

Internet Electronic Journal of Molecular Design

December 2004, Volume 3, Number 12, Pages 789–801

Editor: Ovidiu Ivanciuc

Proceedings of the Internet Electronic Conference of Molecular Design, IECMD 2003
November 23 – December 6, 2003
Part 6

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Majid Monajjemi,¹ Sepideh Ketabi,² Reza Ghiasi,² Karim Zare,¹ Hoda Passdar,³
Mehrnoosh Karimkhani,² and Lyla Saedi¹

¹ Science and Research Branch, Islamic Azad University, P.O. Box 14515–775, Tehran, Iran

² Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran

³ Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

Received: October 15, 2003; Revised: March 14, 2004; Accepted: June 3, 2004; Published: December 31, 2004

Citation of the article:

M. Monajjemi, S. Ketabi, R. Ghiasi, K. Zare, H. Passdar, M. Karimkhani, and L. Saedi, Theoretical study of interaction between adenine and M^+ ($M = \text{Li, Na, K, Rb, Cs}$) and M^{2+} ($M = \text{Mg, Ca, Sr, Ba}$), *Internet Electron. J. Mol. Des.* **2004**, *3*, 789–801, <http://www.biochempress.com>.

Theoretical study of interaction between adenine and M^+ ($M = \text{Li, Na, K, Rb, Cs}$) and M^{2+} ($M = \text{Mg, Ca, Sr, Ba}$)[#]

Majid Monajjemi,^{1,*} Sepideh Ketabi,² Reza Ghiasi,² Karim Zare,¹ Hoda Passdar,³
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¹ Science and Research Branch, Islamic Azad University, P.O. Box 14515–775, Tehran, Iran

² Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran

³ Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

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Internet Electron. J. Mol. Des. 2004, 3 (12), 789–801

Abstract

Motivation. The interaction of alkali and alkaline earth metals with adenine is an interesting target of studies in connection with bioinorganic chemistry and biological chemistry of toxicity and carcinogenicity. We studied interactions of one of the N7 of adenine and its tautomer with alkali metals (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) and alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) by *ab initio* calculations. The stability of these species has been studied in gas phase. The characterization of C8–N9, C8–N7, N7–C5, N4–C3 and N9–C4 bonds has been made with the NBO method and the interactions that cause the strongest stabilization have been studied, as well. The stability of metalated adenine and its tautomer has been studied thermochemically. The present study reports the quantum chemistry analysis of the metal–assisted tautomerization.

Method. We have used *ab initio* and DFT methods at the HF and B3LYP levels of theory.

Results. The interactions of alkali and alkaline earth metals with N7 of adenine and its tautomer stabilize rare tautomer respect to major form. Thermochemical analysis shows that the stability of metalated adenine is more for less electropositive metals. These results show that the basicity of metalated adenine has been increased. NBO calculations show that in metalated adenine N1 is less basic.

Conclusions. Metalation of N7 of adenine and its tautomer by alkali and earth alkali metals cause to stabilize the rare tautomers. Metalation affects some bonding and structural properties, such as bond distances and atomic charges.

Keywords. Adenine; metalated adenine; *ab initio* calculation; natural bond orbital analysis; NBO.

1 INTRODUCTION

Interaction between metal ions and nucleotides has been the subject of intense research because of their significance 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

[#] Presented in part at the Internet Electronic Conference of Molecular Design, IECMD 2003.

* Correspondence author; E-mail: m_monajjemi@yahoo.com.

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 [3,4]. 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]. Therefore, 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 indicate with more complex nucleic acid polymers.

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 to the phosphate as well as the sugar oxygen atoms or to the base nitrogen and oxygen sites [7]. It has been quite well established that the best metal binding site in the base of purine nucleotides is the N7 site of guanine and adenine. The existence of metal–N7 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 METHODS

The system used in calculations consists of adenine and its tautomer complexed with metal cations. The cations were initially placed at the N7 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+G* basis set [11,12] for C, H and N atoms. For alkali and alkaline earth metals (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) standard LANL2DZ basis set is used [13–16] and Na, K, Rb and Cs are described by the effective core potential (ECP) of Wadt and Hay pseudopotential [11,14] with a doublet– ξ valence using the LANL2DZ. All systems have been optimized at the Hartree–Fock level. For the optimized geometries the correlation energies were calculated with the Becke3LYP density functional theory (DFT). Using the GAUSSIAN 98 suite of program has performed the calculations [11]. We limit the optimization to the planar C_s structures of the base... M^{n+} complexes, where the metal cations M^{n+} interact with the nitrogen atom N7 of adenine.

The natural bond orbital analysis (NBO) [17–21] has been performed by using NBO as implement in the GAUSSIAN98. The 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 examining all possible interactions between filled (donor) Lewis type NBOs and empty (acceptor) non Lewis NBOs and estimating their energetic importance by 2nd–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:

$$E = \Delta E_{ij} = q_i \frac{F^2(i, j)}{\epsilon_j - \epsilon_i}$$

where q_i is the donor orbital occupancy, ϵ_i , ϵ_j are diagonal elements (orbital energies) and $F(i, j)$ is the off diagonal NBO Fock matrix element.

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

$$E_I = E(B \dots M^{n+}) - [E(B) + E(M^{n+})] \quad (n = 1 \text{ or } 2)$$

The final interaction energies (E_I) 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:

$$E_{I+BSSE}(B \dots M^{n+}) = E(B \dots M^{n+})_{BM^{n+}} - [E(B)_B + E(M^{n+})_{M^{n+}}] + [E(B')_B - E(B')_{BM^{n+}} + E(M')_{M^{n+}} - E(M')_{BM^{n+}}]$$

where $E(B \dots M^{n+})_{BM^{n+}}$ represents the energy of the complex, $E(B)_B$ the energy of the isolated monomer B with its basis set, $E(B')_B$ the energy of B in its geometry within the complex calculated with its basis set, and $E(B')_{BM^{n+}}$ the energy of B in its geometry within the complex with the complete basis set of the complex ($B \dots M^{n+}$) [34].

Metal ion affinity (MIA) was assumed as the negative of the enthalpy variations (ΔH) for the process:



In other words the MIA corresponds to the dissociation energy of the $B-M^{n+}$ bond.

The variations in zero point energies were considered together thermochemical analysis at 298 K in order to obtain the entropy (ΔS) and free energy (ΔG) variation for the considered process.

3 RESULTS AND DISCUSSION

3.1 Tautomerization 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, Figure 1). As shown in Tables 1 the stabilization of the amino tautomer is larger than that of the imino tautomer. Their relative stabilities are markedly influenced by the metalation. The interaction of the metal with N7 shows that the stabilization of the imino tautomer increases. The first major difference can be found in the relative stability of the tautomer of free and metalated adenine, while the imino tautomer of nonmetalated adenine is destabilized by only 23.03 kcal mol⁻¹ (in HF) with respect to the amino form; metalation caused the destabilization energy to decrease. The differences of energy upon metalation have been shown in Table 1 to increase for different metals (with HF and B3LYP methods). These values show that the results are depending on metals. The stability of the tautomers (I), (II) and (III) is higher for electronegative metals. The stabilization of the imino tautomer of the complexes with bivalent ions is larger than those with monovalent ions.

Table 1. Relative energies (in DFT and Hartree–Fock levels) (kcal/mol) for nonmetalated and metalated structures (I), (II) and (III) in gas phase. Relative Energy of structures (II), (III) is calculated relative to that of structure (I)

M^{n+}	HF			B3LYP		
	I	II	III	I	II	III
–	0.00	65.48	23.03	0.00	50.60	12.96
Li	0.00	60.62	8.28	0.00	46.14	7.19
Na	0.00	60.46	7.94	0.00	45.99	6.92
K	0.00	60.77	8.04	0.00	46.28	7.07
Rb	0.00	60.98	8.15	0.00	46.45	7.14
Cs	0.00	61.21	8.30	0.00	48.42	7.24
Mg	0.00	57.03	-0.08	0.00	42.80	3.62
Ca	0.00	56.21	0.91	0.00	42.80	-3.62
Sr	0.00	56.28	1.16	0.00	41.99	-0.43
Ba	0.00	56.50	1.47	0.00	42.17	0.29

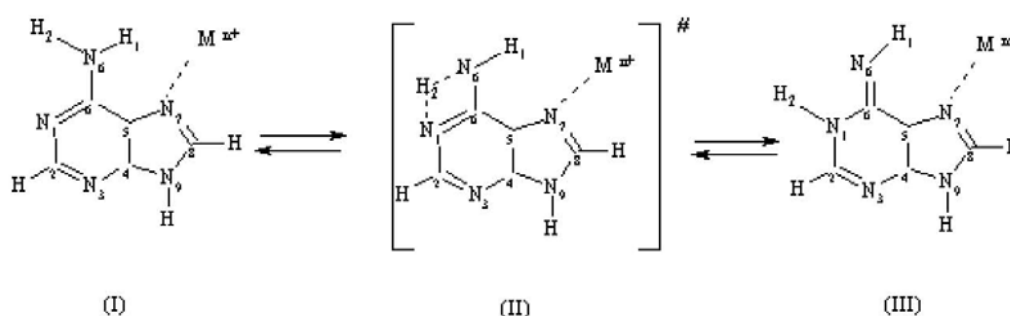


Figure 1. Tautomers of adenine: (I) Amino form (major form); (II) Transition state for transformation of amino form to imino form; (III) Imino form (rare form), M^{n+} interacts with N7.

Transition state. Table 1 shows that the required energy for the transformation of amino to imino tautomer is 65.48 kcal mol⁻¹ (in HF). The metalation caused the energy of the transition state to decrease. This energy is smaller for the more electronegative metals. Also, the calculation shows that the required energy for the transformation of amino to imino tautomer is higher for monovalent ions.

Table 2. E_I (Interaction Energies), BSSE and E_{I+BSSE} (kcal/mol) for metalated structures (I), (II) and (III) at the Hartree-Fock level

M	E_I		BSSE		E_{I+BSSE}	
	I	III	I	III	I	III
Li	-37.70	-50.27	-38.39	-53.11	-76.09	-103.38
Na	-22.67	-32.14	-23.47	-38.52	-46.14	-70.66
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
Mg	-109.05	-155.86	-109.74	-132.74	-218.79	-288.6
Ca	-59.81	-93.11	-59.86	-81.94	-119.67	-175.05
Sr	-47.71	-76.42	-48.26	-70.08	-95.97	-146.5
Ba	-37.45	-61.58	-37.84	-59.37	-75.29	-136.87

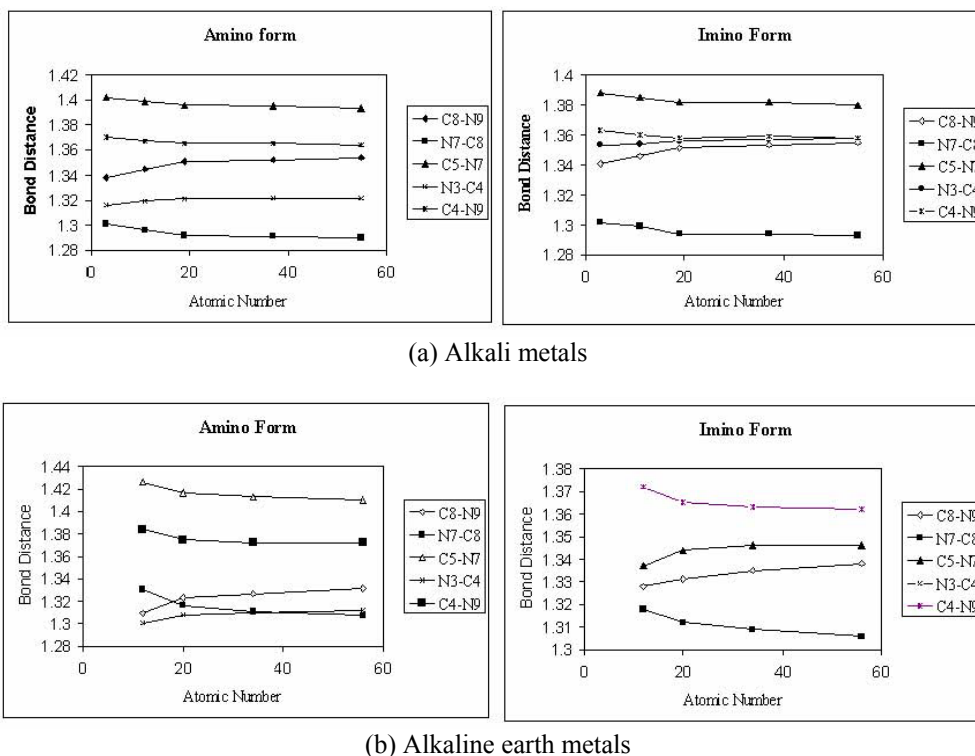
Table 3. Optimized bond distances M–N7 and C6–N6 (Å) and angles M–N7–C4 and C5–C6–N6 (degree) for metalated structures (I), (II) and (III) in gas phase at the Hartree-Fock level

M^{n+}	M–N7			C6–N6			C5–C6–N6			M–N7–C4		
	I	II	III	I	II	III	I	II	III	I	II	III
Li	1.924	1.92	1.93	1.343	1.298	1.261	125.0	142.3	132.7	170.0	162.8	162.8
Na	2.34	2.33	2.34	1.345	1.301	1.263	124.6	142.1	132.4	172.5	163.0	163.4
K	2.81	2.80	2.82	1.344	1.302	1.264	124.2	142.0	132.1	175.7	164.2	164.4
Rb	3.05	3.02	3.06	1.345	1.303	1.264	124.0	142.0	131.9	176.7	164.8	164.7
Cs	3.32	3.28	3.33	1.345	1.303	1.264	123.7	141.9	131.8	177.6	165.5	165.0
Mg	1.946	1.94	1.95	1.345	1.298	1.280	126.6	142.7	132.3	167.0	159.2	144.9
Ca	2.38	2.38	2.40	1.349	1.308	1.274	126.0	142.3	131.9	170.0	156.8	156.0
Sr	2.57	2.56	2.59	1.349	1.309	1.274	125.8	142.3	131.7	171.3	157.5	157.8
Ba	2.78	2.77	2.81	1.350	1.310	1.273	125.5	142.3	131.5	172.9	158.5	159.5

3.2 The 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 the atomic number of M. This increasing is due to the larger dipole moments for metalated adenine with heavy atoms (Table 1). Also, Table 2 shows that the strongest bonding interactions are found for the complexes of adenine with alkaline earth metals.

Table 2 shows the value of BSSE for the metalated imino and amino tautomers. It is clear that for all complexes the BSSE values are small.



(a) Alkali metals

(b) Alkaline earth metals

Figure 2. 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.

3.3 Geometry 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 monotonically increase with the atomic number for the alkaline and alkaline earth metals (Table 3, Figure 2). The increase is more pronounced where this difference is about 1.4 Å in metalated amino and imino tautomer by alkali metal. Table 3 shows that the $C5-C6-N7$ bond angle of any structures (I), (II) and (III) decreases by about 1° in any group, while the $C6-N6$ distance is almost not changed. Correlation between the bond length changes and stabilization energy was found for all types of complexes.

3.3.2 Intramolecular 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 from X-ray measurements. Because the complexes were held planar, the dihedral angles were not allowed to change. The five largest bond length deviations of adenine...M complexes are summarized in Table 4 (distances C4-N9, N3-C4, C5-N7, N7-C8, and C8-N9). Table 4 shows that all important bond length changes are localized in the five-member ring.

Table 4. Optimized bond distances C8–N9, N7–C8, C5–N7, N3–C4 and C4–N9 (Å) for metalated structures (I), (II) and (III) in gas phase at the Hartree–Fock level

M ⁿ⁺	C8–N9			N7–C8			C5–N7		
	I	II	III	I	II	III	I	II	III
–	1.370	1.372	1.365	1.281	1.280	1.284	1.383	1.379	1.372
Li	1.338	1.344	1.341	1.301	1.298	1.302	1.402	1.395	1.388
Na	1.345	1.350	1.346	1.296	1.293	1.299	1.399	1.392	1.385
K	1.351	1.355	1.351	1.292	1.290	1.294	1.396	1.391	1.382
Rb	1.352	1.357	1.353	1.291	1.289	1.294	1.395	1.389	1.382
Cs	1.354	1.358	1.355	1.290	1.288	1.293	1.393	1.388	1.380
Mg	1.309	1.317	1.328	1.330	1.323	1.318	1.426	1.415	1.395
Ca	1.323	1.331	1.331	1.316	1.309	1.312	1.416	1.408	1.394
Sr	1.327	1.335	1.335	1.311	1.305	1.309	1.413	1.405	1.396
Ba	1.332	1.339	1.338	1.307	1.303	1.306	1.410	1.403	1.394

M ⁿ⁺	N3–C4			C4–N9		
	I	II	III	I	II	III
–	1.328	1.344	1.365	1.362	1.356	1.356
Li	1.316	1.329	1.353	1.370	1.365	1.363
Na	1.319	1.332	1.354	1.367	1.362	1.360
K	1.321	1.334	1.356	1.365	1.360	1.358
Rb	1.322	1.335	1.357	1.365	1.358	1.359
Cs	1.322	1.336	1.358	1.364	1.358	1.358
Mg	1.301	1.313	1.337	1.384	1.381	1.372
Ca	1.308	1.319	1.344	1.375	1.371	1.365
Sr	1.310	1.321	1.346	1.372	1.368	1.363
Ba	1.312	1.321	1.346	1.372	1.366	1.362

The C8–N9 and N3–C4 distances in (I) and (III) increases with increasing of the atomic number of alkali and alkaline earth metals. The bond strength of C8–N9 and N3–C4 is the following order: (I) > (II). The N7–C5, N7–C8, and C4–N9 distances in (I), (III) are shorter for heavy alkali and earth alkali metal (Figure 2). So, the double bond characterization of the N7–C8 bond increases in the following order: (I) > (II). The bond strength of the C4–N9 and N7–C5 bonds in (I) is higher than in (II). Characterizations of these bonds have been studied by the NBO method. Table 5 shows hybridization coefficients of these bonds.

3.4 Thermochemical Analysis

A thermochemical analysis has been performed for the metalated and non metalated adenine and its tautomers. The values of ΔH , $T\Delta S$ and ΔG are reported in Table 6 in which the individual terms are computed at 298 K. Although the values of the ΔG and ΔH of the complexes are different, the differences of ΔG and ΔH are almost the same for all complexes, therefore the ΔS values must be the same. As can be seen in Table 6, the computed ΔS are similar for all complexes. The equilibrium constants of the all complexes are given in Table 6. This shows that the equilibrium constant is smaller for the more electropositive metals, which is compatible with the symbiosis effect [22]. The ΔG value increases with increasing metal ion radius which shows that the stability

of the complex decreases (see Table 6).

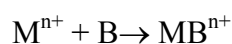
Table 5. Hybridization coefficient of C8-N9, C8-N7, N7-C5, N4-C3 and N9-C4 bonds for metalated amino and imino forms calculated by NBO method at the HF level

M^{n+}		Bond		
		C8-N9	C8-N7	N7-C5
–	σ	$0.609(sp^{2.22})_C + 0.792(sp^{1.94})_N$	$0.776(sp^{1.68})_C + 0.630(sp^{1.97})_N$	$0.773(sp^{1.98})_C + 0.634(sp^{2.4})_N$
	π	–	$0.828(p^{1.00})_C + 0.559(p^{1.00})_N$	–
Na	σ	$0.608(sp^{2.25})_C + 0.793(sp^{1.95})_N$	$0.814(p^{1.00})_C + 0.580(p^{1.00})_N$	$0.768(sp^{2.05})_C + 0.639(sp^{2.36})_N$
	π		$0.773(sp^{1.69})_C + 0.634(sp^{1.93})_N$	
K	σ	$0.607(sp^{2.26})_C + 0.794(sp^{1.95})_N$	$0.771(sp^{1.68})_C + 0.635(sp^{1.90})_N$	$0.766(sp^{2.08})_C + 0.642(sp^{2.33})_N$
	π		$0.803(p^{1.00})_C + 0.595(p^{1.00})_N$	
Rb	σ	$0.607(sp^{2.27})_C + 0.794(sp^{1.95})_N$	$0.771(sp^{1.68})_C + 0.636(sp^{1.89})_N$	$0.765(sp^{2.09})_C + 0.643(sp^{2.33})_N$
	π		$0.800(p^{1.00})_C + 0.599(p^{1.00})_N$	
Cs	σ	$0.606(sp^{2.28})_C + 0.795(sp^{1.95})_N$	$0.771(sp^{1.67})_C + 0.636(sp^{1.89})_N$	$0.764(sp^{2.10})_C + 0.644(sp^{2.32})_N$
	π		$0.797(p^{1.00})_C + 0.603(p^{1.00})_N$	
Mg	σ	$0.615(sp^{2.11})_C + 0.7885(sp^{1.89})_N$	$0.782(sp^{1.74})_C + 0.623(sp^{2.09})_N$	$0.787(sp^{1.90})_C + 0.616(sp^{2.58})_N$
	π		$0.878(p^{1.00})_C + 0.478(p^{1.00})_N$	
Ca	σ	$0.613(sp^{2.15})_C + 0.789(sp^{1.92})_N$	$0.777(sp^{1.72})_C + 0.629(sp^{2.00})_N$	$0.779(sp^{1.96})_C + 0.626(sp^{2.47})_N$
	π		$0.849(p^{1.00})_C + 0.528(p^{1.00})_N$	
Sr	σ	$0.613(sp^{2.16})_C + 0.790(sp^{1.93})_N$	$0.776(p^{1.72})_C + 0.630(sp^{1.98})_N$	$0.777(sp^{1.98})_C + 0.629(sp^{2.44})_N$
	π		$0.840(p^{1.00})_C + 0.542(p^{1.00})_N$	
Ba	σ	$0.612(sp^{2.17})_C + 0.790(sp^{1.93})_N$	$0.775(sp^{1.71})_C + 0.632(sp^{1.96})_N$	$0.775(sp^{2.00})_C + 0.631(sp^{2.42})_N$
	π		$0.831(p^{1.00})_C + 0.555(p^{1.00})_N$	

(b) Imino form

M^{n+}		Bond		
		C8-N9	C8-N7	N7-C5
–	σ	$0.598(sp^{2.33})_C + 0.800(sp^{1.91})_N$	$0.770(sp^{1.69})_C + 0.637(sp^{1.87})_N$	$0.649(sp^{2.27})_C + 0.760(sp^{2.05})_N$
	π		$0.770(p^{1.00})_C + 0.637(p^{1.00})_N$	
Li	σ	$0.606(sp^{2.26})_C + 0.795(sp^{1.93})_N$	$0.777(sp^{1.67})_C + 0.629(sp^{1.99})_N$	$0.634(sp^{2.41})_C + 0.772(sp^{1.95})_N$
	π		$0.821(p^{1.00})_C + 0.570(p^{1.00})_N$	
Na	σ	$0.604(sp^{2.30})_C + 0.796(sp^{1.94})_N$	$0.773(sp^{1.68})_C + 0.634(sp^{1.92})_N$	$0.642(sp^{2.33})_C + 0.766(sp^{2.03})_N$
	π		$0.797(p^{1.00})_C + 0.603(p^{1.00})_N$	
K	σ	$0.605(sp^{2.29})_C + 0.796(sp^{1.93})_N$	$0.774(sp^{1.69})_C + 0.632(sp^{1.95})_N$	$0.639(sp^{2.36})_C + 0.768(sp^{2.00})_N$
	π		$0.807(p^{1.00})_C + 0.590(p^{1.00})_N$	
Rb	σ	$0.603(sp^{2.31})_C + 0.797(sp^{1.94})_N$	$0.772(sp^{1.68})_C + 0.635(sp^{1.92})_N$	$0.643(sp^{2.32})_C + 0.765(sp^{2.04})_N$
	π		$0.794(p^{1.00})_C + 0.607(p^{1.00})_N$	
Cs	σ	$0.603(sp^{2.31})_C + 0.797(sp^{1.94})_N$	$0.772(sp^{1.68})_C + 0.635(sp^{1.91})_N$	$0.644(sp^{2.32})_C + 0.764(sp^{2.05})_N$
	π		$0.791(p^{1.00})_C + 0.611(p^{1.00})_N$	
Mg	σ	$0.610(sp^{2.21})_C + 0.792(sp^{1.92})_N$	$0.785(sp^{1.58})_C + 0.619(sp^{2.11})_N$	$0.627(sp^{2.55})_C + 0.778(sp^{2.04})_N$
	π		$0.867(p^{1.00})_C + 0.496(p^{1.00})_N$	
Ca	σ	$0.609(sp^{2.21})_C + 0.792(sp^{1.93})_N$	$0.779(sp^{1.66})_C + 0.625(sp^{2.02})_N$	$0.631(sp^{2.45})_C + 0.775(sp^{1.99})_N$
	π		$0.843(p^{1.00})_C + 0.537(p^{1.00})_N$	
Sr	σ	$0.609(sp^{2.22})_C + 0.793(sp^{1.93})_N$	$0.778(sp^{1.67})_C + 0.627(sp^{2.00})_N$	$0.633(sp^{2.43})_C + 0.774(sp^{2.00})_N$
	π		$0.834(p^{1.00})_C + 0.550(p^{1.00})_N$	
Ba	σ	$0.608(sp^{2.23})_C + 0.793(sp^{1.93})_N$	$0.777(sp^{1.68})_C + 0.629(sp^{1.98})_N$	$0.635(sp^{2.41})_C + 0.772(sp^{2.00})_N$
	π		$0.826(p^{1.00})_C + 0.562(p^{1.00})_N$	

The result seems correct, because as we have indicated previously, when the metal ion radius increases, the bond length increases and as a result, the bonding strength decreases. Stability constants in Table 6 prove this case. The reaction can be considered as:



Since in this reaction two particles form one, ΔS should have a negative value.

Table 5. (Continued)

M ^{nt+}	Bond		
	N4–C3	N9–C4	
–	σ	$0.656(\text{sp}^{1.80})_{\text{C}} + 0.7547(\text{sp}^{1.89})_{\text{N}}$	$0.609(\text{sp}^{2.67})_{\text{C}} + 0.79(\text{sp}^{1.92})_{\text{N}}$
	π		–
Na	σ	$0.655(\text{sp}^{1.81})_{\text{C}} + 0.7551(\text{sp}^{1.90})_{\text{N}}$	$0.610(\text{sp}^{2.65})_{\text{C}} + 0.792(\text{sp}^{1.90})_{\text{N}}$
	π		
K	σ	$0.655(\text{sp}^{1.82})_{\text{C}} + 0.7555(\text{sp}^{1.90})_{\text{N}}$	$0.611(\text{sp}^{2.63})_{\text{C}} + 0.791(\text{sp}^{1.90})_{\text{N}}$
	π		
Rb	σ	$0.655(\text{sp}^{1.82})_{\text{C}} + 0.7556(\text{sp}^{1.90})_{\text{N}}$	$0.611(\text{sp}^{2.62})_{\text{C}} + 0.791(\text{sp}^{1.90})_{\text{N}}$
	π		
Cs	σ	$0.654(\text{sp}^{1.83})_{\text{C}} + 0.7557(\text{sp}^{1.90})_{\text{N}}$	$0.611(\text{sp}^{2.62})_{\text{C}} + 0.791(\text{sp}^{1.89})_{\text{N}}$
	π		
Mg	σ	$0.658(\text{sp}^{1.74})_{\text{C}} + 0.7525(\text{sp}^{1.86})_{\text{N}}$	$0.604(\text{sp}^{2.80})_{\text{C}} + 0.796(\text{sp}^{1.96})_{\text{N}}$
	π		$0.415(\text{p}^{1.00})_{\text{C}} + 0.909(\text{p}^{1.00})_{\text{N}}$
Ca	σ	$0.657(\text{sp}^{1.77})_{\text{C}} + 0.7532(\text{sp}^{1.88})_{\text{N}}$	$0.606(\text{sp}^{2.73})_{\text{C}} + 0.794(\text{sp}^{1.94})_{\text{N}}$
	π		
Sr	σ	$0.657(\text{sp}^{1.78})_{\text{C}} + 0.7535(\text{sp}^{1.88})_{\text{N}}$	$0.607(\text{sp}^{2.72})_{\text{C}} + 0.794(\text{sp}^{1.93})_{\text{N}}$
	π		
Ba	σ	$0.657(\text{sp}^{1.78})_{\text{C}} + 0.7537(\text{sp}^{1.89})_{\text{N}}$	$0.608(\text{sp}^{2.70})_{\text{C}} + 0.793(\text{sp}^{1.93})_{\text{N}}$
	π		

(b) Imino form			
M ^{nt+}	Bond		
	N4–C3	N9–C4	
–	σ	$0.649(\text{sp}^{1.99})_{\text{C}} + 0.760(\text{sp}^{2.05})_{\text{N}}$	$0.614(\text{sp}^{2.53})_{\text{C}} + 0.788(\text{sp}^{1.84})_{\text{N}}$
	π		
Li	σ	$0.655(\text{sp}^{1.92})_{\text{C}} + 0.755(\text{sp}^{2.08})_{\text{N}}$	$0.611(\text{sp}^{2.62})_{\text{C}} + 0.791(\text{sp}^{1.91})_{\text{N}}$
	π		
Na	σ	$0.654(\text{sp}^{1.95})_{\text{C}} + 0.756(\text{sp}^{2.08})_{\text{N}}$	$0.613(\text{sp}^{2.58})_{\text{C}} + 0.789(\text{sp}^{1.89})_{\text{N}}$
	π		
K	σ	$0.654(\text{sp}^{1.94})_{\text{C}} + 0.755(\text{sp}^{2.08})_{\text{N}}$	$0.612(\text{sp}^{2.59})_{\text{C}} + 0.790(\text{sp}^{1.90})_{\text{N}}$
	π		
Rb	σ	$0.653(\text{sp}^{1.95})_{\text{C}} + 0.756(\text{sp}^{2.08})_{\text{N}}$	$0.613(\text{sp}^{2.57})_{\text{C}} + 0.789(\text{sp}^{1.89})_{\text{N}}$
	π		
Cs	σ	$0.653(\text{sp}^{1.96})_{\text{C}} + 0.757(\text{sp}^{2.08})_{\text{N}}$	$0.613(\text{sp}^{2.57})_{\text{C}} + 0.789(\text{sp}^{1.89})_{\text{N}}$
	π		
Mg	σ	$0.658(\text{sp}^{1.84})_{\text{C}} + 0.752(\text{sp}^{2.03})_{\text{N}}$	$0.611(\text{sp}^{2.62})_{\text{C}} + 0.791(\text{sp}^{1.95})_{\text{N}}$
	π		
Ca	σ	$0.657(\text{sp}^{1.88})_{\text{C}} + 0.753(\text{sp}^{2.06})_{\text{N}}$	$0.611(\text{sp}^{2.63})_{\text{C}} + 0.791(\text{sp}^{1.93})_{\text{N}}$
	π		
Sr	σ	$0.657(\text{sp}^{1.89})_{\text{C}} + 0.753(\text{sp}^{2.06})_{\text{N}}$	$0.611(\text{sp}^{2.62})_{\text{C}} + 0.791(\text{sp}^{1.92})_{\text{N}}$
	π		
Ba	σ	$0.656(\text{sp}^{1.90})_{\text{C}} + 0.754(\text{sp}^{2.06})_{\text{N}}$	$0.611(\text{sp}^{2.61})_{\text{C}} + 0.790(\text{sp}^{1.92})_{\text{N}}$
	π		

3.5 Population Analysis

The Mulliken population analysis, like all atomic charge assignment schemes, is an arbitrary method for assigning atomic charges. Generally, changes in the 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 even 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.

Table 6. Enthalpy ($\Delta H = \text{MIA}$), entropy (TS) and free energy (ΔG) variations for the formation process of (I), (II) and (III) complexes at 298 K, computed at the HF level of theory^{a,b}

M	$\Delta H^{298\text{ K}}$		$T\Delta S^{298\text{ K}}$		$\Delta G^{298\text{ K}}$		K	
	I	III	I	III	I	III	I	III
Li	-37.489	-51.641	-8.711	-6.815	-28.778	-44.826	1.04	1.078
Na	-22.779	-37.557	-8.263	-6.276	-14.516	-31.281	1.024	1.054
K	-12.723	-27.964	-7.685	-8.017	-5.038	-19.947	1.008	1.034
Rb	-9.954	-25.067	-7.468	-7.894	-2.486	-17.173	1.004	1.029
Cs	-7.360	-22.510	-7.023	-7.720	-0.337	-14.790	1.00	1.025
Mg	-109.225	-130.760	-9.042	-5.582	-100.183	-125.178	1.184	1.235
Ca	-60.028	-82.862	-8.665	-8.723	-51.363	-74.139	1.090	1.133
Sr	-47.989	-70.439	-8.488	-8.644	-39.501	-61.795	1.068	1.109
Ba	-37.748	-59.781	-8.194	-8.506	-29.554	-51.275	1.051	1.090

^a all values are in kcal/mol

^b basis set for M = Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba is LANL2DZ and for other atoms is 6-31+G*. Also, electron core potential for M = Na, K, Rb, Cs, Mg, Ca, Sr and Ba has been considered

Table 7. Mulliken population of M, N6, N1 and N7 in metalated adenine at the HF level

M ⁿ⁺	M		N6		N1		N7	
	I	III	I	III	II	III	II	III
-	-	-	-0.082242	-0.396867	-0.482976	-0.422568	-0.420400	-0.550024
Li	0.741244	0.736386	-0.048770	-0.311485	-0.444904	-0.204686	-0.378204	-0.400035
Na	0.896444	0.889606	-0.044159	-0.316927	-0.449955	-0.204618	-0.532491	-0.546330
K	0.989812	0.987405	-0.046806	-0.333062	-0.458440	-0.207573	-0.606816	-0.618647
Rb	0.986867	0.984515	-0.050137	-0.340211	-0.458760	-0.210698	-0.582329	-0.592283
Cs	0.982318	0.981172	-0.055422	-0.346903	-0.461215	-0.214611	-0.530061	-0.541416
Mg	1.678411	1.552677	-0.075650	-0.320833	-0.389965	-0.147151	-0.626793	-0.666646
Ca	1.944982	1.917541	-0.072198	-0.350274	-0.411710	-0.162736	-0.802673	-0.837168
Sr	1.984358	1.973272	-0.062713	-0.352963	-0.419028	-0.167240	-0.810539	-0.836353
Ba	1.956577	1.952173	-0.055803	-0.358206	-0.423471	-0.169887	-0.763977	-0.790060

Table 8. Natural population of M, N6, N1 and N7 in metalated adenine at the HF level

M ⁿ⁺	M		N6		N1		N7	
	I	III	I	III	II	III	II	III
-	-	-	-0.87902	-0.79878	-0.66420	-0.69443	-0.53545	-0.52329
Li	0.98107	0.97983	-0.87156	-0.77968	-0.63658	-0.69066	-0.78118	-0.76022
Na	0.98754	0.98692	-0.87359	-0.79045	-0.64211	-0.69204	-0.71147	-0.69266
K	0.99650	0.99648	-0.87528	-0.80034	-0.64678	-0.69344	-0.66881	-0.65217
Rb	0.99744	0.99749	-0.87601	-0.80381	-0.64849	-0.69401	-0.65262	-0.63653
Cs	0.99883	0.99898	-0.87680	-0.80729	-0.65020	-0.69461	-0.63839	-0.62256
Mg	1.92583	1.89007	-0.86975	-0.77629	-0.60018	-0.66656	-0.98031	-0.91972
Ca	1.98090	1.97862	-0.87403	-0.77261	-0.61278	-0.67799	-0.88350	-0.85297
Sr	1.98835	1.98789	-0.87474	-0.78017	-0.61683	-0.68017	-0.84795	-0.82061
Ba	1.99457	1.99491	-0.87537	-0.78842	-0.62103	-0.68217	-0.81257	-0.78819

The Mulliken charges for M, N1, N6 and N7 on metalated adenine (I) and (II) are given in Table 7. The analysis of the atomic charges is studied by the natural bonding orbital (NBO) method, as well. Atomic charges of the selected atoms of metalated adenine M, N1, N6 and N7 in amino and

imino tautomers are shown in Table 8.

Table 9. Change in natural population of N6, N1 and N7 after metalation, Δ Population

M ⁿ⁺	N6		N1		N7	
	I	III	II	III	II	III
–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Li	0.00746	0.01910	0.02762	0.00377	–0.24573	–0.23693
Na	0.00543	0.00833	0.02209	0.00239	–0.17602	–0.16937
K	0.00374	–0.00156	0.01742	0.00099	–0.13336	–0.12888
Rb	0.00301	–0.00503	0.01571	0.00042	–0.11717	–0.11324
Cs	0.00222	–0.00851	0.01400	–0.00018	–0.10294	–0.09927
Mg	0.00927	0.02249	0.06402	0.02787	–0.44486	–0.39643
Ca	0.00499	0.02617	0.05142	0.01644	–0.34805	–0.32968
Sr	0.00428	0.01861	0.04737	0.01426	–0.3125	–0.29732
Ba	0.00365	0.01036	0.04317	0.01226	–0.27712	–0.26490

Table 10. %Total Lewis, highest energy Lewis NBO lowest and lowest occupancy in amino and imino tautomer

M ⁿ⁺	Amino tautomer			Imino tautomer		
	%Total Lewis	Lowest occupancy	Highest energy Lewis NBO(a.u) ^a	%Total Lewis	Lowest occupancy	Highest energy Lewis NBO(a.u)
–	97.3387%	1.67421	–0.33645	97.7595%	1.77561	–0.35438
Li	97.2982%	1.68960	–0.48286	97.7095	1.77482	–0.50963
Na	97.3165%	1.68416	–0.46731	97.7139	1.77052	–0.49478
K	97.3247%	1.68075	–0.45333	97.7179	1.76840	–0.48114
Rb	97.3276%	1.67969	–0.44796	97.7203	1.76796	–0.47590
Cs	97.3302%	1.67873	–0.44251	97.7219	1.76751	–0.47040
Mg	96.7308%	1.22555	–0.42273	97.5652	1.64639	–0.65745
Ca	97.2434%	1.69331	–0.59682	97.6271	1.76395	–0.62967
Sr	97.2593%	1.69009	–0.58550	97.6393	1.76310	–0.61748
Ba	97.2733%	1.68748	–0.57383	97.6499	1.76226	–0.60494

^a NBO for all elements is BD(2)C4–C5, but for Mg is LP(1)N1

It is possible to identify principal delocalizing acceptor orbitals associated with each donor NBO and their topological relationship to this NBO, *i.e.*, whether it is attached to the same atom (geminal), to an adjacent bonded atom (vicinal) or to a more remote site. These acceptor NBOs will generally correspond to the principal 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). Therefore, the basicity of N6 decreases with metalation.

The Lewis NBO s in Table 10 describes percentage of the total density, with the remaining non Lewis density found primarily in the valence–shell antibonding. In metalated amino tautomers the BD(2)C4–C5 is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into BD*(2) C6–N1, BD*(2) N7–C8, BD*(2) N3–C2, RY*(2) N7, RY*(1) N9, RY*(3) N3, BD*(2) C4– C5, RY*(9) C6, RY*(5) C6, RY*(8) N7. But for the amino tautomer with M = Mg, the LP (1) C5 is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into BD*(2) C4–N9, BD*(2) C6–N1, BD*(2) N7–C8, RY*(1) N7, RY*(8) C4, RY*(5) C6, RY*(5) C5, RY*(9) C6, RY*(7) N7, RY*(3) C5, RY*(8) C5.

In metalated imino tautomers the BD (2) C4–C5 is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into BD*(2) N6–C6, BD*(2) N7–C8, BD*(2) C2–N3, RY*(2) N7, RY*(1) N9, RY*(3) N3, BD*(2) C4–C5, RY*(8) N7, RY*(3) C6, RY*(9) C6. For imino tautomers with $M = \text{Mg}$, the LP (1) N1 is seen to be the lowest occupancy and highest energy Lewis NBO and to be primarily delocalized into BD*(2) C2–N3, BD*(2) N6–C6, RY*(3) C2, RY*(2) C6, RY*(6) C2, RY*(6) C6, RY*(1) N1, RY*(11) C6.

Table 11. The stabilization energy $E(2)$ associated with delocalization for interactions that to give the strongest stabilization

M^{\square}	I		III		E(2) kcal/mol	
	Donor NBO	Acceptor NBO	Donor NBO	Acceptor NBO	I	III
–	BD*(2) C 6–N 1	BD*(2) C 4–C 5	BD*(2) N 8–C 7	BD*(2) C 4–C 5	530.1	275.9
Li	BD*(2) C 6–N 1	BD*(2) N3–C 2	BD*(2) C 4–C 5	BD*(2) C 2–N 3	235.2	262.3
Na	BD*(2) C 6–N 1	BD*(2) N3–C 2	BD*(2) C 4–C 5	BD*(2) C 2–N 3	238.2	309.8
K	BD*(2) C 6–N 1	BD*(2) N3–C 2	BD*(2) C 4–C 5	BD*(2) N 6–C 6	248.0	119.6
Rb	BD*(2) C 6–N 1	BD*(2) N3–C 2	BD*(2) C 4–C 5	BD*(2) N 6–C 6	252.7	122.1
Cs	BD*(2) C 6–N 1	BD*(2) N3–C 2	BD*(2) C 4–C 5	BD*(2) N 6–C 6	258.0	123.8
Mg	LP (1) C 5	BD*(2) C 4–N 9	LP (1) N19	BD*(2) N 7–C 8	343.3	136.2
Ca	BD*(2) C 4–C 5	BD*(2) C 6–N 1	BD*(2) C 4–C 5	BD*(2) N 6–C 6	409.7	230.8
Sr	BD*(2) C 4–C 5	BD*(2) C 6–N 1	BD*(2) C 4–C 5	BD*(2) N 6–C 2	463.7	219.1
Ba	BD*(2) C 4–C 5	BD*(2) C 6–N 1	BD*(2) C 4–C 5	BD*(2) N 6–C 6	526.3	211.6

3.6 Donor Acceptor Interaction Perturbation Theory Energy Analysis

The localized orbitals in the best Lewis structure can interact strongly. A filled bonding or lone pair orbital can act as a donor and an empty or antibonding orbital can act as an acceptor. These interactions can strengthen and weaken bonds. For example, a lone pair donor→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 the best Lewis structure will also show up as donor–acceptor interactions. Table 11 shows the interactions that give the strongest stabilization.

4 CONCLUSIONS

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 (Li, Na, K, Rb and Cs) and alkaline earth metals (Mg, Ca, Sr and Ba) stabilize the imino tautomer compared to the major form.
2. Metalation caused a decrease for the transition state energy of transformation from amino form to imino form.
3. The required energy for transformation of amino to imino tautomer is higher for monovalent ions.

4. Metalation decreases the 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 the amino form decrease with increasing atomic number of the alkali metal.
7. The C4–N9 and N7–C8 distances in the imino form decrease with increasing atomic number of the metal.

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