Superalkalis as Building Block for Efficient Lewis Base

Swapan Sinha  
Haldia Institute of Technology

Subhra Das  
Haldia Institute of Technology

Gourisankar Roymahapatra  
Haldia Institute of Technology

Santanab Giri (✉ santanab.giri@gmail.com)  
Haldia Institute of Technology  https://orcid.org/0000-0002-5155-8819

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Superalkalis as building block for efficient Lewis base

Swapan Sinha, Subhra Das, Gourisankar Roymahapatra, Santanab Giri*

School of Applied Science and Humanities, Haldia Institute of Technology, Haldia, India 721657

* Corresponding Author: Dr. Santanab Giri, Email: santanab.giri@gmail.com, sgiri.chem@hithaldia.in

Abstract

In quest for efficient Lewis base an in-silico investigation on NH$_3$ and its structurally similar different molecules have been carried out. It has been observed that the ionization energy of the groups attached to N-centre play an important role in determining their stability and reactivity. Among different groups, superalkali ligands make better Lewis base. Several conceptual DFT descriptors like electrophilicity, nucleophilicity, dual descriptors have been used to analyse the stability and reactivity of proposed Lewis base. Calculated charge transfer descriptor describes the efficiency of the designed Lewis base to form an adduct with Lewis acid. nc-2e (n=1,2) AdNDP calculation lend additional support to the bonding of the studied molecules.

Keywords Lewis base • DFT • Nucleophilicity index • Charge transfer descriptor • AdNDP

Introduction

Lewis base [1,2], a well-known chemical species that donates electron pairs because of the presence of lone pair. The typical example of Lewis bases are NH$_3$, PH$_3$, N(Me)$_3$, N(tBu)$_3$, etc. Lewis bases play an important role in different catalytic reactions in modern organic synthesis. Nowadays sterically hindered Lewis base and acids are also used to design efficient frustrated Lewis pairs (FLP) [3-11] which has immense application in catalysis and small molecule activation. It is well known fact that with increasing the electron releasing (+I effect) power of substituents on the group 15 elements can increase the basicity or
nucleophilicity of the Lewis base in the gas phase. So, the trend of Lewis basicity for nitrogen series will be \( \text{NH}_3 < \text{N(Me)}_3 < \text{N(Et)}_3 < \text{N(iPr)}_3 < \text{N(tBu)}_3 \) according to their electron-donating power of attaching substituents on nitrogen centre. Very recently a new super Lewis basic Tris(dialkylamino)-substituted terpyridines (TYP) was synthesized by kleeff et.al, where \( \text{NMe}_2 \) which is an electron donating group increases the basicity of TPY [12]. So, it is expected that the efficiency of the Lewis base can be tuned by introducing more powerful electron releasing species. In this regard we can think about a special kind of molecule, superalkali. Superalkali [13-15] is the common term for the last three decades in chemistry, that can easily release electrons with very low ionization energy even lower than the alkali metals. There are many different types of inorganic binuclear, polynuclear, non-metallic, and aromatic superalkalis reported in the literature [16-19]. Not only inorganic, but organic heterocyclic molecules also show superalkali behaviour [20]. Very recently Rohrbach et.al [20] synthesize organic heterocyclic superalkali type neutral super electron donor (SED), which have an efficient catalytic activity in a chemical reaction. Looking at this fact, In this study, we try to design more effective Lewis bases by introducing organic superalkalis at the N-centre. Very recently Reddy et.al [22] proposed superhalogens as a building block of super Lewis acids, which can accept the electron pair efficiently. So, it can be assumed that super alkali will work in a reverse manner. To serve this purpose different organic heterocyclic based superalkali ligands have been used to make the system more nucleophilic with better Lewis base character.

**Theory and computational details**

Conceptual DFT based global and local reactivity descriptors play an important role in describing the stability and reactivity of molecules. One of the most important global reactivity descriptor is hardness (\( \eta \)) [23,24] which is represented as,
Where $I$ is the ionisation energy and $A$ is the electron affinity of the system. In $\Delta SCF$ method, the ionization energy ($I$) and electron affinity ($A$) of the system can be calculated as

\[ I = E_{(N-1)} - E_N \]  \hspace{1cm} (2)

\[ A = E_N - E_{N+1} \]  \hspace{1cm} (3)

Where, $E_N$, $E_{N+1}$, $E_{(N-1)}$ represents the energy of neutral, anion and cation system respectively.

Electrophilicity [25] is also considered to be an important global reactivity descriptor which can be define as-

\[ \eta = I - A \]  \hspace{1cm} (1)

Where $\eta$ is the hardness and $\mu$ is the chemical potential. The chemical potential can be expressed as

\[ \mu = \frac{-(I+A)}{2} \]  \hspace{1cm} (5)

Based on the frontier orbital energy and inverse relation between electrophilicity and nucleophilicity, there exist four different expressions for the calculation of nucleophilicity index ($N$), [26-28] which are as follow

Equation- I = $E_{HOMO} - E_{HOMO \text{(TCE)}}$, where (TCE= Tetracyanoethylene)

\[ II = \frac{1}{\omega} \hspace{1cm} \text{where } \omega = \frac{\mu^2}{2\eta} \]

\[ III = \frac{1}{\omega'} \hspace{1cm} \text{where } \omega' = \frac{I^2}{2(I-A)} \]

\[ IV = \frac{1}{\omega''} \hspace{1cm} \text{where } \omega'' = \frac{(3I+A)^2}{16(I-A)} \]

To see whether our designed system can be able to form Lewis adduct, we have calculated the charge transfer descriptor. Charge transfer ($\Delta N$) [29] descriptor was proposed by Parr
et al.,[30] which is defined as, the fractional number of electrons transferred between the systems A and B in A-B molecule as

$$\Delta N = \frac{(\mu_B - \mu_A)}{2(\eta_A + \eta_B)}$$  \hspace{1cm} (6)

Where $\mu_A$, $\mu_B$ and $\eta_A$, $\eta_B$ are chemical potentials and chemical hardness of A and B respectively. Sign of $\Delta N$ determines the direction of charge/electron transfer. Negative sign refers the direction from A to B and opposite is true for positive $\Delta N$.

Apart from the global reactivity descriptors, different local reactivity descriptors, such as condensed form of Fukui functions [31,32], dual descriptor [33], multiphilic descriptor [34], $(\Delta\omega_k^{\pm})$ were used to analyze the site selectivity. These descriptors can be expressed as follows,

Fukui function for electrophilic attack, $f_k^- = \rho_k^{N-1} - \rho_k^{N}$  \hspace{1cm} (7)

Fukui function for nucleophilic attack, $f_k^+ = \rho_k^{N} - \rho_k^{N+1}$  \hspace{1cm} (8)

where $\rho_N$, $\rho_{N-1}$, $\rho_{N+1}$ are the population of neutral, cation and anionic system on the atom k.

Dual descriptor, $(\Delta f)$ which is defined as an intramolecular local reactivity descriptor, can be calculated from the densities of frontier molecular orbitals as

$$\Delta f(r) = \rho_{LUMO(r)} - \rho_{HOMO(r)}$$  \hspace{1cm} (9)

To account for the intermolecular reactivity, multiphilic descriptor has been calculated by using the following expression,

$$\Delta\omega_k^{\pm} = \omega \times (f_k^+ - f_k^-)$$  \hspace{1cm} (10)

The ground state geometries of all the studied molecules are obtained by using wB97XD [35] as hybrid functional and 6-311+G (d, p) in the form of basis set without imposing any symmetry constrain. Vibrational frequency analysis has been performed at same level of theory to know their existence on the minimum of the potential energy surface. For all the cases we obtained zero imaginary frequency. All the optimizations have been performed by using Gaussian 09 program [36].
Results and discussion

As discussed earlier, our primary goal of this work is to design efficient Lewis base, we have initially taken different N centred molecules with known aliphatic/aromatic groups which are structurally similar to NH$_3$. At first, variation in properties have been analysed with different groups attached to the N. The Lewis basicity of these molecules have analysed by looking at the electrophilicity and nucleophilicity values.

N-centre attached with known organic aliphatic ligand

A total six different molecules analogous to NH$_3$ have been taken whose ground state geometries are shown in figure 1. From the optimized geometries, it is evident that all of them are analogous to NH$_3$. It can be observed from figure 1 that the groups are attached to N center are -H, -OCH$_3$, -CH$_3$, -C$_2$H$_5$, -CH(CH$_3$)$_2$, and -tBu. So, it is expected that -tBu being more powerful electron releasing group, the nucleophilicity of N(tBu)$_3$ will be more than the others. To analyse their properties, we have calculated the vertical ionization energy (VIE), hardness ($\eta$), electrophilicity ($\omega$) and four different nucleophilicity indices (N). The corresponding values are given in Table 1. From the Table 1, it is observed that VIE is gradually decreasing when hydrogens of NH$_3$ are replaced by more electron-donating groups. The vertical ionization energy values for molecules a to f change from 10.79 eV to 7.139 eV. Among the molecules, f has lowest VIE values of 7.139 eV which is expected. This indicates that f can release electron more easily and will be more efficient Lewis base than other molecules.
The calculated η values show a decreasing trend as we move from molecules \( a \) to \( f \). This suggests that the stability of the molecules gradually decreases because of the presence of more and more electron releasing groups. Normally η and ω works in opposite way. But here we have observed that ω also has a decreasing trend. This is probably since the molecules are already electron rich because of the presence of electron releasing group. So, tendency of accepting electron is less. To get into the detail about the reactivity, we have calculated the Nucleophilicity index (N) to analyse the nucleophilicity of the molecules \( a \) to \( f \) which are Lewis bases in nature. Four different equations are used to evaluate Nucleophilicity index (N). Domingo et.al [27] established equation-I for calculating nucleophilicity index (N) by taking highest molecular orbital (HOMO) energies of the studied molecule and TCE (Tetracyanoethylene). According to this expression, \( N>3.0 \) eV is classified as a strong nucleophile whereas 2.0-3.0 eV and less than 2.0 eV values corresponds to moderate and weak nucleophile, respectively. In our case, we have observed that Nucleophilicity is gradually increasing as we move from \( a-f \). Among these, except \( a \) and \( b \), molecules \( c-f \) can
be treated as strong nucleophiles. Similar trend is observed from other expressions used for the calculation of N. A nice correlation has been observed between the VIE and nucleophilicity. As VIE decreases, N increases. This suggests that Lewis basicity can be enhanced by using groups having high electron releasing nature.

**Table 1.** Calculated vertical ionization energy (VIE), chemical hardness (η), electrophilicity (ω) and nucleophilicity index (N) of different N-centred molecules attached with electron-donating aliphatic groups.

| SI No. | Lewis Base | VIE (eV) | η (eV) | ω (eV) | I   | II   | III  | IV  |
|--------|------------|----------|--------|--------|-----|------|------|-----|
| a      |            | 10.790   | 13.035 | 0.700  | 1.911| 1.428| 0.224| 0.230|
| b      |            | 9.167    | 10.809 | 0.655  | 2.561| 1.527| 0.257| 0.259|
| c      |            | 8.361    | 10.055 | 0.553  | 3.450| 1.809| 0.288| 0.294|
| d      |            | 7.876    | 9.458  | 0.524  | 3.686| 1.910| 0.305| 0.311|
| e      |            | 7.491    | 8.976  | 0.502  | 3.872| 1.990| 0.320| 0.326|
| f      |            | 7.139    | 8.602  | 0.468  | 4.063| 2.137| 0.338| 0.346|

**N-centre attached with known organic aromatic ligand**

As for aliphatic groups, we have a correlation between VIE and nucleophilicity index, we wanted to see whether the same is valid for aromatic groups. To serve this purpose, we have taken four different groups namely benzene, imidazole, N-linked imidazole tripodal and C-linked imidazole tripodal [37].

The ground state geometries and their different properties are given in figure 2 and table 2 respectively. The values provided in table 2 reveal that, like aliphatic groups, aromatic
groups are also capable of making good Lewis base. As VIE decreases, nucleophilicity of these molecules are also increasing.

![Fig. 2 The optimized structure of (g) N-linked imidazole tripodal (h) C-linked imidazole tripodal (i) N(IMD)₃ and (j) N(Ph)₃.](image)

**Table 2** Calculated vertical ionisation energy (VIE), chemical hardness (η), electrophilicity (ω), nucleophilicity index (N) of N-centred attached with electron-donating aromatic ligands.

| Sl No. | Lewis Base | VIE (eV) | η (eV) | ω (eV) | N (eV) | I   | II  | III | IV  |
|--------|------------|----------|--------|--------|--------|-----|-----|-----|-----|
| g      | ![Image](image) | 8.487    | 9.123  | 0.845  | 3.021  | 1.184| 0.253| 0.237 |
| h      | ![Image](image) | 8.120    | 8.735  | 0.806  | 3.408  | 1.241| 0.265| 0.248 |
| i      | ![Image](image) | 7.313    | 8.778  | 0.487  | 4.154  | 2.053| 0.328| 0.335 |
| j      | ![Image](image) | 6.854    | 7.748  | 0.573  | 4.377  | 1.745| 0.330| 0.320 |
We observe that all of them are strong nucleophile according to nucleophilicity index described by Domingo et al, and phenyl group which has lower VIE than other studied aromatic groups makes better Lewis base.

**N-centre attached with aromatic heterocyclic superalkali ligand**

From the above results, we can see that, molecules having more electron-donating group make efficient Lewis base. In this aspect, superalkali will be the best candidate for the making of efficient Lewis base as they possess very low VIE values even lower than alkali metals.

**Table 3** calculated vertical ionisation energy (VIE), chemical hardness (\(\eta\)), electrophilicity (\(\omega\)) and nucleophilicity index (N) of N-centred attached with superalkalis ligand. The vertical ionization energy of the individual ligand is shown in the first brackets.

| Sl. No | Lewis Base | VIE (eV) | \(\eta\) (eV) | \(\omega\) (eV) | N (eV) |
|--------|------------|----------|---------------|---------------|--------|
|        |            |          |               | I  | II  | III | IV  |
| k      | ![Structure](image) | 4.688 (5.491) | 6.107 | 0.219 | 6.429 | 4.570 | 0.556 | 0.611 |
| l      | ![Structure](image) | 4.460 (5.193) | 5.611 | 0.244 | 6.747 | 4.099 | 0.564 | 0.600 |
| m      | ![Structure](image) | 4.350 (4.829) | 5.442 | 0.244 | 6.883 | 4.102 | 0.575 | 0.609 |
| n      | ![Structure](image) | 4.173 (4.584) | 5.042 | 0.271 | 7.024 | 3.694 | 0.579 | 0.594 |

Here we have taken four imidazolium based aromatic heterocycles to model Lewis base analogous to \(\text{NH}_3\). Earlier study reveals that these heterocycles have very low VIE values and
can be designated as superalkali\[20\]. The ground state geometries (k – n) given in figure 3 portray similar structural features like NH$_3$, N(Ph)$_3$, etc. To know the stability and reactivity of these molecules, we have calculated $\eta$, $\omega$, N alongwith VIE. The corresponding values are tabulated in table 3. We have also calculated the VIE of individual groups which are provided in first bracket in table 3. The calculated VIE suggests that the groups as well as the molecules are superalkali in nature. In fact, these molecules are having less VIE than the individual groups which are superalkalis. So, it is expected that their nucleophilicity will also be high. Looking at the electrophilicity values it reveal that these molecules have very less tendency to accept electrons. The nucleophilicity values are quite high in comparison to other groups which suggest that these systems can act as better Lewis base.

For further checking, we have calculated all the parameter in MP2 level, which is shown in supporting information table S1-S3. Although the calculated values are not same for both level of theories, the qualitative trend remains same. To analyse the reactivity of these
molecules, especially the local reactivity, we have calculated the local reactivity descriptors like Fukui functions for electrophilic/nucleophilic attack, dual descriptor [33], philicity [38] and multiphilic descriptor [34] for the N-centre. The values are given in Table 4. From the Table 4, the dual descriptor $\Delta f$ and multiphilic descriptor ($\Delta \omega^k$) of nitrogen atom in the design complexes have negative values, which represent that all the systems seem to be nucleophilic character and prefer for electrophilic attack. The dual descriptor plots which has been calculated from the electron densities of the frontier molecular orbitals (figure 4) also tells the same findings.

**Table 4** Calculated Fukui functions, dual descriptor ($\Delta f$), philicity ($\omega_k$) and multiphilic descriptor ($\Delta \omega^k$) at N centre for molecules k-n.

| Sl. No. | Lewis Base | $f_k^+$ | $f_k^-$ | $\Delta f$ | $\omega_k^+=\omega \times f_k^+$ | $\omega_k^-=\omega \times f_k^-$ | $\Delta \omega^k$ |
|--------|------------|---------|---------|------------|---------------------------------|---------------------------------|-----------------|
| k      | ![Lewis Base](image) | -0.008  | 0.001   | -0.009     | 0.0002                          | -0.002                          | -0.002          |
| l      | ![Lewis Base](image) | -0.038  | 0.007   | -0.045     | 0.002                           | -0.009                          | -0.011          |
| m      | ![Lewis Base](image) | -0.044  | 0.012   | -0.056     | 0.003                           | -0.011                          | -0.014          |
| n      | ![Lewis Base](image) | -0.021  | 0.026   | -0.047     | 0.007                           | -0.006                          | -0.013          |
The Blue colour which corresponds to nucleophilic region suggests that N center is electron rich. This indicates that electron donation can be possible like a Lewis base to an electron deficient center like Lewis acid through N center.

Fig. 4 Dual descriptor $\Delta f(r)$ from FMOs of (k) N(C$_3$N$_2$H$_4$)$_3$, (l) N(C$_5$N$_2$H$_8$)$_3$, (m) N(C$_5$N$_2$H$_8$)$_3$ and (n) N(C$_7$N$_2$H$_{12}$)$_3$. The blue colour represents the nucleophilic region and red colour represents the electrophilic region of the molecules.

To confirm this, we have calculated the charge transfer descriptor for a Lewis acid-base pair where BF$_3$ is acting as Lewis acid. According to Parr et.al. for a A-B system, negative $\Delta N$ suggests the fractional number of charges transferred occurs from A to B. In our case, we have designated Lewis base as A and Lewis acid as B. The corresponding $\Delta N$ values for the pairs are given in table 5.

Negative $\Delta N$ values for all the pairs suggests that charge/electron transfers from our designed molecules to BF$_3$. This reflect their Lewis base nature. We have observed that, the amount of charge transfer is more for the molecules having superalkali as ligand. Molecule n which has
the lowest VIE can able to transfer more charge to the Lewis acid. So, from these results, we can say that efficient Lewis base can be designed by using superalkali ligands.

**Table 5** calculated charge transfer descriptor ($\Delta N$) of all design Lewis base with BF$_3$.

| Lewis base-acid pair       | $\Delta N$ (eV) | Lewis base-acid pair       | $\Delta N$ (eV) |
|----------------------------|----------------|----------------------------|----------------|
| NH$_3$-BF$_3$               | -0.048         | N(OMe)$_3$-BF$_3$          | -0.082         |
| N(tBu)$_3$-BF$_3$          | -0.061         | N(IMD)$_3$-BF$_3$          | -0.082         |
| N-linked imidazole tripodal-BF$_3$ | -0.062       | N(Ph)$_3$-BF$_3$           | -0.085         |
| C-linked imidazole tripodal-BF$_3$ | -0.066       | N(C$_3$N$_2$H$_4$)$_3$-BF$_3$ | -0.120         |
| N(Me)$_3$-BF$_3$            | -0.071         | N(C$_5$N$_2$H$_8$)$_3$-BF$_3$ (isomer 1) | -0.123         |
| N(Et)$_3$-BF$_3$            | -0.076         | N(C$_5$N$_2$H$_8$)$_3$-BF$_3$ (Isomer 2) | -0.124         |
| N(iPr)$_3$-BF$_3$           | -0.080         | N(C$_7$N$_2$H$_{12}$)$_3$-BF$_3$ | -0.202         |

**nc-2e AdNDP Analysis**

To study the bonding features of the newly designed Lewis base system, we analyze the 2c-2e bond to ensure that the bonding between N and carbon centre of the superalkalis ligands is covalent in nature. The 2c-2e bond was calculated using the AdNDP method in Multiwfn software [39,40]. The calculated occupation number, 1.98 $|e|$ clearly demonstrates that the ligands form a covalent bond with the nitrogen center. The calculated 2c-2e bonds (k) N(C$_3$N$_2$H$_4$)$_3$ and (l) N(C$_5$N$_2$H$_8$)$_3$ along with their occupation numbers are shown in figure 5. To confirm the presence of lone pair on N center, we have performed 1c-2e bond analysis, which are shown in figure 6.
**Fig. 5** AdNDP localization results of design Lewis base (k) \( \text{N} \left( \text{C}_3\text{N}_2\text{H}_4 \right)_3 \) and (l) \( \text{N} \left( \text{C}_5\text{N}_2\text{H}_8 \right)_3 \) and their corresponding occupation number is 1.98 \( |e| \).

**Fig. 6** AdNDP localization (1c-2e bond) results of \( \text{NH}_3 \) and other designed Lewis base (k) \( \text{N} \left( \text{C}_3\text{N}_2\text{H}_4 \right)_3 \) and (l) \( \text{N} \left( \text{C}_5\text{N}_2\text{H}_8 \right)_3 \). (m) \( \text{N} \left( \text{C}_7\text{N}_2\text{H}_8 \right)_3 \) and (n) \( \text{N} \left( \text{C}_7\text{N}_2\text{H}_{12} \right)_3 \).
Conclusion
From this study, we conclude that there is an inverse relation between ligand ionization energy with nucleophilicity of N-centre amine. Having lower ionisation energy, superalkali ligand makes better Lewis base with very high nucleophilicity. Among all the studied molecules, tetramethyl imidazolium-based superalkali ligand makes an efficient Lewis base. Local reactivity descriptors like dual and multiphilic descriptors tell us N center reactivity which favours the electrophilic attack. From the charge transfer descriptor, it proves that design Lewis bases can from the adduct with Lewis acid. As the size of the heterocyclic ligands are big, it is expected that, these molecules can capable of creating frustrated Lewis pair with high reactivity.

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Authors’ contributions: Swapan Sinha and Subhra Das did the modelling of the molecules, calculate the descriptors, finalized the data. Santanab Giri and Gourisankar Roymahapatra both designed the problem, Checked the data, wrote the manuscript.
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