# Theoretical study of interaction between adenine and $\mathbf{M}^{+}(\mathbf{M}=\mathbf{L i}, \mathbf{N a}, \mathbf{K}, \mathbf{R b}, \mathbf{C s})$ and $\mathbf{M}^{2+}(\mathbf{M}=\mathbf{M g}, \mathbf{C a}, \mathbf{S r}$, Ba) 

M. Monajjemi ${ }^{1}$, S. Ketabi1 ${ }^{2}$, R. Ghiasil ${ }^{2}$, K. Zare $^{\text {I }}$, H. Passdar $1^{3}$ M.Karimkhani1 ${ }^{2}$ L.Saedi $^{l}$

1Science and Research Branch, Islamic Azad University, P.O. Box 14515-775,Tehran, Iran
2Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran
3Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran
<m monajjemi@yahoo.com>


#### Abstract

Ab Initio calculations indicate that metalation of the exocyclic amino group of adenine by the elements of group IA $\left(\mathrm{Li}^{+}, \mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Rb}^{+}, \mathrm{Cs}^{+}\right)$and group IIA $\left(\mathrm{Mg}^{2+}, \mathrm{Ca}^{2+}, \mathrm{Sr}^{2+}, \mathrm{Ba}^{2+}\right)$ causes to stabilize imino tautomer respect to amino tautomer. Metalation decreases the energy of transformation of amino to imino tauotmer. Thermochemical analysis shows that stability of metalated adenine is less for more electropositive metal. Characterization of intermolecular (C-N) and intramolecular (C-N) bonds has been studied with NBO method. The present study reports the quantum chemistry analysis of the metal-assisted tautomerization


Keywords.: Adenine, metalated adenine, ab Initio calculation, natural bond orbital analysis (NBO).
Abbreviations and notations
NBO, Natural bond orbital
BSSE,Basis set superposition error

## 1 INTRODUCTION

Interaction between metal ions and nucleotides have been the subject of intense research because of their sinificance for genetic events such as DNA replication and transcription ${ }^{1}$. The relative stability of tautomers purine base is very important in the structure of DNA. The occurrence of rare tautomers has been put forward as a possible mechanism of spontaneous mutation ${ }^{2}$. Metalation can change the probability of the formation of rare (minor) tautomers of bases and could affect the ability of nucleobase to be protonated or deprotonated ${ }^{3}$. Formation of rare nucleobase tautomers can occur under the influence of a metal entity.

Alkali cations, at high concentration, interact with the nucleic acid bases, destroying the base pair hydrogen bonding and, consequently, compromise the structure integrity of the nucleic acid polymer ${ }^{4-6}$. Furthermore, the presence of these ions in the cell nucleus
has an inhibitory effect on the chain initiation process by RNA polymerase ${ }^{4,5}$.So the alkali ions affect syntheses, replication, structure integrity, and cleavage of nucleic acid. For these reasons, knowledge of the thermochemical and structure features that govern the interaction between alkali cations and nucleic acid bases can indications with more complex nucleic acid polimers.
in this paper we have characterized the metal adenine and rare tautomer of adenine bindings.Although the calculations assume the gas phase conditions,our extended model system is close to cation bindings in nucleotides and DNA.

Metal binding may occur through a specific coordination of metal ion, either directly tp the phosphate as well as the suger oxygen atoms and to the base nitrogen and oxygen sites ${ }^{7}$.it has been quite well established that the best metal bindig site in the base of purine nucleotides is the $\mathrm{N}_{7}$ site of guanine and adenine.the existence of metal- $\mathrm{N}_{7}$ binding has been widely documented by several spectroscopic investigations including NMR $^{8}$ and RAMAN and by X-ray ${ }^{9}$ structural studies on metal-nucleotide complexes ${ }^{10}$.

## 2 Method And Calculation

The system used in calculations consist of adenine and its tautomer complexed with metal cations.the cation were initially placed at the $\mathrm{N}_{7}$ position of the base.the cations under investigation include metal ions of group (Ia) and (IIa).
All systems were optimized by using the standard split-valence $6-31+\mathrm{G}^{*}$ basis set ${ }^{11,12}$ for $\mathrm{C}, \mathrm{H}, \mathrm{andN}$ atoms. . For alkali and earth alkali metals $\left(\mathrm{Li}^{+}, \mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Rb}^{+}, \mathrm{Cs}^{+}, \mathrm{Mg}^{2+}, \mathrm{Ca}^{2+}\right.$, $\mathrm{Sr}^{2+}, \mathrm{Ba}^{2+}$ ) standard LANL2DZ basis set is used ${ }^{13-16}$ and $\mathrm{Na}, \mathrm{K}, \mathrm{Rb}$ and Cs are described by effective core potential (ECP) of Wadt and Hay pseudopotential ${ }^{11,14}$ with a doublet- $\xi$ valance using the LANL2DZ. All systems have been optimized at the Hartree-Fock level. For the optimized geometries the correlation energies were calculated by Becke3LYP density functional theory (DFT). The calculations have been performed by using the GAUSSIAN 98 suite of program ${ }^{11}$. We limit the optimization to the planar $\mathrm{C}_{\mathrm{s}}$ structures of the base $\ldots \mathrm{M}^{\mathrm{n+}}$ complexes, where metal cations $\mathrm{M}^{\mathrm{n}+}$ interact with the nitrogen atom N 7 of adenine.

The natural bond orbital (NBO) ${ }^{17-21}$ analysis has been performed by using NBO as implement in the GAUSSIAN98. NBO calculations have been performed at Hartree-Fock level. The second-order perturbative estimates of donor-acceptor (bond-antibond) interactions have been done in the NBO basis. This is carried out by examine all possible interactions between filled (donor) Lewis type NBOs and empty (acceptor) non Lewis NBOs and estimating their energetic importance by $2^{\text {nd }}$-order perturbation theory. Since these interactions lead to loss of occupancy form of the localized NBOs of the idealized Lewis structure into the empty non Lewis orbitals (and thus to departures from the idealized Lewis structure description) they are referred as delocalization corrections to the zeroth order natural Lewis structure. For each donor NBO (i) and acceptor NBO ( j ) the stabilization energy $E(2)$ associated with delocalization (2e-stabilization) $i \rightarrow j$ is estimated as:

$$
\mathrm{E}(2)=\Delta \mathrm{E}_{\mathrm{ij}}=\mathrm{q}_{\mathrm{i}} /\left[\mathrm{F}(\mathrm{i}, \mathrm{j})^{2}\left(\varepsilon_{\mathrm{j}}-\varepsilon_{\mathrm{i}}\right)\right]
$$

Where $\mathrm{q}_{\mathrm{i}}$ is the donor orbital occupancy, $\varepsilon_{\mathrm{i}}, \varepsilon_{\mathrm{j}}$ are diagonal elements (orbital energies) and $F(i, j)$ is the off diagonal NBO Fock matrix element.

The interaction energies $\left(\mathrm{E}_{\mathrm{I}}\right)$ were determined as the difference between the optimized energy of the base...metals cation $\left[\mathrm{E}\left(\mathrm{B} . . \mathrm{M}^{\mathrm{n+}}\right)\right]$ systems and the sum of the energies of the base $[E(B)]$ and the metal cation $\left[E\left(M^{n+}\right)\right]$ :

$$
\mathrm{E}_{\mathrm{I}}=\mathrm{E}\left(\mathrm{~B} \ldots \mathrm{M}^{\mathrm{n}+}\right)-\left[\mathrm{E}(\mathrm{~B})+\mathrm{E}\left(\mathrm{M}^{\mathrm{n}+}\right)\right](\mathrm{n}=1 \text { or } 2)
$$

The final interaction energies $\left(\mathrm{E}_{\mathrm{I}}\right)$ have been calculated as the difference between the energy of the complex and the sum of the energies of the monomers, and have been corrected from the inherent basis set superposition error (BSSE) which is calculated, by using the Boys-Bernardi counterpoise technique:
$\mathrm{E}_{\mathrm{I}+\mathrm{BSSE}}\left(\mathrm{B} \ldots \mathrm{M}^{+}\right)=\mathrm{E}\left(\mathrm{B} \ldots \mathrm{M}^{+}\right)_{\mathrm{BM}}-\left[\mathrm{E}(\mathrm{B})_{\mathrm{B}}+\mathrm{E}\left(\mathrm{M}^{+}\right)_{\mathrm{M}}\right]+\left[\mathrm{E}\left(\mathrm{B}^{\prime}\right)_{\mathrm{B}}-\mathrm{E}\left(\mathrm{B}^{\prime}\right)_{\mathrm{BM}}+\mathrm{E}\left(\mathrm{M}^{\prime}\right)_{\mathrm{M}}\right.$ $\left.-E\left(\mathrm{M}^{\prime}\right)_{\mathrm{BM}}\right]$
Where $\mathrm{E}\left(\mathrm{B} \ldots \mathrm{M}^{+}\right)_{\mathrm{BM}}$ represents the energy of the complex, $\mathrm{E}(\mathrm{B})_{\mathrm{B}}$ the energy of the isolated monomer $B$ with its basis set, $E\left(B^{\prime}\right)_{B}$ the energy of $B$ in its geometry within the complex calculated with its basis set, and $\mathrm{E}\left(\mathrm{B}^{\prime}\right)_{\mathrm{BM}}$ the energy of B in its geometry within the complex with the complete basis set of the complex (B... $\mathrm{M}^{+}$) ${ }^{34}$.

Metal ion affinity (MIA) was assumed as the negative of the enthalpy variations $(\Delta \mathrm{H})$ for the process:

$$
\mathrm{B}+\mathrm{M}^{\mathrm{n}+} \rightarrow \mathrm{BM}^{\mathrm{n}+}
$$

In other words the MIA corresponds to the dissociation energy of the $\mathrm{B}-\mathrm{M}^{+}$bond.
The variations in zero point energies were considered together thermochemical analysis at 298 K in order to obtain the entropic $(\Delta \mathrm{S})$ and free energy $(\Delta \mathrm{G})$ variation for the considered process.

## 3 RESULTS AND DISCUSSION 3.1Tutomerization Energies and Tautomeric Equilibria of Metalated

## Adenine

Ground states. Computed energies of species (I), (II) and (III) for nonmetalated and metalated amino, imino tautomers are compared by HF and DFT methods (Table 1,Figure1). As shown in Tables 1 stabilization of amino tautomer is more than imino tautomer. Their relative stabilities are markedly influenced by the metalation. The interaction of metal with N7 shows that stabilization of imino tautomer increases. The first major difference can be found in the relative stability of the tatutomer of free and metalated adenine, while the imino tautomer of nonmetalated adenine is destabilized by only $23.03 \mathrm{kcal} \mathrm{mol}^{-1}$ (in HF)with respect to the amino form,metalation caused the destabilization energy decreases. The differences of energy upon metalation have been shown in Table1 which increase for different metals (with HF method and B3LYP). These values show that the results are depending on metals. Stability of tautomers (I), (I) and (III) is more for electronegative metals. The stabilization of imino tautomer of the complexes with bivalent ions is larger than those with monovalent ions.
Transition state. Tablel shows that the required energy for transfoirmation of amino to imino tautomer is $65.48 \mathrm{kcal} \mathrm{mol}^{-1}$ (in HF). Metalation caused energy of transition state decreases. This energy is less for the more electronegative metals. Also, calculation shows that the required energy for transformation of amino to imino tautomer is more for monovalent ions.

### 3.2The Interaction Energies of Metalated adenine.

Table 2 shows the interaction energies of metalated adenine. The interaction energies of the metalated adenine are systematically increased with atomic number of M . This increasing is duo to larger dipole moments for metalated adenine with heavy atoms
(Table 1).Also; Table 2 shows that the strongest bonding interactions for adenine... $\mathrm{M}^{\mathrm{n}+}$ complexes were found for the metal ions of earth alkali.

Table 2 shows the value of BSSE for the metalated imino and amino tautomers. Clearly for the all complexes, values of BSSE are rather small.

### 3.3Geometry Parameters

### 3.3.1 Intermolecular Parameters.

All the intermolecular distances M-N7 for metalated amino and imino tautomers have been shown in Table 3.The intermolecular M-N7 distances in monotonically increases with the atomic number for the alkaline and earth alkali metals (Table 3, Figure 2). The increasing is more pronounced where this difference is about $1.4 \AA$ in metalated amino and imino tautomer by alkali metal. Table 3 shows the C5-C6-N7 bond angle of any structures (I), (II) and (III) decreases by about $1^{\circ}$ in any group, while that he C6-N6 distance is almost not changed. Correlation between the bond length changes and stabilization energy was found for all types of complexes.

### 3.3.2Intramolecular Parameters

The geometries of isolated bases and bases in the complexes differ considerably. See Table 4.We analyzed only bond lengths and bond angles among complexes because only these geometric parameters could be determined form X-ray measurement. Because the complexes were hold planar, the dihedrals angles were not allowed to change. The five largest bond length deviations of adenine...M complexes are summarized in Table 4 (distances of C4-N9, N3-C4, C5-N7, N7-C8 and C8-N9). Table 4 shows that all most important bond length changes take place in the five member ring. shown in Table 8. The C8-N9, N3-C4 distance in (I) and (III) increase with increasing of atomic number of alkali and earth alkali metals. The bond strength of C8-N9, N3-C4 is the following order: (I)> (II).The N7-C5, N7-C8, C4-N9 distances in (I), (III) decreases with increasing of atomic number of alkali and earth alkali metal (Figure 2). So, the double bond characterization of N7-C8 bond increases in the following order: (I)> (II). The bond strength of C4-N9, N7-C5 bonds is (I)> (II). Characterizations of these bonds have been studied by NBO method. Table 5 shows hybridation coefficients of these bonds.

### 3.4 Thermochemical Analysis

Thermochemical analysis is studied for metalated and nonmetalated adenine and it tautomers. The values of $\Delta \mathrm{H}, \mathrm{T} \Delta \mathrm{S}$ and $\Delta \mathrm{G}$ are reported in Table 6 in which the individual terms are referred to a temperature of 298 K . As can be verified, the $\Delta \mathrm{S}$ values are similar for all complexes. Although the relative difference of the $\Delta \mathrm{G}$ are almost the same as the $\Delta \mathrm{H}$. The equilibrium constants of the all complexes are given in Table6. This shows that the equilibrium constant is less for the more electropositive metals which is compatible with symbiosis effect ${ }^{22}$. The value of $\Delta \mathrm{G}$ increases with increasing metal ion radius which shows that the stability of the complex decline. See Table 6. It sounds right,
because as we have indicated previously, with metal ion radius increment bond length increases. As a result, the bonding strength decreases. Stability constants in Table 6 prove this case. The reaction can be considered as:

$$
\mathrm{M}^{+\mathrm{n}}+\mathrm{B} \longrightarrow \mathrm{MB}^{+\mathrm{n}}
$$

Since in this reaction two particles form one, $\Delta \mathrm{S}$ should be a negative value.

### 3.5 Population Analysis

Mulliken population analysis, like all atomic charge assignment schemes, is an arbitrary method for assigning atomic charges. Generally, changes in Mulliken population provide a reasonable estimation of changes in electron density within closely related molecules. Mulliken population analysis assigns atomic charges by dividing molecular orbital overlap evenly between each pair of atoms involved in a chemical bond. To identify any artifacts in the Mulliken population analysis, a natural bond orbital was also performed. The Mulliken charges for M, N1, N4 and N8 on methalated adenine (I), (II) are given in Table7. The analysis of the atomic charges is studied by the natural bonding orbital (NBO) method, as well. Atomic charges of selected atoms of metalated adenine M, N1, N6 and N7 in amino, imino tautomers have been shown in Tables 8.

Identify principle delocalizing acceptor orbitals associate with each donor NBO and their topological relationship to this NBO, i.e., whether attached to the same atom (geminal), to an adjacent bonded atom (vicinal) or to a more remote site, is possible. These acceptor NBO s will generally correspond to the principle delocalization tails of the non Lewis molecular orbital (NLMO) associated with the parent donor NBO. Calculations show that metalation cause to decrease N6 charge in amino form ( Table 9). So, basicity of N6 decreases with metalation.

The Lewis NBO s in Table 10describes percentage of the total density, with the remaining non Lewis density found primarily in the valence-shell antibonding. In metalated amino tautomers the $\mathrm{BD}(2) \mathrm{C} 4-\mathrm{C} 5$ is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into BD*(2)C6-N1,BD* (2) N 7-C 8, BD* (2) N3-C2, RY* (2) N 7,RY*(1) N9 , RY* (3) N3, BD* (2) C 4-C 5, $\mathrm{RY}^{*}(9) \mathrm{C} 6, \mathrm{RY}^{*}(5) \mathrm{C} 6, \mathrm{RY}^{*}(8) \mathrm{N} 7$. But, for amino tautomer with $\mathrm{M}=\mathrm{Mg}$, the LP ( 1) C 5 is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into $\mathrm{BD}^{*}$ ( 2) C $4-\mathrm{N} 9, \mathrm{BD}^{*}(2) \mathrm{C} 6-\mathrm{N} 1, \mathrm{BD}^{*}(2) \mathrm{N} 7-\mathrm{C} 8, \mathrm{RY}^{*}($ 1) $\mathrm{N} 7, \mathrm{RY}^{*}(8) \mathrm{C} 4, \mathrm{RY}^{*}(5) \mathrm{C} 6, \mathrm{RY}^{*}(5) \mathrm{C} 5, R Y^{*}(9) \mathrm{C} 6, R Y^{*}(7) \mathrm{N} 7, R Y^{*}(3) \mathrm{C} 5$ , RY* (8) C 5.

In metalated imino tautomers the $\mathrm{BD}(2) \mathrm{C} 4-\mathrm{C} 5$ is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into BD* (2) N 6- C 6 , BD* (2) N 7-C8, BD*( 2) C 2-N3, RY* (2) N 7 , RY* (1) N9, RY* (3) N3, BD* (2) C 4- C 5, RY* (8) N 7 , RY* (3) C $6, \mathrm{RY}^{*}$ ( 9) C 6.For imino tautomer with $\mathrm{M}=\mathrm{Mg}$, the LP (1) N 1 is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into $\mathrm{BD}^{*}(2) \mathrm{C} 2-\mathrm{N} 3, \mathrm{BD}^{*}(2) \mathrm{N} 6-\mathrm{C} 6, \mathrm{RY}^{*}(3) \mathrm{C} 2, \mathrm{RY}^{*}(2) \mathrm{C}$ $6, \mathrm{RY}^{*}(6) \mathrm{C} 2, \mathrm{RY}^{*}(6) \mathrm{C} 6, \mathrm{RY}^{*}(1) \mathrm{N} 1, \mathrm{RY}^{*}(11) \mathrm{C} 6$.

### 3.6Donor Acceptor Interaction Perturbation Theory Energy Analysis

The localized orbitals in your best Lewis structure can interact strongly. A filled bonding or lone pair orbital can act as a donor and an empty or filled bonding,
antibonding or lone pair orbital can act as an acceptor. These interactions can strengthen and weaken bonds. For example, a lone pair donor $\rightarrow$ antibonding acceptor orbital interaction will weaken the bond associated with the antibonding orbitals. Conversely, an interaction with a bonding pair as the acceptor will strengthen the bond. Strong electron delocalization in your best Lewis structure will also show up as donor-acceptor interactions. Table 11 shows the interactions that give the strongest stabilization.

## 4 CONCLUSIONS

Therefore in this paper we have shown:

1. ab initio calculations indicate that metalation of nitrogen atom N7 of adenine by the elements of group IA ( $\mathrm{Li}, \mathrm{Na}, \mathrm{K}, \mathrm{Rb}$ and Cs ) and earth alkali metals( $\mathrm{Mg}, \mathrm{Ca}, \mathrm{Sr}$ and Ba ) stabilize imino tautomer respect to major form.
2. Metalation caused energy of transition state of transformation of amino form to imino form decreases
3. The required energy for transformation of amino to imino tautomer is more for monovalent ions.
4. Metalation decreases basicity of the nitrogen atom N6 of the major form.
5. The strongest bonding interactions have been found for metalated adenine with heavy alkali metals.
6. The N7-C8, C5-N7 and C4-N9 distances in amino form decreases with increasing atomic number of alkali metal.
7. The C4-N9,N7-C8 distances in imino form decreases with increasing atomic number of metal.

## 5 REFERENCES

[1] Nakano,S.I.;Fujimoto,N.;Hara,H.;Sugimoto,N.Nucleic Acids Res.1999,27,2957
[2] Monajjemi M, et al. J.Mol.Struct (THEOCHEM). 2002; 581: 51
[3] Sponer J, Sponer JE, Gorb L, Leszczynski J, Lippert B. J.Phys.Chem A. 1999; 103: 11406
[4] Sponer J, Sponer JE, Gorb L, Leszczynski J, Lippert B. J.Phys.Chem A. 1999; 103: 11406
[5] Kaim W, Schwedersky B, Bioinorganic Chemistry: Inorganic elements in the Chemistry of Life; John Wiley \& Sons : Chichester, 1994
[6] Lobew LA, Zakour AR, In Nucleic Acid-Metal Ion Interactions; John Wiley \& Sons; New Yourk, 1980: pp 115-144
[7] Cowan,J.A.Inorganic Biochemistry.VCH Publishers:New York,1993
[8] (a)Jia,X.;Zon,G.;Marzilli,L.G.Inorg.chem.1991,30,228.(b)Froystein,N.A.;Davis,J.T;Reid,B.R. ;Sletten,E.Acta chem.scand.1993,47,649
[9] Duguid,J.;Bloomfiel,V.A.;Benevides,J.;Thomas,G.J.Biophys.J.1993,65,1916
[10](a)Abrescia,N.G.A.;Malinina,L.;Fernandez,L.G.Huynh-
Dinh,T.;Neidle,S.;Subrina,J.A.Nucleic Acids
Res.1999,27,1593.(b)Egli,M.;Williams,L.D.Biochemistry 199130,1364
[11] Gaussian 98, Revision A.6, Frisch MJ, Trucks GW, Schlegel BH, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, HeadGordon M, Replogle ES, and Pople JA, Gaussian, Inc., Pittsburgh PA, 1998
[12] Clark T, Chandrasekhar J, Spitznagel GW, Schleger PVR. J.Comp.Chem. 1983; 4: 294
[13] Schaefer A, Horn H, Ahlrichs R. J.Chem.Phys. 1992; 93: 2571
[14]] Hay PJ and Wadt WR.J.Chem.Phys.1985; 82: 270.
[15] Hay PJ, Wadt WR. J.Chem.Phys. 1985; 82: 284
[16]Hay PJ, Wadt WR. J.Chem.Phys. 1985; 82: 299
[17]Carpenter JE, Weinhold F. J.Mol.Struct (THEOCHEM).1988; 169: 41
[18]Foster JP, Weinhold F. J.Am.Chem.Soc.1980; 102: 7211
[19] Reed AE, Weinhold F. J.Chem.Phys.1983; 78: 4066
[20] Reed AE, Curtiss LA, Weinhold F. Chem.Rev1988; 88: 899
[21] Redd AE, Weinstock RB, Weinhold F. J.Chem.Phys. 1985; 83: 735
[22] Huheey JE, .Keiter EA and Keiter RL, Inorganic Chemistry, Principles of structure and Reactivity, Fourth Edition, Harpar and Row, New York, 1994 pp 348-350,518-519

Figure1. Structures of Adenine: (I) Amino form (major form); (II) Transition state for transformation of amino form to imino form ;(III) Imino form (Rare form) that $\mathrm{M}^{\mathrm{nt}}$ interacts with N7.

(I)


(II)

(III)

Figure2. Dependencies of C8-N9, N7-C8, C5-N7, N3-C4 and C4-N9 distances on the atomic number of metal in amino and imino forms.
(a)Alkali metals


(b)Earth alkali metals



Tablel. Relative Energies a (in DFT and Hartree-Fock levels) (kcal/mol) and Dipole moment (in Hartree-Fock levels) (Debye) for nonmetalated and metalated
structures (I), (III) and (III) in gas phase.

| $\mathrm{M}^{\mathrm{n}^{+}}$ | HF |  |  | B3LYP |  |  | Dipole moment(Debye) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | I | II | III | I | II | III | I | II | III |
| - | 0.00 | 65.48 | 23.03 | 0.00 | 50.60 | 12.96 | 2.5186 | 2.5743 | 4.0164 |
| Li | 0.00 | 60.62 | 8.28 | 0.00 | 46.14 | 7.19 | 14.4769 | 12.5010 | 10.2406 |
| Na | 0.00 | 60.46 | 7.94 | 0.00 | 45.99 | 6.92 | 15.2483 | 12.9582 | 10.6375 |
| K | 0.00 | 60.77 | 8.04 | 0.00 | 46.28 | 7.07 | 16.1618 | 13.6193 | 11.2644 |
| Rb | 0.00 | 60.98 | 8.15 | 0.00 | 46.45 | 7.14 | 14.1815 | 11.6312 | 9.3335 |
| Cs | 0.00 | 61.21 | 8.30 | 0.00 | 48.42 | 7.24 | 12.8829 | 10.3256 | 8.0774 |
| Mg | 0.00 | 57.03 | -0.08 | 0.00 | 42.80 | 3.62 | 22.9415 | 20.7754 | 14.5971 |
| Ca | 0.00 | 56.21 | 0.91 | 0.00 | 42.80 | -3.62 | 25.4176 | 22.2576 | 19.0748 |
| Sr | 0.00 | 56.28 | 1.16 | 0.00 | 41.99 | -0.43 | 21.9169 | 18.8237 | 16.0074 |
| Ba | 0.00 | 56.50 | 1.47 | 0.00 | 42.17 | 0.29 | 19.6946 | 16.6244 | 14.0581 |

${ }^{\text {a }}$ Relative Energy of structures (II),(III) calculated respect to structure(I) .

Table1. Relative Energies ${ }^{\text {a }}$ (in DFT and Hartree-Fock levels) (kcal/mol) and Dipole moment (in Hartree-Fock levels) (Debye) for nonmetalated and metalated structures (I), (II) and (III) in gas phase.

| $M^{\text {n+ }}$ | HF |  |  | B3LYP |  |  | Dipole moment(Debye) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | I | II | III | 1 | II | III | I | II | III |
|  | 0.00 | 65.48 | 23.03 | 0.00 | 50.60 | 12.96 | 2.5186 | 2.5743 | 4.0164 |
|  | 0.00 | 60.62 | 8.28 | 0.00 | 46.14 | 7.19 | 14.4769 | 12.5010 | 10.2406 |
| Li |  |  |  |  |  |  |  |  |  |
| Na | 0.00 | 60.46 | 7.94 | 0.00 | 45.99 | 6.92 | 15.2483 | 12.9582 | 10.6375 |
| K | 0.00 | 60.77 | 8.04 | 0.00 | 46.28 | 7.07 | 16.1618 | 13.6193 | 11.2644 |
| Rb | 0.00 | 60.98 | 8.15 | 0.00 | 46.45 | 7.14 | 14.1815 | 11.6312 | 9.3335 |
| Cs | 0.00 | 61.21 | 8.30 | 0.00 | 48.42 | 7.24 | 12.8829 | 10.3256 | 8.0774 |
| Mg | 0.00 | 57.03 | -0.08 | 0.00 | 42.80 | 3.62 | 22.9415 | 20.7754 | 14.5971 |
| Ca | 0.00 | 56.21 | 0.91 | 0.00 | 42.80 | -3.62 | 25.4176 | 22.2576 | 19.0748 |
| Sr | 0.00 | 56.28 | 1.16 | 0.00 | 41.99 | -0.43 | 21.9169 | 18.8237 | 16.0074 |
| Ba | 0.00 | 56.50 | 1.47 | 0.00 | 42.17 | 0.29 | 19.6946 | 16.6244 | 14.0581 |

${ }^{\text {a }}$ Relative Energy of structures (II),(III) calculated respect to structure(I) .
Table2. $\mathbf{E}_{\mathrm{I}}$ (Interaction Energies), BSSE and $\mathbf{E}_{\mathrm{I}+\mathrm{BSSE}}(\mathrm{kcal} / \mathrm{mol})$ for metalated structures (I), (II) and (III) in Hartree-Fock level.

| M | $E_{1}$ |  | BSSE |  | $E_{\text {I+BSSE }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | I | III | I | II | I | II |
| Li | - | - | - | - | - | - |
|  | 37.7 | 50.2 | 38.3 | 53.1 | 76.0 | 103. |
|  | 0 | 7 | 9 | 1 | 9 | 38 |
| Na |  | -32.14 | -23.47 | -38.52 | -46.14 | -70.66 |
|  | - |  |  |  |  |  |
|  | 22.6 |  |  |  |  |  |
|  | 7 |  |  |  |  |  |
| K | -11.68 | -18.56 | -13.22 | -28.17 | -24.9 | -46.73 |
| Rb | -9.74 | -15.82 | -10.48 | -25.33 | -20.22 | -41.15 |
| Cs | -7.33 | -12.66 | -8.90 | -22.80 | -16.23 | -35.46 |


| $\mathbf{M g}$ | - | - | - | - | - | -288.6 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 109.0 | 155.86 | 109.7 | 132.7 | 218.79 |  |
|  | 5 |  | 4 | 4 |  |  |
| $\mathbf{C a}$ | -59.81 | -93.11 | -59.86 | -81.94 | - | - |
|  |  |  |  |  | 119.67 | 175.05 |
| $\mathbf{S r}$ | -47.71 | -76.42 | -48.26 | -70.08 | -95.97 | -146.5 |
| $\mathbf{B a}$ | -37.45 | -61.58 | -37.84 | -59.37 | -75.29 | - |
|  |  |  |  |  |  | 136.87 |

Table3.Optimized bond distances of M-N7, C6-N6 ( $\AA$ ) and angle of M-N7-C4, C5-C6-N6 (degree) for metalated structures (I), (II) and (III) at gas phase in HartreeFock level.

| M-N7-C4 |  |  | C5-C6-N6 |  |  | C6-N6 |  |  |  |  | M-N7 |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| III | II | I | III | II | I | III | II | I | III | II | III |  |  |
| 162.8 | 162.8 | 170.0 | 132.7 | 142.3 | 125.0 | 1.261 | 1.298 | 1.343 | 1.93 | 1.92 | 1.924 | $\mathbf{L i}$ |  |
| 163.4 | 163.0 | 172.5 | 132.4 | 142.1 | 124.6 | 1.263 | 1.301 | 1.345 | 2.34 | 2.33 | 2.34 | $\mathbf{N a}$ |  |
| 164.4 | 164.2 | 175.7 | 132.1 | 142.0 | 124.2 | 1.264 | 1.302 | 1.344 | 2.82 | 2.80 | 2.81 | $\mathbf{K}$ |  |
| 164.7 | 164.8 | 176.7 | 131.9 | 142.0 | 124.0 | 1.264 | 1.303 | 1.345 | 3.06 | 3.02 | 3.05 | $\mathbf{R b}$ |  |
| 165.0 | 165.5 | 177.6 | 131.8 | 141.9 | 123.7 | 1.264 | 1.303 | 1.345 | 3.33 | 3.28 | 3.32 | $\mathbf{C s}$ |  |
| 144.9 | 159.2 | 167.0 | 132.3 | 142.7 | 126.6 | 1.280 | 1.298 | 1.345 | 1.95 | 1.94 | 1.946 | $\mathbf{M g}$ |  |
| 156.0 | 156.8 | 170.0 | 131.9 | 142.3 | 126.0 | 1.274 | 1.308 | 1.349 | 2.40 | 2.38 | 2.38 | $\mathbf{C a}$ |  |
| 157.8 | 157.5 | 171.3 | 131.7 | 142.3 | 125.8 | 1.274 | 1.309 | 1.349 | 2.59 | 2.56 | 2.57 | $\mathbf{S r}$ |  |
| 159.5 | 158.5 | 172.9 | 131.5 | 142.3 | 125.5 | 1.273 | 1.310 | 1.350 | 2.81 | 2.77 | 2.78 | $\mathbf{B a}$ |  |

Table4. Optimized bond distances of C8-N9, N7-C8, C5-N7, N3-C4 and C4-N9 ( $\AA$ ) for metalated structures (I), (II) and (III) at gas phase in Hartree-Fock level.

|  | C5-N7 |  | N7-C8 |  |  |  |  | C8-N9 |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| III | II | I | III | II | I | III | II | I |  |  |
|  |  |  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  | $\mathbf{M}^{+}$ |  |
| 1.372 | 1.379 | 1.383 | 1.284 | 1.280 | 1.281 | 1.365 | 1.372 | 1.370 |  |  |
|  |  |  |  |  |  |  |  |  | $\mathbf{-}$ |  |
| 1.388 | 1.395 | 1.402 | 1.302 | 1.298 | 1.301 | 1.341 | 1.344 | 1.338 | $\mathbf{L i}$ |  |
| 1.385 | 1.392 | 1.399 | 1.299 | 1.293 | 1.296 | 1.346 | 1.350 | 1.345 | $\mathbf{N a}$ |  |
| 1.382 | 1.391 | 1.396 | 1.294 | 1.290 | 1.292 | 1.351 | 1.355 | 1.351 | $\mathbf{K}$ |  |
| 1.382 | 1.389 | 1.395 | 1.294 | 1.289 | 1.291 | 1.353 | 1.357 | 1.352 | $\mathbf{R b}$ |  |
| 1.380 | 1.388 | 1.393 | 1.293 | 1.288 | 1.290 | 1.355 | 1.358 | 1.354 | $\mathbf{C s}$ |  |
| 1.395 | 1.415 | 1.426 | 1.318 | 1.323 | 1.330 | 1.328 | 1.317 | 1.309 | $\mathbf{M g}$ |  |
| 1.394 | 1.408 | 1.416 | 1.312 | 1.309 | 1.316 | 1.331 | 1.331 | 1.323 | $\mathbf{C a}$ |  |
| 1.396 | 1.405 | 1.413 | 1.309 | 1.305 | 1.311 | 1.335 | 1.335 | 1.327 | $\mathbf{S r}$ |  |


| 1.394 | 1.403 | 1.410 | 1.306 | 1.303 | 1.307 | 1.338 | 1.339 | 1.332 | $\mathbf{B a}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |


| C4-N9 |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | N3-C4 |  |  | $\mathbf{M}^{\mathbf{n +}}$ |
| III | II | I | III | II | II |  |
| 1.356 | 1.356 | 1.362 | 1.365 | 1.344 | 1.328 |  |
|  |  |  |  |  |  | $\mathbf{-}$ |
| 1.363 | 1.365 | 1.370 | 1.353 | 1.329 | 1.316 | $\mathbf{L i}$ |
| 1.360 | 1.362 | 1.367 | 1.354 | 1.332 | 1.319 | $\mathbf{N a}$ |
| 1.358 | 1.360 | 1.365 | 1.356 | 1.334 | 1.321 | $\mathbf{K}$ |
| 1.359 | 1.358 | 1.365 | 1.357 | 1.335 | 1.322 | $\mathbf{R b}$ |
| 1.358 | 1.358 | 1.364 | 1.358 | 1.336 | 1.322 | $\mathbf{C s}$ |
| 1.372 | 1.381 | 1.384 | 1.337 | 1.313 | 1.301 | $\mathbf{M g}$ |
| 1.365 | 1.371 | 1.375 | 1.344 | 1.319 | 1.308 | $\mathbf{C a}$ |
| 1.363 | 1.368 | 1.372 | 1.346 | 1.321 | 1.310 | $\mathbf{S r}$ |
| 1.362 | 1.366 | 1.372 | 1.346 | 1.321 | 1.312 | $\mathbf{B a}$ |

Table 5. Hybridation Coefficient of C8-N9, C8-N7, N7-C5, N4-C3 andN9-C4 bonds of metalaed amino and imino forms calculated by NBO method in HF level.

## (a)Amino form

| $\mathbf{M}^{\text {n+ }}$ | C8-N9 | C8-N7 |  |
| :---: | :---: | :---: | :---: |
|  |  |  | N7-C5 |
|  | $\begin{array}{cc} \sigma & 0.6096\left(\mathrm{sp}^{2.22}\right)_{\mathrm{c}}+0.7927\left(\mathrm{sp}^{1.94}\right)_{\mathrm{N}} \\ \pi & - \end{array}$ | $\begin{gathered} 0.7761\left(\mathrm{sp}^{1.68}\right)_{\mathrm{c}}+0.6306\left(\mathrm{sp}^{1.97}\right)_{\mathrm{N}} \\ \left.0.8288\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}^{+}+0.5596\left(\mathrm{p}^{1.00}\right.}\right)_{\mathrm{N}} \end{gathered}$ | $0.7733\left(\mathrm{sp}_{1.98}\right)_{\mathrm{C}}+0.6341\left(\mathrm{sp}^{2.4}\right)_{\mathrm{N}}$ |
|  | $\begin{array}{ll} \hline \sigma & 0.6085\left(\mathrm{sp}^{2.25}\right)_{\mathrm{C}}+\left(0.7936 \mathrm{sp}^{1.95}\right)_{\mathrm{N}} \\ \pi & \\ \hline \end{array}$ | $\begin{aligned} & 0.8143(\mathrm{p} 1.06)_{\mathrm{C}}+0.5804(\mathrm{p} 1.00)_{\mathrm{N}} \\ & 0.7733\left(\mathrm{sp}^{1.69}\right)_{\mathrm{C}}+0.6340\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}} \\ & \hline \end{aligned}$ | $0.7688\left(\mathrm{sp}^{2.05}\right)_{\mathrm{C}}+0.6395\left(\mathrm{sp}^{2.36}\right)_{\mathrm{N}}$ |
| K | $\begin{array}{ll}\sigma & 0.6075\left(\mathrm{sp}^{2.26}\right)_{\mathrm{C}}+0.7943\left(\mathrm{sp}^{1.95}\right)_{\mathrm{N}} \\ \pi & \end{array}$ | $\begin{aligned} & 0.7719\left(\mathrm{sp}^{1.68}\right)_{\mathrm{C}}+0.6358\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}} \\ & 0.8037\left(\mathrm{p}^{.00}\right)_{\mathrm{C}}+0.5950\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}} \end{aligned}$ | $0.7664\left(\mathrm{sp}^{2.08}\right)_{\mathrm{C}}+0.6423\left(\mathrm{sp}^{2.33}\right)_{\mathrm{N}}$ |
| Rb | $\begin{array}{ll} \sigma & 0.6071\left(\mathrm{sp}^{2.27}\right)_{\mathrm{C}}+0.7946\left(\mathrm{sp}^{1.95}\right)_{\mathrm{N}} \\ \pi & \\ \hline \end{array}$ | $0.7714\left(\mathrm{sp}^{1.68}\right)_{\mathrm{C}}+0.6363\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ $0.8003\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.5996\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}}$ | $0.7655\left(\mathrm{sp}^{2.099}\right)_{\mathrm{C}}+0.6434\left(\mathrm{sp}^{2.33}\right)_{\mathrm{N}}$ |
|  | $\begin{array}{ll} \hline \sigma & 0.6067\left(\mathrm{sp}^{2.28}\right)_{\mathrm{C}}+0.7950\left(\mathrm{sp}^{1.95}\right)_{\mathrm{N}} \\ \pi \end{array}$ | $0.7711\left(\mathrm{sp}^{1.67}\right)_{\mathrm{C}}+0.6367\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ $0.7972\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.6038\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}}$ | $0.7647\left(\mathrm{sp}^{2.10}\right)_{\mathrm{C}}+0.6444\left(\mathrm{sp}^{2.32}\right)_{\mathrm{N}}$ |
|  | $\begin{array}{ll} \sigma & 0.6151\left(\mathrm{sp}^{2.11}\right)_{\mathrm{C}}+0.78859\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}} \\ \pi & \\ \hline \end{array}$ | $\begin{aligned} & 0.7821\left(\mathrm{sp}^{1.74}\right)_{\mathrm{c}}+0.6231\left(\mathrm{sp}^{2.09}\right)_{\mathrm{N}} \\ & 0.8782(\mathrm{p} \mathrm{1.00})+0.4784(\mathrm{p} 1.00)_{\mathrm{N}} \\ & \hline \end{aligned}$ | $0.7871\left(\mathrm{sp}^{1.90}\right)_{\mathrm{c}}+0.6168\left(\mathrm{sp}^{2.58}\right)_{\mathrm{N}}$ |
| Ca | $\sigma \quad 0.6136\left(\mathrm{sp}^{2.15}\right)_{\mathrm{C}}+0.7896\left(\mathrm{sp}^{1.92}\right)_{\mathrm{N}}$ | $0.7773\left(\mathrm{sp}^{1.72}\right)_{\mathrm{c}}+0.6291\left(\mathrm{sp}^{2.00}\right)_{\mathrm{N}}$ | $0.7792\left(\mathrm{sp}^{1.96}\right)_{\mathrm{C}}+0.6268\left(\mathrm{sp}^{2.47}\right)_{\mathrm{N}}$ |


| $\mathbf{M}^{\text {n+ }}$ |  |  | $\mathrm{N} 9-\mathrm{C} 4$ |
| :---: | :---: | :---: | :---: |
|  |  | N4-C3 |  |
| - | $\begin{aligned} & \sigma \\ & \pi \end{aligned}$ | $0.6561\left(\mathrm{sp}^{1.80}\right)_{\mathrm{C}^{+}} 0.7547\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ | $0.6096\left(\mathrm{sp}^{2.67}\right)_{\mathrm{C}}+0.792\left(\mathrm{sp}^{1.92}\right)_{\mathrm{N}}$ |
| Na |  | $0.6556\left(\mathrm{sp}^{1.81}\right)_{\mathrm{C}}+0.7551\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}}$ | $0.6106\left(\mathrm{sp}^{2.65}\right)_{\mathrm{C}^{+}} 0.7920\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}}$ |
| K | $\begin{aligned} & \sigma \\ & \pi \end{aligned}$ | $0.6552\left(\mathrm{sp}^{1.82}\right)_{\mathrm{C}^{+}} 0.7555\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}}$ | $0.6112\left(\mathrm{sp}^{2.63}\right)_{\mathrm{C}^{+}} 0.7914\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}}$ |
| Rb | $\begin{aligned} & \sigma \\ & \pi \end{aligned}$ | $0.6550\left(\mathrm{sp}^{1.82}\right)_{\mathrm{C}}+0.7556\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}}$ | $0.6115\left(\mathrm{sp}^{2.62}\right)_{\mathrm{C}}+0.7912\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}}$ |
| Cs | $\begin{aligned} & \sigma \\ & \pi \end{aligned}$ | $0.6549\left(\mathrm{sp}^{1.83}\right)_{\mathrm{C}^{+}} 0.7557\left(\mathrm{sp}^{1.90}\right)_{\mathrm{N}}$ | $0.6118\left(\mathrm{sp}^{2.62}\right)_{\mathrm{C}}+0.7910\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ |
| Mg | $\sigma$ $\pi$ | $0.6586\left(\mathrm{sp}^{1.74}\right)_{\mathrm{C}^{+}} 0.7525\left(\mathrm{sp}^{1.86}\right)_{\mathrm{N}}$ | $\begin{aligned} & 0.6042\left(\mathrm{sp}^{2.80}\right)_{\mathrm{C}^{+}} 0.7968\left(\mathrm{sp}^{1.96}\right)_{\mathrm{N}} \\ & 0.4151\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.9098\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}} \\ & \hline \end{aligned}$ |
| Ca | $\sigma$ $\pi$ | $0.6577\left(\mathrm{sp}^{1.77}\right)_{\mathrm{C}^{+}}+0.7532\left(\mathrm{sp}^{1.88}\right)_{\mathrm{N}}$ | $0.6068\left(\mathrm{sp}^{2.73}\right)_{\mathrm{C}}+0.7949\left(\mathrm{sp}^{1.94}\right)_{\mathrm{N}}$ |
| Sr | $\sigma$ $\pi$ | $0.6575\left(\mathrm{sp}^{1.78}\right)_{\mathrm{C}^{+}+0.7535\left(\mathrm{sp}^{1.88}\right)_{\mathrm{N}}}$ | $0.6074\left(\mathrm{sp}^{2.72}\right)_{\mathrm{C}}+0.7944\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ |
|  | $\begin{aligned} & \sigma \\ & \pi \end{aligned}$ | $0.6572\left(\mathrm{sp}^{1.78}\right)_{\mathrm{C}^{+}} 0.7537\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ | $0.6080\left(\mathrm{sp}^{2.70}\right)_{\mathrm{C}^{+}} 0.7939\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ |

## (b)Imino form

| $\mathrm{M}^{\text {n+ }}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | C8-N9 | C8-N7 | N7-C5 |
| - | $\stackrel{\sigma}{\pi}$ | $0.5988\left(\mathrm{sp}^{2.33}\right)_{\mathrm{C}^{+}} 0.8009\left(\mathrm{sp}^{1.91}\right)_{\mathrm{N}}$ | $\begin{gathered} \hline 0.7706\left(\mathrm{sp}^{1.69}\right)_{\mathrm{C}^{+}}+0.6373\left(\mathrm{sp}^{1.87}\right)_{\mathrm{N}} \\ 0.7706\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.6373\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}} \end{gathered}$ | $0.6490\left(\mathrm{sp}^{2.27}\right)_{\mathrm{C}}+0.7608\left(\mathrm{sp}^{2.05}\right)_{\mathrm{N}}$ |
| Li | $\cdots$ | $0.6066\left(\mathrm{sp}^{2.26}\right)_{\mathrm{C}}+0.7950\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ | $\begin{aligned} & 0.7773\left(\mathrm{sp}^{1.67}\right)_{\mathrm{C}}+0.6291\left(\mathrm{sp}^{1.99}\right)_{\mathrm{N}} \\ & 0.8210\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.5709\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}} \\ & \hline \end{aligned}$ | $0.6345\left(\mathrm{sp}^{2.41}\right)_{\mathrm{C}}+0.7729\left(\mathrm{sp}^{1.95}\right)_{\mathrm{N}}$ |
| Na | $\sigma$ $\pi$ | $0.6041\left(\mathrm{sp}^{2.30}\right)_{\mathrm{C}}+0.7969\left(\mathrm{sp}^{1.94}\right)_{\mathrm{N}}$ | $\begin{aligned} & 0.7730\left(\mathrm{sp}^{1.68}\right)_{\mathrm{C}^{+}} 0.6344\left(\mathrm{sp}^{1.92}\right)_{\mathrm{N}} \\ & 0.7976\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.6031\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}} \end{aligned}$ | $0.6427\left(\mathrm{sp}^{2.33}\right)_{\mathrm{C}}+0.7661\left(\mathrm{sp}^{2.03}\right)_{\mathrm{N}}$ |
| K | $\sigma$ $\pi$ | $0.6052\left(\mathrm{sp}^{2.29}\right)_{\mathrm{C}}+0.7960\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ | $\begin{aligned} & 0.7744\left(\mathrm{sp}^{1.69}\right)_{\mathrm{C}}+0.6327\left(\mathrm{sp}^{1.95}\right)_{\mathrm{N}} \\ & 0.8074\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.5901\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}} \end{aligned}$ | $0.6397\left(\mathrm{sp}^{2.36}\right)_{\mathrm{C}}+0.7686\left(\mathrm{sp}^{2.00}\right)_{\mathrm{N}}$ |
|  | $\sigma$ $\pi$ | $0.6037\left(\mathrm{sp}^{2.31}\right)_{\mathrm{C}}+0.7972\left(\mathrm{sp}^{1.94}\right)_{\mathrm{N}}$ | $\begin{aligned} & 0.7725\left(\mathrm{sp}^{1.68}\right)_{\mathrm{C}}+0.6350\left(\mathrm{sp}^{1.92}\right)_{\mathrm{N}} \\ & 0.7944\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.6074\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}} \end{aligned}$ | $0.6438\left(\mathrm{sp}^{2.32}\right)_{\mathrm{C}}+0.7652\left(\mathrm{sp}^{2.04}\right)_{\mathrm{N}}$ |


| Cs | $\sigma$ | $0.6033\left(\mathrm{sp}^{2.31}\right)_{\mathrm{C}}+0.7975\left(\mathrm{sp}^{1.94}\right)_{\mathrm{N}}$ | $0.7721\left(\mathrm{sp}^{1.68}\right)_{\mathrm{C}}+0.6355\left(\mathrm{sp}^{1.91}\right)_{\mathrm{N}}$ | $0.6447\left(\mathrm{sp}^{2.32}\right)_{\mathrm{C}}+0.7644\left(\mathrm{sp}^{2.05}\right)_{\mathrm{N}}$ |
| :--- | :--- | :--- | :--- | :--- |
|  | $\pi$ |  | $0.7913\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.6114\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}}$ |  |
| Mg | $\sigma$ | $0.6105\left(\mathrm{sp}^{2.21}\right)_{\mathrm{C}}+0.7920\left(\mathrm{sp}^{1.92}\right)_{\mathrm{N}}$ | $0.7853\left(\mathrm{sp}^{1.58}\right)_{\mathrm{C}}+0.6191\left(\mathrm{sp}^{2.11}\right)_{\mathrm{N}}$ | $0.6273\left(\mathrm{sp}^{2.55}\right)_{\mathrm{C}}+0.7788\left(\mathrm{sp}^{2.04}\right)_{\mathrm{N}}$ |
|  | $\pi$ | $0.8679\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.4968\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}}$ |  |  |
| Ca | $\sigma$ | $0.6095\left(\mathrm{sp}^{2.21}\right)_{\mathrm{C}}+0.7928\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ | $0.7799\left(\mathrm{sp}^{1.66}\right)_{\mathrm{C}}+0.6259\left(\mathrm{sp}^{2.02}\right)_{\mathrm{N}}$ | $0.6312\left(\mathrm{sp}^{2.45}\right)_{\mathrm{C}}+0.7756\left(\mathrm{sp}^{1.99}\right)_{\mathrm{N}}$ |
|  | $\pi$ |  | $0.8431\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.5377\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}}$ |  |
| Sr | $\sigma$ | $0.609\left(\mathrm{sp}^{2.22}\right)_{\mathrm{C}}+0.7932\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ | $0.7785\left(\mathrm{sp}^{1.67}\right)_{\mathrm{C}}+0.6277\left(\mathrm{sp}^{2.00}\right)_{\mathrm{N}}$ | $0.6332\left(\mathrm{sp}^{2.43}\right)_{\mathrm{C}}+0.7740\left(\mathrm{sp}^{2.00}\right)_{\mathrm{N}}$ |
|  | $\pi$ | $0.8348\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.5505\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}}$ |  |  |
| Ba | $\sigma$ | $0.6084\left(\mathrm{sp}^{2.23}\right)_{\mathrm{C}}+0.7936\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ | $0.7772\left(\mathrm{sp}^{1.68}\right)_{\mathrm{C}}+0.6292\left(\mathrm{sp}^{1.98}\right)_{\mathrm{N}}$ | $0.6351\left(\mathrm{sp}^{2.41}\right)_{\mathrm{C}}+0.7725\left(\mathrm{sp}^{2.00}\right)_{\mathrm{N}}$ |
|  | $\pi$ |  | $0.8267\left(\mathrm{p}^{1.00}\right)_{\mathrm{C}}+0.5626\left(\mathrm{p}^{1.00}\right)_{\mathrm{N}}$ |  |


| $\mathbf{M}^{\text {n+ }}$ |  |  |
| :---: | :---: | :---: |
|  | N3-C4 | N9-C4 |
| $\begin{aligned} & \sigma \\ & -\quad \pi \end{aligned}$ | $0.6493\left(\mathrm{sp}^{1.99}\right)_{\mathrm{C}}+0.7606\left(\mathrm{sp}^{2.05}\right)_{\mathrm{N}}$ |  |
| $\begin{array}{ll} \hline \mathbf{L i} & \sigma \\ & \pi \end{array}$ | $0.6557\left(\mathrm{sp}^{1.92}\right)_{\mathrm{C}}+0.7550\left(\mathrm{sp}^{2.08}\right)_{\mathrm{N}}$ | $0.6116\left(\mathrm{sp}^{2.62}\right)_{\mathrm{C}}+0.7912\left(\mathrm{sp}^{1.91}\right)_{\mathrm{N}}$ |
| $\begin{array}{ll} \mathrm{Na} & \sigma \\ & \pi \\ \hline \end{array}$ | $0.6540\left(\mathrm{sp}^{1.95}\right)_{\mathrm{C}}+0.7565\left(\mathrm{sp}^{2.08}\right)_{\mathrm{N}}$ | $0.6132\left(\mathrm{sp}^{2.58}\right)_{\mathrm{C}}+0.7899\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ |
| $\begin{array}{ll} \mathbf{K} & \sigma \\ & \pi \\ \hline \end{array}$ | $0.6548\left(\mathrm{sp}^{1.94}\right) \mathrm{C}^{+0.7558\left(\mathrm{sp}^{2.08}\right)_{\mathrm{N}}}$ | $0.6125\left(\mathrm{sp}^{2.59}\right)_{\mathrm{C}}+0.7904\left(\mathrm{sp}{ }^{1.90}\right)_{\mathrm{N}}$ |
| $\begin{array}{cc} \hline \mathbf{R b} & \sigma \\ & \pi \end{array}$ | $0.6537\left(\mathrm{sp}^{1.95}\right)_{\mathrm{C}}+0.7567\left(\mathrm{sp}^{2.08}\right)_{\mathrm{N}}$ | $0.6134\left(\mathrm{sp}^{2.57}\right)_{\mathrm{C}}+0.7898\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ |
| $\begin{array}{ll} \text { Cs } & \sigma \\ & \pi \\ \hline \end{array}$ | $0.6534\left(\mathrm{sp}^{1.96}\right)_{\mathrm{C}}+0.7570\left(\mathrm{sp}^{2.08}\right)_{\mathrm{N}}$ | $0.6136\left(\mathrm{sp}^{2.57}\right)_{\mathrm{C}}+0.7896\left(\mathrm{sp}^{1.89}\right)_{\mathrm{N}}$ |
| $\begin{array}{lc} \hline \mathbf{M g} & \sigma \\ & \pi \\ \hline \end{array}$ | $0.6585\left(\mathrm{sp}^{1.84}\right)_{\mathrm{C}}+0.7525\left(\mathrm{sp}^{2.03}\right)_{\mathrm{N}}$ | $0.6118\left(\mathrm{sp}^{2.62}\right)_{\mathrm{C}}+0.7910\left(\mathrm{sp}^{1.95}\right)_{\mathrm{N}}$ |
| $\begin{array}{ll} \mathrm{Ca} & \sigma \\ & \pi \\ \hline \end{array}$ | $0.6578\left(\mathrm{sp}^{1.88}\right)_{\mathrm{C}}+0.7532\left(\mathrm{sp}^{2.06}\right)_{\mathrm{N}}$ | $0.6114\left(\mathrm{sp}^{2.63}\right)_{\mathrm{C}}+0.7913\left(\mathrm{sp}^{1.93}\right)_{\mathrm{N}}$ |
| $\begin{array}{ll} \text { Sr } & \sigma \\ & \pi \\ \hline \end{array}$ | $0.6573\left(\mathrm{sp}^{1.89}\right)_{\mathrm{C}}+0.7536\left(\mathrm{sp}^{2.06}\right)_{\mathrm{N}}$ | $0.6116\left(\mathrm{sp}^{2.62}\right)_{\mathrm{C}}+0.7911\left(\mathrm{sp}^{1.92}\right)_{\mathrm{N}}$ |
| $\begin{array}{cc} \hline \mathbf{B a} & \sigma \\ & \pi \end{array}$ | $0.6569\left(\mathrm{sp}^{1.90}\right)_{\mathrm{C}}+0.7540\left(\mathrm{sp}^{2.06}\right)_{\mathrm{N}}$ | $0.6119\left(\mathrm{sp}^{2.61}\right)_{\mathrm{C}}+0.7909\left(\mathrm{sp}^{1.92}\right)_{\mathrm{N}}$ |

Table6. Enthalpy ( $\Delta H=$ MIA), Entropy (TS) and Free Energy ( $\Delta \mathbf{G}$ ) variations for the formation process of (I),(II) and (III) complexes ,at 298 K , computed in HF level of theory ${ }^{\text {a,b }}$

| K |  | $\Delta \mathbf{G}^{298 \mathrm{~K}}$ |  | T $\Delta \mathbf{S}^{298} \mathrm{~K}$ |  | $\Delta \mathbf{H}^{298 \mathrm{~K}}$ |  |  |
| :---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  | III | I | III | I | III | I | III | I |


| 1.078 | 1.04 | -44.826 | -28.778 |
| :--- | :--- | :--- | :--- |
|  |  |  | - |

${ }^{\text {a }}$ All values are in $\mathrm{kcal} / \mathrm{mol}$.
${ }^{\mathrm{b}}$ basis set for $\mathrm{M}=\mathrm{Li}, \mathrm{Na}, \mathrm{K}, \mathrm{Rb}, \mathrm{Cs}, \mathrm{Mg}, \mathrm{Ca}, \mathrm{Sr}$ and Ba is LANL2DZ and for other atoms is $6-31+\mathrm{G}^{*}$.Also, electron core potential for $\mathrm{M}=\mathrm{Na}, \mathrm{K}, \mathrm{Rb}, \mathrm{Cs}, \mathrm{Mg}, \mathrm{Ca}, \mathrm{Sr}$ and Ba has been considered.

Table7. Mulliken population of $\mathbf{M}, \mathbf{N 6 , N 1}$ and $\mathbf{N} 7$ in Metalated adenine in HF level

| N6 |  |  | M |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{n n}$ | III | I |  | III |  |
| $\mathbf{M}^{\mathbf{n +}}$ |  |  |  |  |  |
| -0.396867 | -0.082242 |  | - | - |  |
|  |  |  |  |  | $\mathbf{l}$ |
| -0.311485 | -0.048770 |  | 0.736386 | 0.741244 | $\mathbf{L i}$ |
| -0.316927 | -0.044159 |  | 0.889606 | 0.896444 | $\mathbf{N a}$ |
| -0.333062 | -0.046806 |  | 0.987405 | 0.989812 | $\mathbf{K}$ |
| -0.340211 | -0.050137 |  | 0.984515 | 0.986867 | $\mathbf{R b}$ |
| -0.346903 | -0.055422 |  | 0.981172 | 0.982318 | $\mathbf{C s}$ |
| -0.320833 | -0.075650 |  | 1.552677 | 1.678411 | $\mathbf{M g}$ |
| -0.350274 | -0.072198 |  | 1.917541 | 1.944982 | $\mathbf{C a}$ |
| -0.352963 | -0.062713 |  | 1.973272 | 1.984358 | $\mathbf{S r}$ |
| -0.358206 | -0.055803 |  | 1.952173 | 1.956577 | $\mathbf{B a}$ |


| N7 |  | N1 |  | $M^{\text {n+ }}$ |
| :---: | :---: | :---: | :---: | :---: |
| III | II | III | II |  |


| -0.550024 | -0.420400 | -0.422568 | -0.482976 |  |
| :--- | :--- | :--- | :--- | :--- |
|  |  |  |  | $=$ |
| -0.400035 | -0.378204 | -0.204686 | -0.444904 | $\mathbf{L i}$ |
| -0.546330 | -0.532491 | -0.204618 | -0.449955 | $\mathbf{N a}$ |
| -0.618647 | -0.606816 | -0.207573 | -0.458440 | $\mathbf{K}$ |
| -0.592283 | -0.582329 | -0.210698 | -0.458760 | $\mathbf{R b}$ |
| -0.541416 | -0.530061 | -0.214611 | -0.461215 | $\mathbf{C s}$ |
| -0.666646 | -0.626793 | -0.147151 | -0.389965 | $\mathbf{M g}$ |
| -0.837168 | -0.802673 | -0.162736 | -0.411710 | $\mathbf{C a}$ |
| -0.836353 | -0.810539 | -0.167240 | -0.419028 | $\mathbf{S r}$ |
| -0.790060 | -0.763977 | -0.169887 | -0.423471 | $\mathbf{B a}$ |

Table8. Natural population of M, N6,N1 and N7 in Metalated adenine in HF level

| N6 |  |  | M |  | ${ }^{\mathbf{n +}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| III | I |  | III | I |  |
| -0.79878 | -0.87902 |  | - | - |  |
|  |  |  |  |  | $=$ |
| -0.77968 | -0.87156 |  | 0.97983 | 0.98107 | $\mathbf{L i}$ |
| -0.79045 | -0.87359 |  | 0.98692 | 0.98754 | $\mathbf{N a}$ |
| -0.80034 | -0.87528 |  | 0.99648 | 0.99650 | $\mathbf{K}$ |
| -0.80381 | -0.87601 |  | 0.99749 | 0.99744 | $\mathbf{R b}$ |
| -0.80729 | -0.87680 |  | 0.99898 | 0.99883 | $\mathbf{C s}$ |
| -0.77629 | -0.86975 |  | 1.89007 | 1.92583 | $\mathbf{M g}$ |
| -0.77261 | -0.87403 |  | 1.97862 | 1.98090 | $\mathbf{C a}$ |
| -0.78017 | -0.87474 |  | 1.98789 | 1.98835 | $\mathbf{S r}$ |
| -0.78842 | -0.87537 |  | 1.99491 | 1.99457 | $\mathbf{B a}$ |


| N7 |  |  | N1 |  | ${ }^{\mathbf{n}+}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| III | II |  | III | II |  |
| -0.52329 | -0.53545 |  | -0.69443 | -0.66420 |  |
|  |  |  |  |  | $\mathbf{n}$ |
| -0.76022 | -0.78118 |  | -0.69066 | -0.63658 | $\mathbf{L i}$ |
| -0.69266 | -0.71147 |  | -0.69204 | -0.64211 | $\mathbf{N a}$ |
| -0.65217 | -0.66881 |  | -0.69344 | -0.64678 | $\mathbf{K}$ |
| -0.63653 | -0.65262 |  | -0.69401 | -0.64849 | $\mathbf{R b}$ |
| -0.62256 | -0.63839 |  | -0.69461 | -0.65020 | $\mathbf{C s}$ |
| -0.91972 | -0.98031 |  | -0.66656 | -0.60018 | $\mathbf{M g}$ |
| -0.85297 | -0.88350 |  | -0.67799 | -0.61278 | $\mathbf{C a}$ |
| -0.82061 | -0.84795 |  | -0.68017 | -0.61683 | $\mathbf{S r}$ |
| -0.78819 | -0.81257 |  | -0.68217 | -0.62103 | $\mathbf{B a}$ |

Table9. Change in Natural Population of N6,N1 and N7 after metalation , $\Delta_{\text {Population }}$.

| N1 |  |  | N6 |  | ${ }_{c}^{\text {n+ }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| III | II |  | III | I |  |
| 0.00000 | 0.00000 |  | 0.00000 | 0.00000 |  |
|  |  |  |  |  | $=$ |
| 0.00377 | 0.02762 |  | 0.01910 | 0.00746 | $\mathbf{L i}$ |
| 0.00239 | 0.02209 |  | 0.00833 | 0.00543 | $\mathbf{N a}$ |
| 0.00099 | 0.01742 |  | -0.00156 | 0.00374 | $\mathbf{K}$ |
| 0.00042 | 0.01571 |  | -0.00503 | 0.00301 | $\mathbf{R b}$ |
| -0.00018 | 0.01400 |  | -0.00851 | 0.00222 | $\mathbf{C s}$ |
| 0.02787 | 0.06402 |  | 0.02249 | 0.00927 | $\mathbf{M g}$ |
| 0.01644 | 0.05142 |  | 0.02617 | 0.00499 | $\mathbf{C a}$ |
| 0.01426 | 0.04737 |  | 0.01861 | 0.00428 | $\mathbf{S r}$ |
| 0.01226 | 0.04317 | 0.01036 | 0.00365 | $\mathbf{B a}$ |  |


| N7 |  | $M^{\text {n+ }}$ |
| :---: | :---: | :---: |
| III | II |  |
| 0.00000 | 0.00000 |  |
| -0.23693 | -0.24573 | Li |
| -0.16937 | -0.17602 | Na |
| -0.12888 | -0.13336 | K |
| -0.11324 | -0.11717 | Rb |
| -0.09927 | -0.10294 | Cs |
| -0.39643 | -0.44486 | Mg |
| -0.32968 | -0.34805 | Ca |
| -0.29732 | -0.3125 | Sr |
| -0.26490 | -0.27712 | Ba |

Table 10. \%Total Lewis, Highest energy Lewis NBO Lowest and Lowest occupancy in amino and imino tautomer

|  | Amino tautomer |  |  |
| :--- | :---: | :---: | :---: |
| $\mathbf{M}^{\mathbf{n +}}$ | \%Total Lewis | Lowest occupancy | Highest energy Lewis NBO(a.u) ${ }^{\text {a,b }}$ |
| - | 97.3387 | 1.67421 | -0.33645 |


| Li | 97.2982 | 1.68960 | -0.48286 |
| :---: | :---: | :---: | :---: |
| Na | 97.3165 | 1.68416 | -0.46731 |
| K | 97.3247 | 1.68075 | -0.45333 |
| Rb | 97.3276 | 1.67969 | -0.44796 |
| Cs | 97.3302 | 1.67873 | -0.44251 |
| Mg | 96.7308 | 1.22555 | -0.42273 |
| Ca | 97.2434 | 1.69331 | -0.59682 |
| Sr | 97.2593 | 1.69009 | -0.58550 |
| Ba | 97.2733 | 1.68748 | -0.57383 |


| Imino tautomer |  |  |  |
| :---: | :---: | :---: | :---: |
| $\mathbf{M}^{\mathbf{n +}}$ | \%Total Lewis | Lowest occupancy | Highest energy Lewis NBO(a.u) |
|  |  |  |  |
| - | 97.7595 | 1.77561 | -0.35438 |
| Li | 97.7095 | 1.77482 | -0.50963 |
| Na | 97.7139 | 1.77052 | -0.49478 |
| K | 97.7179 | 1.76840 | -0.48114 |
| Rb | 97.7203 | 1.76796 | -0.47590 |
| Cs | 97.7219 | 1.76751 | -0.47040 |
| Mg | 97.5652 | 1.64639 | -0.65745 |
| Ca | 97.6271 | 1.76395 | -0.62967 |
| Sr | 97.6393 | 1.76310 | -0.61748 |
| Ba | 97.6499 | 1.76226 | -0.60494 |

NBO for all elements is BD (2) C 4- C 5
But for Mg is LP (1) C 5 in (I) and . is BD (2) C 4- C 5 But for Mg is LP (1) N 1

Table11. The stabilization energy $\mathbf{E}$ (2) associated with delocalization for interactions that to give the strongest stabilization.

| III |  | I |  | $\mathbf{M}^{\text {n+ }}$ |
| :---: | :---: | :---: | :---: | :---: |
| Acceptor NBO | Donor NBO | Acceptor NBO | Donor NBO |  |
| BD*(2) C 4-C 5 | BD* (2) N 8-C7 | BD* (2) C 4-C 5 | BD* (2) C 6-N 1 |  |
| $\mathrm{BD}^{*}$ (2) C $2-\mathrm{N} 3$ | BD* (2) C 4-C 5 | BD* (2) N3-C2 | BD* (2) C 6-N 1 | Li |
| $\mathrm{BD}^{*}(2) \mathrm{C} 2-\mathrm{N} 3$ | BD* (2) C 4-C 5 | BD* (2) N3-C2 | $\mathrm{BD}^{*}(2) \mathrm{C} 6-\mathrm{N} 1$ | Na |
| $\mathrm{BD}^{*}$ (2) N 6-C 6 | BD* (2) C 4-C 5 | BD* (2) N3-C2 | $\mathrm{BD}^{*}(2) \mathrm{C} 6-\mathrm{N} 1$ | K |
| BD* (2) N 6-C 6 | BD* (2) C 4-C 5 | BD* (2) N3-C2 | BD* (2) C 6-N 1 | Rb |
| BD* (2) N 6-C 6 | BD* (2) C 4-C 5 | BD* (2) N3-C2 | BD* (2) C 6-N 1 | Cs |
| BD* (2) N 7-C8 | LP ( 1) N19 | BD* (2) C 4-N 9 | LP (1) C 5 | Mg |
| BD* (2) N 6-C 6 | BD* (2) C 4-C 5 | BD* (2) C 6-N 1 | BD* (2) C 4-C 5 | Ca |
| $\mathrm{BD}^{*}(2) \mathrm{N} 6-\mathrm{C} 2$ | BD* (2) C 4-C 5 | BD* (2) C 6-N 1 | BD* (2) C 4-C 5 | Sr |


| $\mathbf{E}(\mathbf{2}) \mathbf{k c a l} / \mathbf{m o l}$ |  | $\mathbf{M}^{\mathbf{n +}}$ |
| :---: | :---: | :---: |
| III | I |  |
| 275.90 | 530.13 | - |
| 262.30 | 235.23 | Li |
| 309.88 | 238.26 | Na |
| 119.66 | 248.02 | K |
| 122.15 | 252.75 | Rb |
| 123.82 | 258.01 | Cs |
| 136.28 | 343.35 | Mg |
| 230.83 | 409.76 | Ca |
| 219.14 | 463.73 | Sr |
| 211.60 | 526.30 | Ba |

