Adsorption of neutral and protonated Lewis bases on Na₈-nanocluster: basicity enhancement of the Lewis bases

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Abstract. Structural and energetic properties of Na_n (n = 1–8) nanoclusters were studied employing the B3LYP method and using 6-31+(d,p) basis set. Comparison of the calculated binding energies per atom (E_b) of the cluster shows that the Na₈ cluster with D_{2d} symmetry group is the most stable structure among the Na_n clusters. Adsorption of neutral and protonated forms of ammonia, methylamine, ethylamine, hydrazine, guanidine, pyridine, methanolamine, and methanimine on Na₈ cluster was studied. Interaction of the neutral Lewis bases with Na₈ was very weak such that the interaction energies were smaller than -50 kJ mol^{-1} . However, the protonated bases interact with Na₈ more strongly with interaction energies generally in the range of -90 to -350 kJ mol^{-1} . The protonated forms of methanolamine undergo dissociative adsorption on Na₈ with adsorption energies of about -800 kJ mol^{-1} . Since the protonated bases are stabilized more than the corresponding neutral ones upon adsorption on Na₈ cluster, the basicity of the Lewis bases enhances in the presence of Na₈. The calculated proton affinities of the isolated Lewis bases were smaller than 990 kJ mol^{-1} while in the presence of the Na₈ cluster, the basicity increases so that the calculated proton affinities were higher than 1000 kJ mol^{-1} .

Keywords. Na₈-nanocluster; proton affinity; lewis base; DFT; adsorption.

1. Introduction

Strong acids and bases are important molecules having a wide application in chemistry. These compounds catalyze many important organic and inorganic reactions in chemical industries and laboratories.^{1,2} Hence, design and synthesis of superacids and superbases and study of their structural and chemical properties are still an active research field in chemistry.^{3–6} The main strategy to achieve a Brønsted superbase is to design a stable positively charged protonated molecule which can accommodate the positive charge. However, the design of unstable neutral molecules, with steric repulsion for example, which are stabilized upon protonation is another strategy to achieve superbases.⁷ Recently, we designed some organic superbases using 1,3,5-cycloheptatriene motif in which the positive charge is delocalized in the 7-membered aromatic ring.⁸ Also, the entering proton may interact with different sites *via* hydrogen bonding interaction leading to a stable protonated molecule.⁹ The proton sponges are an important class of superbases whose basicities are

due to two hydrogen bonding interactions in the protonated molecule.^{10,11} Electron donating substituents stabilize the protonated molecule *via* field/inductive, polarization and resonance effects and consequently increase the basicity of the molecule.^{12–15} Phosphorous ylides,¹⁶ phosphazenes,¹⁷ phosphorous carbenes,¹⁸ guanidines,^{19–21} guanidino phosphazenes,²² nitriles,^{23,24} and imidazolines²⁵ are important classes of superbases which have been studied as well. In the present work, we intend to achieve strong bases using the nanoclusters of sodium, Na_n, to delocalize the positive charge of the corresponding protonated molecules.

Sodium clusters have been studied extensively and their melting points, polarizabilities, stabilities, and structures have been determined.^{26–31} Most of these studies have been performed using computational methods. Their results show that many of the Na_n properties are size-dependent. Solov'yov *et al.*,²⁸ studied structural and energetic properties of Na_n clusters with $n \leq 20$ using B3LYP and MP2 methods and showed that Na₈ and Na₂₀ are more stable than others. Bonacic-Koutecky *et al.*,²⁹ studied small clusters of Na_n ($n \leq 9$) and reported that Na₈ is the most stable cluster. Also, Na_n clusters with a larger size have been studied with

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Figure 1. The structures of different isomers of Na_n ($n = 2-8$) clusters optimized by the B3LYP/6-31+G(d,p) method.

different theoretical methods. The results of these studies determined other magic clusters of sodium with 13, 55, 71, 115, 147, 178, and 297 atoms.^{30,31} Most of these studies focused on the structural, physical, energetic, and chemical properties of Na_n clusters. Jalili *et al.*,³² studied adsorptions of O and O_2 on the sodium clusters with 2–6 atoms and calculated adsorption energies. They found that the energy values exhibit an even–odd oscillation versus the number of sodium atoms.

In this work, adsorption of some simple amines and their protonated forms on the Na_8 cluster is studied and the adsorption energies are computed. The proton affinities and gas phase basicities of the amines in the absence

and presence of the Na_8 cluster are calculated and compared.

2. Computational details

The molecules, clusters, and complexes were structurally optimized using density functional theory (DFT) by the B3LYP functional in the gas phase. The 6-31+G(d,p) basis set with diffuse and polarization functions was used for all calculations. Different isomers of Na_n with $n = 1-8$ were investigated. For each cluster, different structures including linear, triangular, rectangular, pyramidal, and regular polygonal geometries were provided as input files. However, some

of the structures were converted to others during geometry optimization. Only neutral clusters were studied. For clusters with an odd number of atoms (Na_3 , Na_5 , Na_7) the multiplicity was considered as 2 and for other clusters as 1. To compare the stabilities of the sodium clusters, their bonding energies per atom (E_b) were calculated using equation (1).³³

$$E_b = - \frac{(E_{\text{Na}_n} - nE_{\text{Na}})}{n} \quad (1)$$

where E_{Na} is the energy of Na atom. Because of the minus sign, the E_b values are generally positive, therefore, a larger value of E_b indicates higher stability.

The frequency calculations were performed at the same level of theory and 298 K to obtain thermodynamic properties including enthalpies (ΔH_{ads}) and Gibbs free energies (ΔG_{ads}) of the adsorptions as well as the proton affinities (PA) and gas phase basicities (GB). The ΔH_{ads} values for adsorption of the bases on the Na_8 cluster were calculated using the following equation:

$$\Delta H_{\text{ads}} = H_{\text{complex}} - (H_{\text{base}} + H_{\text{Na}_8}) \quad (2)$$

Here, H_{complex} is the enthalpy of the Na_8 -base complex, H_{base} is enthalpy of the Lewis base, and H_{Na_8} is the enthalpy of the Na_8 cluster. To investigate the interaction of the bases with the Na_8 cluster, the bases were put close to Na_8 from different directions and the geometry optimization was performed using OPT keyword. Although we considered several isomers for each complex, some of them were converted to the same structure, therefore, we reported only one isomer for some complexes. To compare with the B3LYP data, interaction of Na_8 with simple bases NH_3 , CH_2NH , and N_2H_4 was also studied by MP2 method. All the calculations were carried out using Gaussian 09 software.³⁴

3. Results and Discussion

The energetic and structural properties of different isomers of clusters Na_n ($n = 1-8$) were investigated. The optimized structures of the clusters Na_{2-8} have been collected in Figure 1. The calculated binding energies per atom (E_b) of the clusters Na_{2-8} have been summarized in Table 1. Comparison of the E_b values shows that the planar isomers are the most stable isomers among the clusters Na_{2-6} . The pentagonal bipyramidal isomer, $\text{Na}_7\text{-e}$, is the most stable structure of the Na_7 clusters. Furthermore, the cluster $\text{Na}_8\text{-e}$ with D_{2d} symmetry point group is the most stable structure among the Na_{1-8} isomers. This result is in agreement with the previous studies which reported that Na_8 is one of the magic clusters of the sodium clusters.²⁸ Therefore, the adsorption of bases and their protonated forms on the cluster $\text{Na}_8\text{-e}$ are studied. Although $\text{Na}_8\text{-e}$ is the most stable cluster, it is possible that interaction with the Lewis bases changes the stability trend. However, because the abundance of

Table 1. The calculated binding energy per atom (E_b) for different isomers of Na_n ($n = 2-8$) clusters.

Cluster	E_b (kJ mol ⁻¹)	Cluster	E_b (kJ mol ⁻¹)
Na_2	36.22	$\text{Na}_6\text{-c}$	44.65
$\text{Na}_3\text{-a}$	30.98	$\text{Na}_6\text{-d}$	40.58
$\text{Na}_3\text{-b}$	31.55	$\text{Na}_6\text{-e}$	48.73
$\text{Na}_4\text{-a}$	38.11	$\text{Na}_6\text{-f}$	37.38
$\text{Na}_4\text{-b}$	40.81	$\text{Na}_7\text{-a}$	36.79
$\text{Na}_4\text{-c}$	36.60	$\text{Na}_7\text{-b}$	45.99
$\text{Na}_4\text{-d}$	40.81	$\text{Na}_7\text{-c}$	43.82
$\text{Na}_4\text{-e}$	40.33	$\text{Na}_7\text{-d}$	47.10
$\text{Na}_4\text{-f}$	39.76	$\text{Na}_7\text{-e}$	50.81
$\text{Na}_5\text{-a}$	43.42	$\text{Na}_7\text{-f}$	45.99
$\text{Na}_5\text{-b}$	39.48	$\text{Na}_8\text{-a}$	37.67
$\text{Na}_5\text{-c}$	43.42	$\text{Na}_8\text{-b}$	42.59
$\text{Na}_5\text{-d}$	42.52	$\text{Na}_8\text{-c}$	47.43
$\text{Na}_5\text{-e}$	35.46	$\text{Na}_8\text{-d}$	44.69
$\text{Na}_5\text{-f}$	42.51	$\text{Na}_8\text{-e}$	54.66
$\text{Na}_6\text{-a}$	43.58	$\text{Na}_8\text{-f}$	49.67
$\text{Na}_6\text{-b}$	43.25		

the less stable isomers is negligible, the cluster $\text{Na}_8\text{-e}$ is the only dominant isomer which interacts with the Lewis bases.

Figure 2 shows the optimized structures for the adsorption of ammonia, methylamine, ethylamine, methanimine, guanidine, hydrazine, pyridine, and hydroxylamine on the Na_8 cluster. The bases interact with Na_8 from different sites, therefore, different complexes were considered and their interactions were studied.

The calculated values of enthalpy (ΔH_{ads}), Gibbs free energy (ΔG_{ads}), and entropy (ΔS_{ads}) for adsorption of the bases on the Na_8 are summarized in Table 2. For comparison, interaction energies of Na_8 with simple bases NH_3 , CH_2NH , N_2H_4 and their protonated forms were also computed by the MP2 method. The MP2-calculated data are in good agreement with the corresponding values computed by B3LYP method. The calculated values of ΔH_{ads} are smaller than -50 kJ mol⁻¹ indicating that the interactions are weak. There are weak van der Waals molecular interactions playing between dipole moments of the bases and induced dipole moment in Na_8 cluster leading to a dipole-induced dipole type van der Waals interaction. As expected, the ΔS_{ads} values are negative due to reduced freedom and formation of the base- Na_8 complexes. Therefore, although the ΔH_{ads} values show that the reactions are exothermic, the ΔG_{ads} values are smaller than ΔH_{ads} and in some cases are positive values. Hence, the formation of some of the complexes does not proceed spontaneously. For example, three isomers were considered for the interaction

Figure 2. The optimized structures for the adsorption of ammonia, methylamine, ethylamine, guanidine, hydrazine, pyridine, and hydroxylamine on the Na_8 cluster.

of CH_3NH_2 with Na_8 while comparison of their ΔG_{ads} values reveals that only $\text{Na}_8\text{-CH}_3\text{NH}_2\text{-a}$ is stable. Interaction of the bases from both their N and H atoms was investigated for methylamine, ethylamine, and pyridine. For other amines, only complexes with N–Na interaction were obtained, after structure optimization. In the

case of NH_2OH , the interactions were via both the O and N atoms. Also, we tried to study the interaction of π -electrons of the pyridine with Na_8 , however, the complexes with this kind of interaction were not stable and they converted to the structures **a** and **b** during optimizations. Comparison of the ΔH_{ads} values reveals that

Table 2. Calculated values of enthalpies (ΔH_{ads}), Gibbs free energies (ΔG_{ads}), and entropies (ΔS_{ads}) for the adsorption of the bases on the Na_8 cluster.

Interaction	ΔH_{ads} (kJ mol ⁻¹)	ΔG_{ads} (kJ mol ⁻¹)	ΔS_{ads} (J/K mol)
$\text{Na}_8 + \text{NH}_3 \rightarrow \text{Na}_8\text{-NH}_3$	-37.02 (-38.78) ^a	-7.50 (-12.55)	-99.01 (-84.61)
$\text{Na}_8 + \text{CH}_3\text{NH}_2 \rightarrow \text{Na}_8\text{-CH}_3\text{NH}_2\text{-a}$	-32.78	-3.20	-99.21
$\text{Na}_8 + \text{CH}_3\text{NH}_2 \rightarrow \text{Na}_8\text{-CH}_3\text{NH}_2\text{-b}$	-35.13	1.51	-122.90
$\text{Na}_8 + \text{CH}_3\text{NH}_2 \rightarrow \text{Na}_8\text{-CH}_3\text{NH}_2\text{-c}$	-1.24	25.06	-88.22
$\text{Na}_8 + \text{C}_2\text{H}_7\text{N} \rightarrow \text{Na}_8\text{-C}_2\text{H}_7\text{N-a}$	-31.31	-0.23	-104.23
$\text{Na}_8 + \text{C}_2\text{H}_7\text{N} \rightarrow \text{Na}_8\text{-C}_2\text{H}_7\text{N-b}$	0.96	22.39	-71.87
$\text{Na}_8 + \text{CH}_2\text{NH} \rightarrow \text{Na}_8\text{-CH}_2\text{NH}$	-28.56 (-35.17)	-1.28 (-5.18)	-91.50 (-100.59)
$\text{Na}_8 + \text{CH}_5\text{N}_3 \rightarrow \text{Na}_8\text{-CH}_5\text{N}_3\text{-a}$	-46.78	-13.89	-110.30
$\text{Na}_8 + \text{CH}_5\text{N}_3 \rightarrow \text{Na}_8\text{-CH}_5\text{N}_3\text{-b}$	-40.01	-0.97	-130.91
$\text{Na}_8 + \text{N}_2\text{H}_4 \rightarrow \text{Na}_8\text{-N}_2\text{H}_4\text{-a}$	-32.25	-7.81	-81.97
$\text{Na}_8 + \text{N}_2\text{H}_4 \rightarrow \text{Na}_8\text{-N}_2\text{H}_4\text{-b}$	-41.30 (-41.75)	-15.46 (-14.01)	-86.65 (-93.05)
$\text{Na}_8 + \text{C}_5\text{H}_5\text{N} \rightarrow \text{Na}_8\text{-C}_5\text{H}_5\text{N-a}$	-29.66	0.05	-99.65
$\text{Na}_8 + \text{C}_5\text{H}_5\text{N} \rightarrow \text{Na}_8\text{-C}_5\text{H}_5\text{N-b}$	0.65	18.30	-59.18
$\text{Na}_8 + \text{NH}_2\text{OH} \rightarrow \text{Na}_8\text{-NH}_2\text{OH-a}$	-25.53	4.76	-101.62
$\text{Na}_8 + \text{NH}_2\text{OH} \rightarrow \text{Na}_8\text{-NH}_2\text{OH-b}$	-22.39	11.19	-112.65
$\text{Na}_8 + \text{NH}_2\text{OH} \rightarrow \text{Na}_8\text{-NH}_2\text{OH-c}$	-29.11	0.10	-97.99

^aThe data in parenthesis have been calculated by MP2/6-31+G(d,p) method.

interactions from the N atom of the amine are stronger than the H–Na interactions. For example, ΔH_{ads} values for interactions of methylamine and ethylamine with Na_8 *via* their H atoms are -1.24 and 0.96 kJ mol⁻¹ while the corresponding values for N–Na interactions are -35.13 and -33.56 kJ mol⁻¹, respectively. Similarly, the interaction *via* N atom of pyridine ($\text{Na}_8\text{-C}_5\text{H}_5\text{N-a}$) is about 30 kJ mol⁻¹ stronger than its interaction *via* H atom ($\text{Na}_8\text{-C}_5\text{H}_5\text{N-b}$). Comparison of the H–Na and N–Na bond lengths also reveals the difference in the interaction energy so that the H–Na bond length are considerably longer than the corresponding N–Na bond lengths.

Interaction of the protonated bases with Na_8 was also considered. Figure 3 shows the optimized structures of the complexes resulting from the interaction of the protonated bases with Na_8 . Comparison of Figures 2 and 3 reveals that neutral bases interact through their N atoms while the corresponding protonated molecules interact with Na_8 both H and N atoms.

The calculated values of enthalpy (ΔH_{ads}), Gibbs free energy (ΔG_{ads}), and entropy (ΔS_{ads}) for interaction between the protonated bases and Na_8 are summarized in Table 3. Interestingly, interactions of the protonated amines with Na_8 are much stronger than those for the neutral amines. Although the interaction energies for the protonated amines are large, no chemical bond was observed between the protonated amines and Na_8 . The stability of these complexes is due to the capability of Na_8 to accommodate the positive charge without forming a chemical bond. However, in the case of $(\text{NH}_2\text{OH})\text{-H}^+$, dissociative adsorption was observed

which resulted in the formation of adsorbed NH_3 , H_2O , OH , and NH_2 species. These species interact with Na_8 more strongly compared to NH_2OH so that complexes with ΔH_{ads} of about -800 kJ mol⁻¹ were observed. Interaction of protonated pyridine, $\text{C}_5\text{H}_5\text{NH}^+$, with Na_8 leads in the formation of two complexes, $\text{Na}_8\text{-}[\text{C}_5\text{H}_5\text{NH}]^+\text{-a}$ and $\text{Na}_8\text{-}[\text{C}_5\text{H}_5\text{NH}]^+\text{-b}$. In the $\text{Na}_8\text{-}[\text{C}_5\text{H}_5\text{NH}]^+\text{-a}$, $\text{C}_5\text{H}_5\text{NH}^+$ interacts *via* two C atoms while in the $\text{Na}_8\text{-}[\text{C}_5\text{H}_5\text{NH}]^+\text{-b}$, it interacts with Na_8 *via* its N atom and one of the C atoms. Although the latter interaction is stronger, in both cases $\text{C}_5\text{H}_5\text{NH}^+$ deforms and loses its planarity. Comparison of the energy values of Tables 2 and 3 shows that Na_8 stabilizes the protonated molecules more than the corresponding neutral ones. Therefore, this property of Na_8 can be used to enhance the gas phase basicity of the amines.

Proton affinity (PA) and gas phase basicity (GB) are two indices used as a measure of basicity of a molecule in gas phase. PA and GB of a molecule (M) are defined as the enthalpy and Gibbs free energy of the following reaction in gas phase, respectively.³⁵

The PAs and GBs of the isolated amines and adsorbed amines were calculated. The calculated PAs and GBs of the amines in the absence and presence of the Na_8 cluster are compared in Table 4. Since there is a linear correlation between PAs and GBs, only the PAs are discussed. The calculated proton affinities of the isolated bases have been compared with those reported in literature. There is a good agreement between the calculated proton affinities and the reported experimental

Figure 3. The optimized structures for the interaction of the protonated bases with Na_8 . In the case of NH_2OH complexes, the atoms in the parenthesis are the protonation sites.

Table 3. Calculated values of enthalpies (ΔH_{ads}), Gibbs free energies (ΔG_{ads}), and entropies (ΔS_{ads}) of the adsorption of the protonated bases on the Na_8 cluster.

Interaction	ΔH_{ads} (kJ mol ⁻¹)	ΔG_{ads} (kJ mol ⁻¹)	ΔS_{ads} (J/K mol)
$\text{Na}_8 + \text{NH}_4^+ \rightarrow \text{Na}_8\text{-NH}_4^+\text{-a}$	-156.43 (-140.05) ^a	-130.69 (-112.33)	-86.32 (-92.96)
$\text{Na}_8 + [\text{CH}_3\text{NH}_3]^+ \rightarrow \text{Na}_8\text{-[CH}_3\text{NH}_3]^+$	-130.04	-106.05	-80.47
$\text{Na}_8 + [\text{C}_2\text{H}_7\text{NH}]^+ \rightarrow \text{Na}_8\text{-[C}_2\text{H}_7\text{NH}]^+$	-120.08	-91.70	-95.17
$\text{Na}_8 + [\text{CH}_2\text{NH}_2]^+ \rightarrow \text{Na}_8\text{-[CH}_2\text{NH}_2]^+\text{-a}$	-348.24	-308.61	-132.90
$\text{Na}_8 + [\text{CH}_2\text{NH}_2]^+ \rightarrow \text{Na}_8\text{-[CH}_2\text{NH}_2]^+\text{-b}$	-355.42 (-338.73)	-315.99 (-296.11)	-132.24 (-142.95)
$\text{Na}_8 + [\text{CH}_5\text{N}_3\text{-H}]^+ \rightarrow \text{Na}_8\text{-[CH}_5\text{N}_3\text{-H]}^+\text{-a}$	-87.80	-59.02	-96.53
$\text{Na}_8 + [\text{CH}_5\text{N}_3\text{-H}]^+ \rightarrow \text{Na}_8\text{-[CH}_5\text{N}_3\text{-H]}^+\text{-b}$	-109.77	-70.32	-132.32
$\text{Na}_8 + [\text{N}_2\text{H}_4\text{-H}]^+ \rightarrow \text{Na}_8\text{-[N}_2\text{H}_4\text{-H]}^+$	-152.96 (-142.86)	-120.95 (-114.15)	-107.36 (-96.27)
$\text{Na}_8 + [\text{C}_5\text{H}_5\text{NH}]^+ \rightarrow \text{Na}_8\text{-[C}_5\text{H}_5\text{NH]}^+\text{-a}$	-139.40	-103.29	-121.10
$\text{Na}_8 + [\text{C}_5\text{H}_5\text{NH}]^+ \rightarrow \text{Na}_8\text{-[C}_5\text{H}_5\text{NH]}^+\text{-b}$	-189.23	-147.69	-139.33
$\text{Na}_8 + [\text{NH}_2\text{OH}_2]^+ \rightarrow \text{Na}_8\text{-[NH}_2\text{OH}_2]^+\text{(O)}$	-800.07	-776.03	-80.63
$\text{Na}_8 + [\text{NH}_3\text{OH}]^+ \rightarrow \text{Na}_8\text{-[NH}_3\text{OH]}^+\text{-a (N)}$	-808.80	-778.36	-102.11
$\text{Na}_8 + [\text{NH}_3\text{OH}]^+ \rightarrow \text{Na}_8\text{-[NH}_3\text{OH]}^+\text{-b (N)}$	-197.39	-162.36	-117.50

In the case of NH_2OH complexes, the atoms in the parenthesis are the protonation sites.

^aThe data in parenthesis have been calculated by MP2/6-31+G(d,p) method.

Figure 4. NBO charge distribution analysis of the complexes $\text{Na}_8\text{--}[\text{NH}_4]^+$, $\text{Na}_8\text{--}[\text{CH}_2\text{NH}_2]^+\text{-a}$, and $\text{Na}_8\text{--}[\text{C}_5\text{H}_5\text{NH}]^+\text{-a}$. q is the total charge on the Na_8 cluster.

Table 4. Comparison of the calculated proton affinities (PA) and gas phase basicities (GB) of the isolated bases with the corresponding values of the adsorbed bases.

Protonation reaction	PA = $-\Delta H$ (kJ mol $^{-1}$)	GB = $-\Delta G$ (kJ mol $^{-1}$)
$\text{NH}_3 + \text{H}^+ \rightarrow [\text{NH}_4]^+$	856.54 (853.6) ^a	828.29
$\text{Na}_8\text{-NH}_3 + \text{H}^+ \rightarrow \text{Na}_8\text{-NH}_4^+$	975.95 (965.09) ^b	952.25 (932.64) ^b
$\text{CH}_3\text{NH}_2 + \text{H}^+ \rightarrow [\text{CH}_3\text{NH}_3]^+$	901.31 (899.0) ^a	869.61
$\text{Na}_8\text{-CH}_3\text{NH}_2\text{-a} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{CH}_3\text{NH}_3]^+$	998.56	972.45
$\text{Na}_8\text{-CH}_3\text{NH}_2\text{-c} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{CH}_3\text{NH}_3]^+$	1032.61	999.49
$\text{C}_2\text{H}_7\text{N} + \text{H}^+ \rightarrow [\text{C}_2\text{H}_7\text{NH}]^+$	915.67 (912.0) ^a	884.14
$\text{Na}_8 + \text{C}_2\text{H}_7\text{N-a} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{C}_2\text{H}_7\text{NH}]^+$	1004.44	975.61
$\text{Na}_8 + \text{C}_2\text{H}_7\text{N-b} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{C}_2\text{H}_7\text{NH}]^+$	1036.70	998.18
$\text{CH}_2\text{NH} + \text{H}^+ \rightarrow [\text{CH}_2\text{NH}_2]^+$	871.50	839.00
$\text{Na}_8\text{-CH}_2\text{NH} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{CH}_2\text{NH}_2]^+\text{-a}$	1191.17	1147.33
$\text{Na}_8\text{-CH}_2\text{NH} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{CH}_2\text{NH}_2]^+\text{-b}$	1198.36 (1175.70) ^b	1155.04 (1131.52) ^b
$\text{CH}_5\text{N}_3 + \text{H}^+ \rightarrow [\text{CH}_5\text{N}_3\text{-H}]^+$	996.09 (986.3) ^a	966.93
$\text{Na}_8\text{-CH}_5\text{N}_3\text{-a} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{CH}_5\text{N}_3\text{-H}]^+\text{-a}$	1037.11	1012.05
$\text{Na}_8\text{-CH}_5\text{N}_3\text{-b} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{CH}_5\text{N}_3\text{-H}]^+\text{-b}$	1065.85	1036.27
$\text{N}_2\text{H}_4 + \text{H}^+ \rightarrow [\text{N}_2\text{H}_4\text{-H}]^+$	872.16 (853.2) ^a	843.65
$\text{Na}_8\text{-N}_2\text{H}_4\text{-a} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{N}_2\text{H}_4\text{-H}]^+$	991.44	956.72
$\text{Na}_8\text{-N}_2\text{H}_4\text{-b} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{N}_2\text{H}_4\text{-H}]^+$	982.39 (977.33) ^b	949.06 (946.05) ^b
$\text{C}_5\text{H}_5\text{N} + \text{H}^+ \rightarrow [\text{C}_5\text{H}_5\text{NH}]^+$	936.06	904.13
$\text{Na}_8\text{-C}_5\text{H}_5\text{N-a} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{C}_5\text{H}_5\text{NH}]^+\text{-a}$	1045.79	1007.47
$\text{Na}_8\text{-C}_5\text{H}_5\text{N-a} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{C}_5\text{H}_5\text{NH}]^+\text{-b}$	1095.62	1051.87
$\text{NH}_2\text{OH} + \text{H}^+ \rightarrow [\text{NH}_2\text{OH}_2]^+$ (O)	705.19 (703.9) ^c	674.49
$\text{Na}_8\text{-NH}_2\text{OH-c} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{NH}_2\text{OH}_2]^+$ (O)	1476.15	1450.42
$\text{NH}_2\text{OH} + \text{H}^+ \rightarrow [\text{NH}_3\text{OH}]^+$ (N)	810.45 (814.7) ^c	779.23
$\text{Na}_8\text{-NH}_2\text{OH-a} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{NH}_2\text{OH}_2]^+\text{-a}$ (N)	1593.72	1562.35
$\text{Na}_8\text{-NH}_2\text{OH-b} + \text{H}^+ \rightarrow \text{Na}_8\text{-}[\text{NH}_2\text{OH}_2]^+\text{-b}$ (N)	985.45	952.78
$\text{Na}_8 + \text{H}^+ \rightarrow \text{Na}_8\text{-H}^+$	1178.43	1150.91

In the case of NH_2OH complexes, the atoms in the parenthesis are the protonation sites.

^aFrom Ref [36].

^bThis work: calculated by MP2/6-31+G(d,p).

^cFrom Ref [37]: calculated by CBS-Q method.

ones. Guanidine, CH_5N_3 , with $\text{PA} = 996.1$ and NH_2OH with $\text{PA} = 810.5 \text{ kJ mol}^{-1}$ are the strongest and weakest bases among the molecules, respectively. However, the proton affinities of the bases in the absence of Na_8 are smaller than 1000 kJ mol^{-1} . A dramatic increase in PAs was observed for the bases adsorbed on Na_8 so that the calculated PAs of the adsorbed bases are generally larger than 1000 kJ mol^{-1} , the threshold of superbasicity. The basicity enhancement may be due to the ability of the Na_8 cluster to stabilize the positively charged protonated bases. By accommodation of some part of the positive charge, Na_8 cluster stabilizes the protonated amines and consequently increases their basicity. Figure 4 shows the NBO charge distribution for complexes of NH_4^+ , CH_2NH_2^+ , and $\text{C}_5\text{H}_5\text{NH}^+$ adsorbed on Na_8 . The total charges on the Na_8 cluster in the mentioned complexes are $+0.2$, $+1.75$, and $+1.43$, respectively. These results show that in the absence of Na_8 , these molecules bear the whole positive charge while in the complexes, the Na_8 cluster accommodates some part of the positive charge and stabilizes the protonated molecule. Basicity enhancement is to some extent proportional to the amount of the charge transferred to the Na_8 cluster. For example, increase in PA for NH_3 and CH_2NH are 120 and 320 kJ mol^{-1} which are proportional to the transferred charges of 0.2 and 1.75 , respectively (Figure 4). Also, PA of Na_8 was calculated using B3LYP/6-31+G(d,p) and obtained to be $1178.4 \text{ kJ mol}^{-1}$. This high basicity of Na_8 reflects its ability to bear a positive charge and increase basicity of the Lewis bases.

4. Conclusions

Structural and energetic properties of different isomers of Na_n clusters with $n = 1-8$ were investigated theoretically. It was found that for the smaller clusters with $n = 2-6$, the planar structures are more stable while the 3D clusters of Na_7 and Na_8 were the most stable isomers. According to the E_b values, the Na_8 cluster with D_{2d} symmetry was the most stable cluster, therefore, the interaction of the neutral and protonated bases with this cluster was studied. Interaction of the neutral bases with Na_8 was very weak such that the interaction energies were smaller than -50 kJ mol^{-1} . On the other hand, the protonated bases interact with Na_8 more strongly with interaction energies generally larger than -100 kJ mol^{-1} . These results showed that the Na_8 cluster stabilizes the protonated bases better than the corresponding neutral ones. Therefore, this property of Na_8 , electropositivity, was used to enhance basicity of the Lewis bases. The calculated PAs of the adsorbed bases on Na_8 were mainly higher than 1000 kJ mol^{-1} indicating the superbasicity of the adsorbed amines.

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