Y. Li, D. Wu and Z.-J. Wu, *Inorg. Chem.*, 2012, **51**, 6081.
9. J. Tong, Y. Li, D. Wu, Z.-R. Li and X.-R. Huang, *J. Chem. Phys.*, 2009, **131**, 164301.
10. N. Hou, Y. Li, Wu and D. Z.-R. Li, *Chem. Phys. Lett.*, 2013, **575**, 32.
11. G. N. Reddy and S. Giri, *Phys. Chem. Chem. Phys.*, 2016, **18**, 24356.
12. (a) R. Parida, G. N. Reddy, A. Ganguly, G. Roymahapatra, A. Chakraborty and S. Giri, *Chem. Commun.*, 2018, **54**, 3903; (b) R. Parida, S. Das, L. J. Karas, J. I-Chia Wu, G. Roymahapatra and S. Giri, *Inorg. Chem. Front.*, 2019, **6**, 3336.
13. A. K. Srivastava, S. N. Tiwari and N. Misra, *Int. J. Quantum. Chem.*, 2018, **118(6)**, e25507.
14. W. V. E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, 1951, **73**, 876.
15. A. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
16. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785.
17. M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163.
18. V. A. Rassolov, J. A. Pople, M. A. Ratner and T. L. Windus, *J. Chem. Phys.*, 1998, **109**, 1223.
19. T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.
20. M. J. Frisch, M. Head-Gordon and J. A. Pople, *Chem. Phys. Lett.*, 1990, **166**, 275.
21. M. Head-Gordon and T. Head-Gordon, *Chem. Phys. Lett.*, 1994, **220**, 122.
22. D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem.*



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- Phys.*, 2008, **10**, 5207.
23. A. Munoz-Castro, *J. Phys. Chem. C*, 2012, **116**, 17197.
24. D. A. Kleinman, *Phys. Rev.*, 1962, **126**, 1977.
25. C. Adant, M. Dupuis and J. L. Bredas, *Int. J. Quant. Chem.*, 1995, **56**, 497.
26. M. J. Frisch *et. al.*, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.
27. N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comput. Chem.*, 2008, **29(5)**, 839.
28. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580.

