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1. Group 15 Analogous of N-Heterocyclic Carbene with two π Accepting Orbitals: A Case Study

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ABSTRACT

N-heterocyclic nitrenium cation are found to have high π accepting ability (Borpuzari MP, Guha AK, Kar R (2015) Struct Chem 26:859–871). However, the tuning of π accepting ability of this class of ligand is not extensively studied. In this report, we have explore the ligation ability of N-heterocyclic nitrenium cation with boron atom at its backbone and reported first time, the presence of two π accepting orbitals, which may open up new possibilities towards catalytic applications which require the stabilization of electron-rich metal centres.

KEYWORDS

N-heterocyclic carbene, DFT, Reactivity, N-heterocyclic nitrenium ion.

Introduction

As ligands are generally recognized to be the heart of co-ordination chemistry, organometallic chemistry and homogeneous catalysis, therefore, the demand for new ligands always obviously remains a major research avenue to explore.

The initial discovery of stable N-heterocyclic carbenes [1] (NHC) quickly triggered many researchers to undergo the exploration of highly flexible ligation properties of NHC and in the past few years, it naturally, causes an upswing in the highly demanding field of organometallic chemistry [2], which is due to its superior σ donation ability of N-Heterocyclic Carbene (NHC) over amine and phosphine. Moreover, NHC is quickly expanded its field from organometallic chemistry to organic reactions and widely used in the highly demanding transesterification, nucleophilic aromatic substitution, and cycloaddition chemistry etc. [3] Due to its prime importance, several experimental and theoretical works are performed to explore the ligation property of NHC [4].

From these studies, it can be quickly realised that the σ donation ability of NHC is higher; however, their π acceptance is lower and the lower π acceptance ability of NHC can be logically understand from the high occupancy of the formally empty p(π) orbital on the carbenic "ene" centre [5].

Due to the lower π accepting ability of NHC, a given metal will simply be more electron rich in NHC-metal complex as compared to the corresponding phosphine complex and, therefore, can be realistically used to stabilise electron poor metal centre. Moreover, it can be quickly became aware of the fact that the ligation property of NHC has profound effect on the outcome of many organometallic catalytic reactions [6].

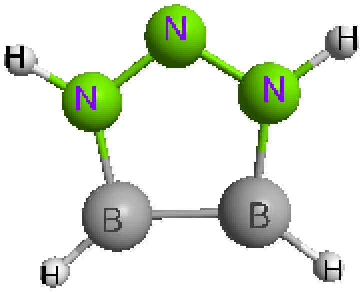
Therefore, various strategies such as introduction of different substituent in the ring and modification of the backbone, have been usually employed to tune the ligation properties of NHC [7]. Moreover, it is reported that the presence of boron atom at the backbone of NHC have a great influence on the ligation properties of the ligand. Recently, the attention of researchers is greatly focused on the various main group derivatives of NHC [8-21].

Among them, the most important is N-heterocyclic nitrenium cation. Moreover, its ligating property is supposed to be similar as that of 1. Recently, transition metal complexes of N-heterocyclic nitrenium cation have been structurally characterized where the ligand bind to the transition metals in a tridentate fashion. [14, 16-17]

Based on experimental and theoretical study, it is easily concluded that these ligands have weaker σ donation abilities than NHC but stronger π accepting abilities. [14, 16-17] Recently, Choudhury has mentioned the importance of the chemistry of these group 15 analog of carbene [22]. Moreover, it is reported that N-heterocyclic nitrenium cation can act as a double base due to the presence of two lone pair on the nitrenium "ene centre" [23-24]. However, the tuning of its π accepting ability is not elaborately studied. Therefore, in this article we have chosen to study the π accepting ability of N-heterocyclic nitrenium cation.

Computational Details

We have chosen to study N-heterocyclic nitrenium cation with boron atom at its backbone (Fig. 1). The geometries of all the molecules are fully optimized at B3LYP/6-311++G** level of theory. This level of theory is recently used to study Group 15 analogous of NHC [24]. Frequency calculations indicates that all the geometries are minima at the potential energy surfaces. The reported charge of the atom is obtained from Lowdin based population scheme. The stabilization energy obtained from Eq. 1 is zero point energy corrected. All the calculations are performed using GAMESS suite of program [25].



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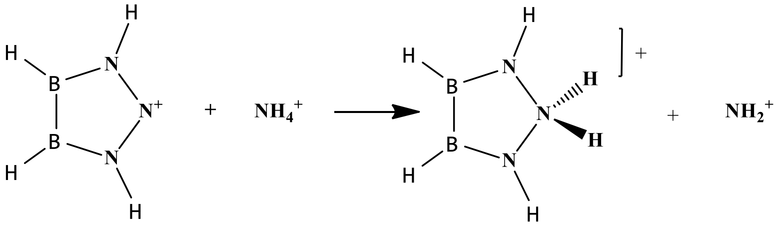


Eq. 1

Fig 1. Optimized geometries of 1 at B3LYP/6-311++G level of theory**

Results and Discussion

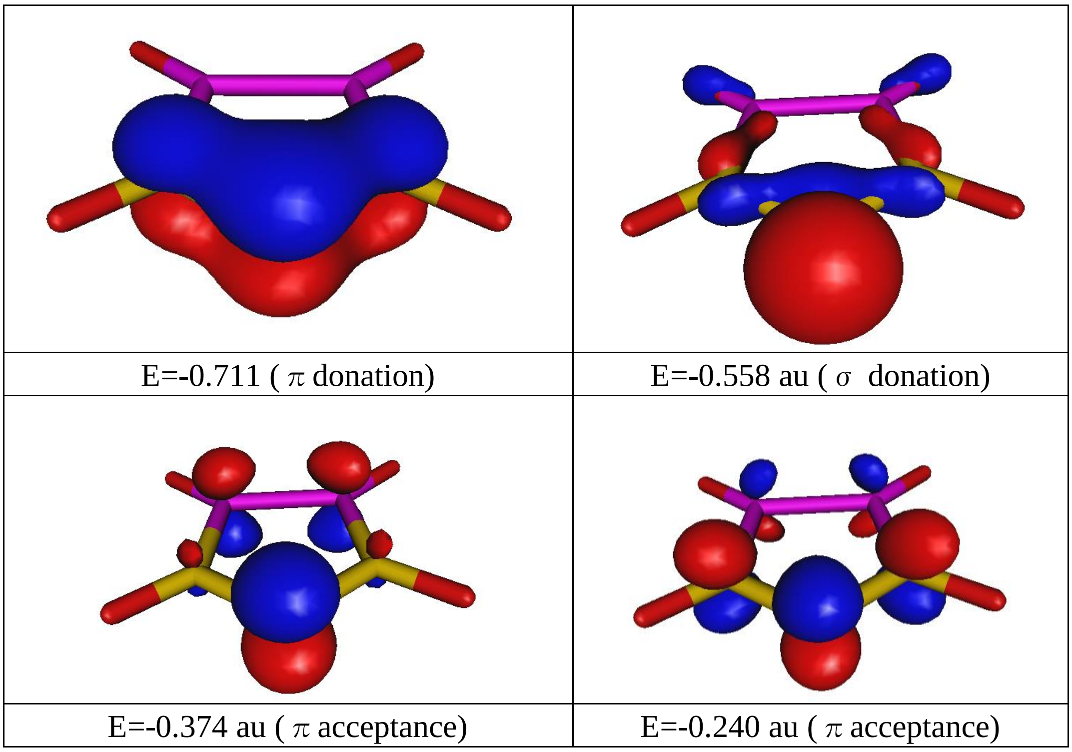
It is found from our calculation that the 1 is perfectly planar. Moreover, the central N atom of 1 i.e. the "ene" centre carries a slight positive Lowdin charge of 0.19e, suggesting that the positive charge is solely concentrated at the central N atom hence signifying that the "ene" centre is electrophilic in nature and energetically more favourable for electron acceptance.

Stability of this ligand is of major importance. Hence, we have calculated its stability by using isodesmic reaction (Eq. 1). The stabilization energy of this ligand can be calculated by the endothermicity of the reaction, Eq. 1. The higher the endothermicity, the higher will be the stability of 1. This way of assessing the stability has been widely employed in Group 15 analogous of NHC. [24]. It is evident from the stabilization energy (stabilization energy=150.53 kcal/mol) obtained by Eq. 1 that 1 is thermodynamically stable. Moreover, to assess the stability of the singlet state of this ligand, we have also calculated the singlet-triplet gap of this molecule. It is evident from our calculations that the singlet-triplet gap of 1 (singlet-triplet gap=35.63 kcal/mol) significant enough for realizing the stability of the singlet ground state. This implies that this ligand is stable and may be probable candidate for synthesis.

To address the ligation property of this ligand, we have calculated the energy of the σ donating and π accepting molecular orbitals centred on the central N atom of 1. The frontier molecular orbitals of 1 are shown in Fig. 2. It is evident from Fig. 2 that the σ donation and π donation abilities of these group 15 analogs are poor. However, their π acceptance ability is strikingly better. Interestingly, we have obtained two π accepting orbitals. It is already reported that Group 15 analogous of NHC may contain two lone pair [23-24], but no literature is present which demonstrate that Group 15 analogous of NHC contain two π accepting orbitals.

Here, we have first time reported the presence of two π accepting orbitals in Group 15 analogous of NHC and thus, we may infer that this ligand can act as a Lewis double acid.

From the Fig. 2, it can be concluded π accepting ability of both the π accepting orbitals are significantly high. This indicates that 1 is very suitable as a ligand to stabilize electron rich metal centre such as Pd (0). This bonding fashion may open up new possibilities towards catalytic applications which require the stabilization of electron-rich metal centres.



E=-0.711 (π donation)

E=-0.558 au (σ donation)

E=-0.374 au (π acceptance)

E=-0.240 au (π acceptance)

Fig. 2. Frontier MOs responsible for σ donation and π acceptance

Conclusions

In conclusion, quantum chemical calculations predict that group 15 analogs of NHC with boron atom in the backbone is significantly stable and therefore, indicates the great possibility of synthesis. Moreover, we have observed two π accepting orbitals and one σ donating and one π donating orbital. The presence of two donating orbital indicates that this ligand may act as Lewis double base. On the other hand, we have first time reported that this ligand possesses two π accepting orbitals and therefore, may act as a Lewis double acid.

Moreover, the presence two π accepting orbitals may indicates that this ligand is very suitable in stabilizing electron rich metal centre such as Pd (0) and thus, can be used in influence the outcome of gold-catalyzed reactions. [6(a)]

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