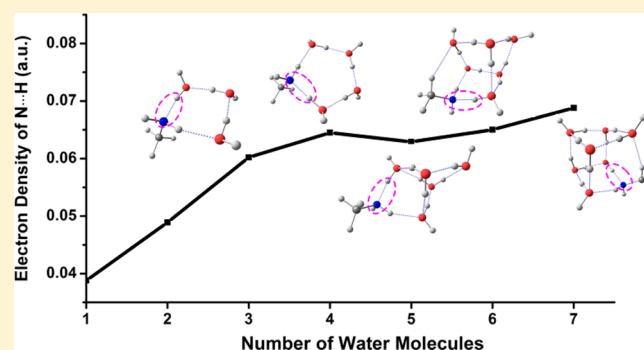


Stability of Hydrated Methylamine: Structural Characteristics and $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ Hydrogen Bonds

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S Supporting Information

ABSTRACT: Methylamine is the simplest aliphatic amine found in human urine, blood, and tissues. It is thought to play a significant part in central nervous system disturbances observed during renal and hepatic disease. In this work we have investigated the methylamine hydration clusters using a basin hopping (BH) algorithm with the density functional theory (DFT). The results presented herein yield a detailed understanding of the structure and stability for a system consisting of one methylamine molecule and up to seven waters: the most stable geometries arise from a fusion of tetramer or pentamer rings; by the geometrical parameters and topological parameters analysis, the strengths of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bonds of the global minima increase as the sizes of clusters increase, except for $n = 5$ where there is a slight fluctuation. This work may shed light on the form mechanism of methylamine existing in organisms and the hydration structures of larger molecules containing amino functional groups and their interaction with the water molecules nearby.



I. INTRODUCTION

Methylamine has been detected in human urine, blood, and tissues.^{1–6} It can be derived from several metabolic reactions, such as the deamination of adrenaline, sarcosine, creatinine, choline, and lecithin.^{7–9} It has been suggested that methylamine and other related short-chain aliphatic amines may play a significant role in the central nervous system disturbances observed during hepatic and renal disease, especially when the blood–brain barrier is compromised.¹⁰ In addition, amino functional groups (NH_2) occur frequently in biomolecules, for example, amino acids molecules.^{11,12} The biological functions of methylamine and other biomolecules containing NH_2 are intimately connected to their hydrated structures.^{13–18} Therefore, studying the hydration of methylamine is essential for biological science.

Much attention has been focused on the hydration behavior of methylamine. Methylamine shows the most favorable solvation free energy of hydration compared with other methylated amines (i.e., ammonia, dimethylamine, trimethylamine),^{19,20} not following the trend expected on the basis of the hydrophobicity of the methyl groups. So considerable effort has been invested in the reproduction of the experimental solvation free energies of hydration of ammonia and methylated amines using computational methods.^{11,21–29} At the same time, there is a lot of work studying the structures of methylamine

hydrates. For instance, according to a Monte Carlo (MC) simulation, the first hydration shell of an amino group in aqueous methylamine solution contains three water molecules, two of them being involved in hydrogen bonds with the NH_2 group.³⁰ A molecular dynamics (MD) simulation also revealed two water molecules forming hydrogen bonds with an amino group in its first hydration shell ($\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$).¹¹ According to *ab initio* MD simulation, the first hydration shell of an amino group contains three water molecules participating in hydrogen bonding. One H_2O molecule forms a hydrogen bond with the nitrogen atom of the NH_2 group and the other two molecules form hydrogen bonds with hydrogen atoms of the NH_2 group.³¹ It was also reported that the amino group forms a smaller number of hydrogen bonds with water molecules. For instance, a MC simulation predicted 2.51 hydrogen bonds per NH_2 group (1.2 bonds per N atom and 1.31 bonds per two H atoms).³² A MD simulation gave 1.77 hydrogen bonds formed by the nitrogen atom of NH_2 group with water molecules.²⁵ Data on hydration of the hydrophobic methyl group in methylamine are also reported. For instance, the hydration number of a methyl group determined in a MC

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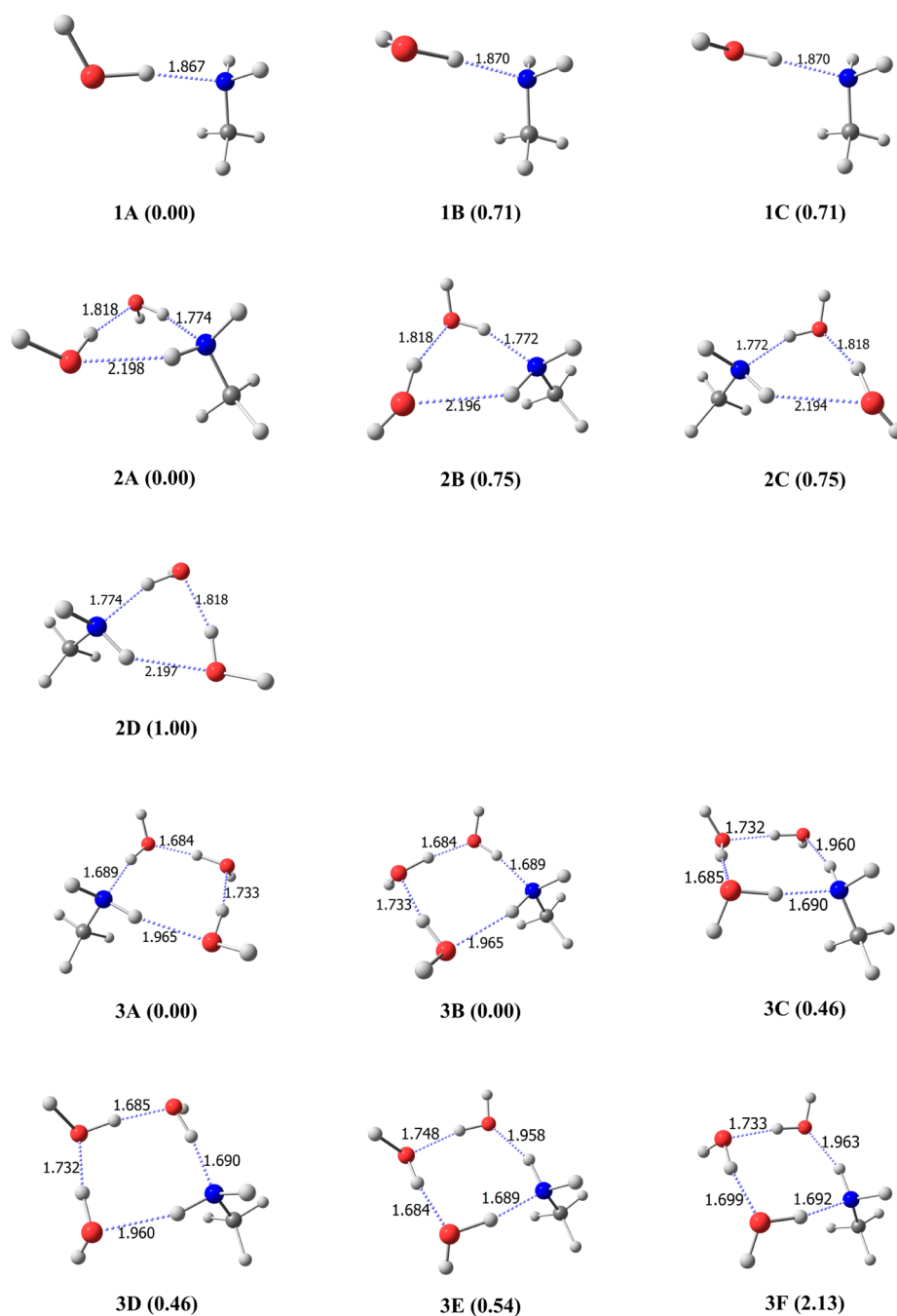


Figure 1. Low energy isomers of $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_n$ ($n = 1-3$) calculated at the PW91/6-311++G(3df,3pd) level of theory arranged in order of increasing electronic energy (kJ mol^{-1}).

simulation³⁰ is 18–20 (cf. 10 according to MD simulation²⁵). Recently, Marta et al. have researched the structures of the methylamines in water clusters by density functional theory (DFT).³³ Their primary focus was the dissociation of a water molecule to generate the hydroxide ion following the transfer of a proton to the amine group and found that the dissociated forms were not found to have the most stable configuration.

Although there have been numerous studies as shown above, the stability of methylamine with several water molecules has been poorly studied so far. This also concerns the whole structures and the hydrogen bonding of this species with water molecules. In this work, we investigate the structures and stability of methylamine hydration in the gas phase. For $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_n$ where $n = 1-7$, we used a basin hopping

(BH) algorithm with the DFT method to locate the global and many low lying local minima for each cluster size. Our analysis mainly focuses on two specific topics: (i) the characteristics of the stable configurations; (ii) the strength of $\text{H}_2\text{N} \cdots \text{H}-\text{O}$ hydrogen bonds of global minima and their variation with the size of the clusters increase.

II. METHODS

To search for the low-lying structures of the $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_n$ ($n = 1-7$) system, we used the BH global optimization technique combined with DFT for geometry optimization. The BH algorithm had been used to explore the atomic and molecular systems in our previous works.^{34–39} This algorithm

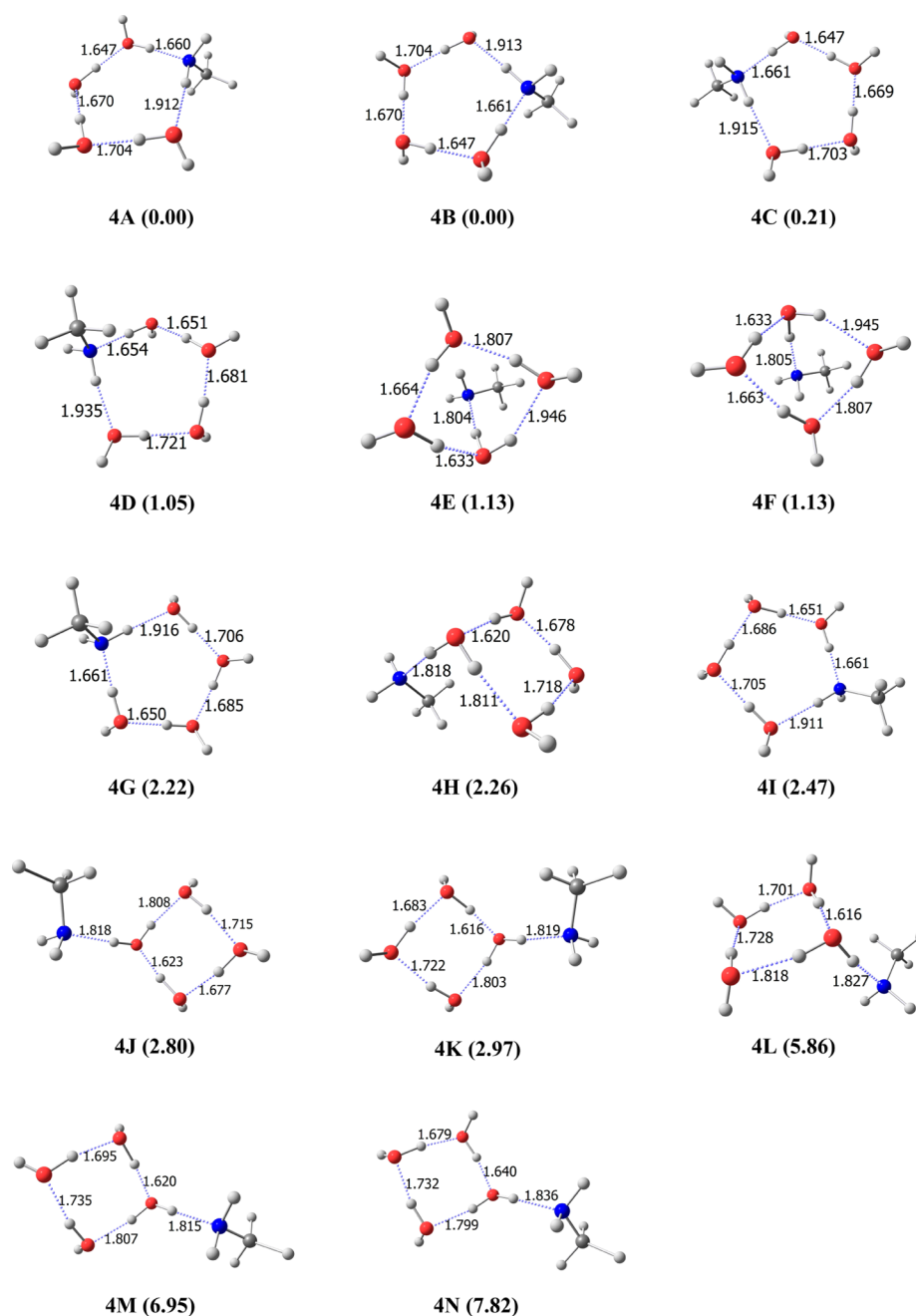


Figure 2. Low energy isomers of $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_4$ calculated at the PW91/6-311++G(3df,3pd) level of theory arranged in order of increasing electronic energy (kJ mol^{-1}).

fundamentally combined the Metropolis random sampling technique and local optimization procedures. Two steps were included: a new structure was generated via the random displacement of atoms and then optimized to the local minimum; this local energy minimum was used as a criterion to accept the initial generated structure spaces with Boltzmann weight at a finite temperature. During this process, generalized gradient approximation in the Perdure–Burke–Ernzerhof (PBE)⁴⁰ functional and the double numerical plus d-functions (DND) basis set, implemented in the DMol³ code,⁴¹ were chosen for structure optimization of $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_n$ ($n = 1-7$) system. For each cluster, three separate BH searches consisting of 1000 sampling steps at 3000 K starting with randomly generated molecular configurations, were performed,

all leading to consistent sets of low-lying isomers for each species.

The top 50 lowest-lying isomers of each size were reoptimized using the functional PW91⁴² and 6-311++G(3df,3pd) basis set for all of elements using the Gaussian 09 software package.⁴³ All the reported clusters here were local minima on the potential energy surface, and there was no imaginary frequency for the optimized structures. The isomers below 9 kJ mol^{-1} of the global minima were selected for this work and were ranked according to their relative energies. Lastly, single-point energy calculations were performed on the optimized geometries using the functional DF-MP2-F12 and VDZ-F12 basis set, implemented in Molpro 2010.1.^{44,45} Zero-point corrected energies were evaluated using thermodynamic corrections at the PW91/6-311++G(3df,3pd) level of theory.

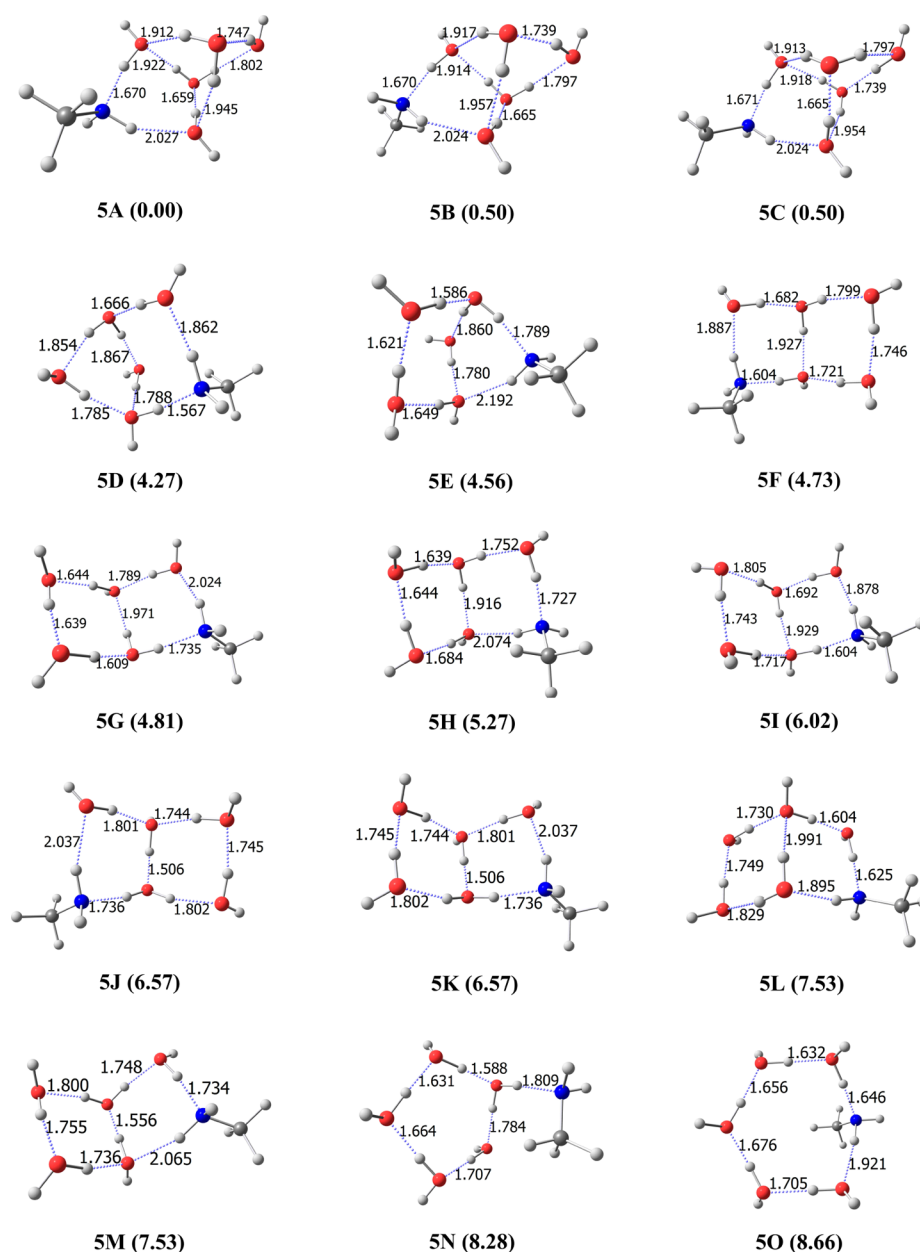


Figure 3. Low energy isomers of $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_5$ calculated at the PW91/6-311++G(3df,3pd) level of theory arranged in order of increasing electronic energy (kJ mol^{-1}).

For finding an appropriate method to optimize the structures, six methods (MP2, PW91, B3LYP, CAM-B3LYP, M062X, and wB97XD) were performed for the relatively small clusters, $\text{CH}_3\text{NH}_2(\text{H}_2\text{O})_3$. The results of all the functionals were compared with those of MP2 to investigate their performance. Considering the structure of the global minimum, the ordering of the isomers by electronic energy and the relative deviation of the electronic energy, PW91 performed well. The detailed information about the benchmark was shown in the Supporting Information. Besides, the choice of the PW91⁴² computational method was based on its satisfactory performance on clusters in the gas phase, including the prediction of Gibbs energies, structural characteristics and vibrational spectra.^{46–52}

In addition, to better clarify the nature of the intermolecular $\text{H}_2\text{N} \cdots \text{H}-\text{O}$ hydrogen bond interactions in the global minima, the topological parameters at bond critical points (BCPs) were

analyzed using the atoms in molecules (AIM) methodology,^{54,55} as implemented in the Multiwfn program.⁵³

III. RESULTS AND DISCUSSION

A. Structures and Energetics. The isomers within 9 kJ mol^{-1} of the global minimum are ordered in increasing relative energy and labeled as nA, nB, nC, etc. All of the relative energies are corrected by zero-point energy.

As shown in Figure 1, the most stable structure for the dimers (i.e., 1A) possesses a hydrogen bond with length of 1.96 \AA . When a second water molecule is added, a cyclic structure is formed where the methylamine molecule acts not only as a hydrogen bond acceptor but also as a hydrogen bond donor. The capacity of methylamine to act as a donor is lower than that of water; thus, the length of the $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond in all four structures with two water molecules (i.e., 2A, 2B, 2C, or 2D) is longer than that of the $\text{H}-\text{O} \cdots \text{H}$ hydrogen bond

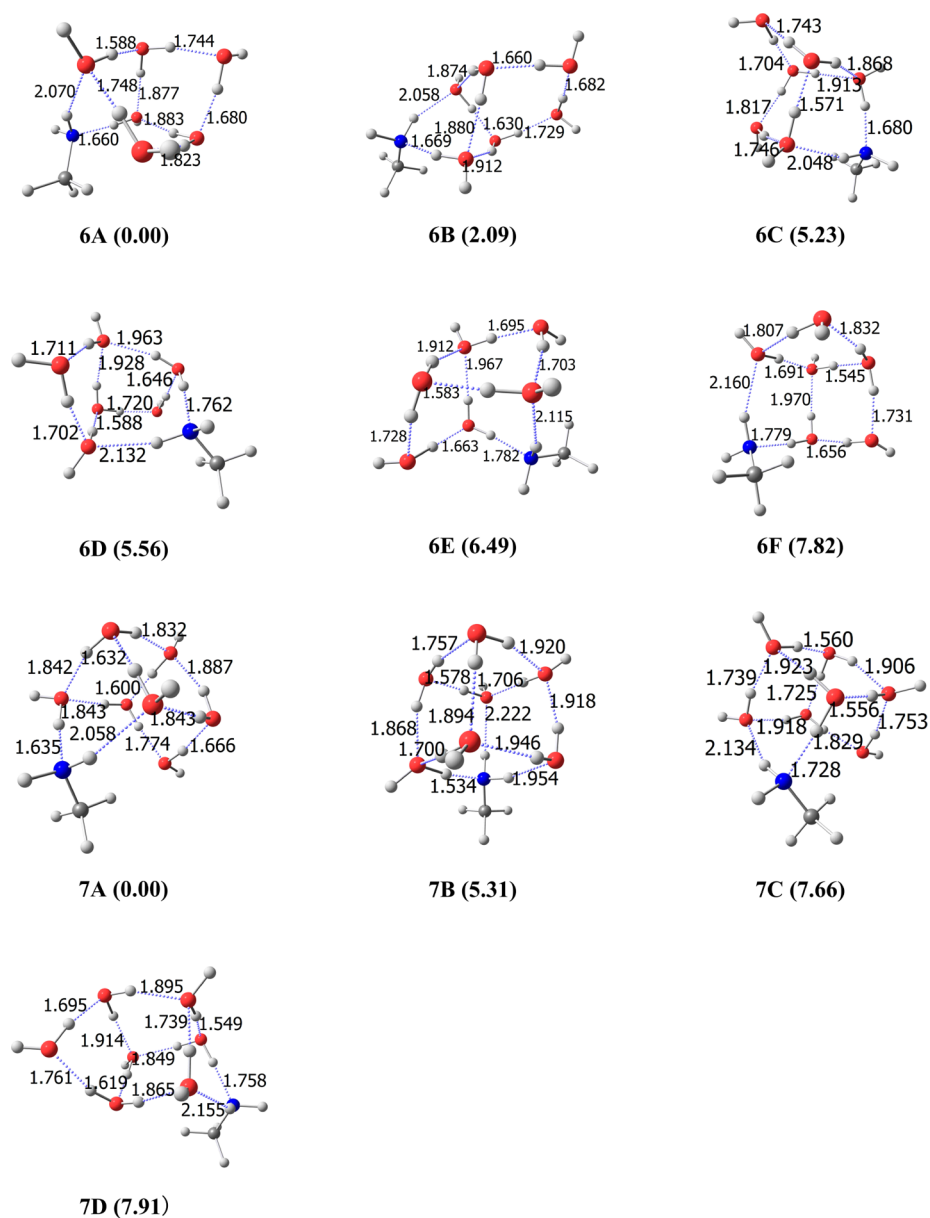


Figure 4. Low energy isomers of $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_n$ ($n = 6-7$) calculated at the PW91/6-311++G(3df,3pd) level of theory arranged in order of increasing electronic energy (kJ mol^{-1}).

(approximately 2.20 versus 1.82 Å). The other hydrogen bond (i.e., $\text{H}_2\text{N} \cdots \text{H}-\text{O}$) is shorter than that in the complex with one water molecule (1A, 1B, or 1C) because of the cooperative effect of hydrogen bonds between these three molecules.^{56,57} By adding a third water molecule, it is possible to obtain more compact structures. In this case, six different cyclic structures have been found, and the methylamine molecules are all incorporated into the cycle being part of the hydrogen bond network. As shown in Figure 2, two types of conformations have been obtained for complexes with four water molecules. In one type of structure, a methylamine molecule participates to form a pentameric ring with five hydrogen bonds. In the other type of structure, the methylamine molecule interacts with a tetrameric ring by forming an $\text{O}-\text{H} \cdots \text{N}$ hydrogen bond. The former type of structure is more stable than the latter type of structure. In Figure 3, we can see that the diversity of structures increases for the complexes with five water molecules. Further, there is a dramatic change in the structure. That is, a cage-like

structure becomes the global minimum (5A), followed by book-like structures. The energy of the cyclic structure (5O, with relative energy to 5A: 8.67 kJ mol^{-1}) is higher than the former two types of structures. The methylamine molecule was not incorporated into the cyclic portion of the complexes with six or seven water molecules, as shown in Figure 4. Within 8.37 kJ mol^{-1} of the stable global minima, these isomers all form three-dimensional structures. Complex 7A is found to be a symmetric cubic cluster, and it is very similar to the cubic water octamer.⁵⁸

For all of the structures, there are one or two pairs of symmetric structures in each set of conformations for the $\text{CH}_3\text{NH}_2 \cdots (\text{H}_2\text{O})_n$ ($n = 1-5$) complexes (e.g., 2B and 2C). They all have nearly identical energies each pair. The structures of the global minima up to four water molecules are cyclic configurations; however, when the number of water molecules increases beyond four, the three-dimensional structures become the most stable configurations. In addition, if observing

carefully enough, we can find that all of the structures have a common feature: the stable geometries arise from a fusion of tetrameric or pentameric rings except for those with $n = 1$ and 2, which possess too few molecules.

From the structures described above, the structure of $\text{CH}_3\text{NH}_2\cdots(\text{H}_2\text{O})_5$ is a special case where the structure of the global minimum has a dramatic change. The structure SO, in which methylamine incorporates itself into the cyclic part of the hydrogen bond network forming a hexameric ring, has higher relative energy. This is consistent with the conclusions about the characteristic of the stable structures.

B. $\text{H}_2\text{N}\cdots\text{H}$ Hydrogen Bonds. Analysis of Geometrical Parameters. Most of the intermolecular interactions of the clusters involve hydrogen bonds. To study the role of methylamine in the water clusters, our present analyses are primarily related to the $\text{N}\cdots\text{H}$ intermolecular interaction, i.e., the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bond. Other hydrogen bonds may influence the $\text{N}\cdots\text{H}$ interaction by the cooperative effect.

Table 1 presents the geometrical parameters and vibrational frequencies of the global minima of the methylamine hydrate

Table 1. General Characteristics of the Global Minima: Intermolecular $\text{N}\cdots\text{H}$ Distances (Å), $\text{H}-\text{O}$ Bond Lengths (Å), Stretching Vibrational Frequency (cm^{-1}), and Changes to Them by the Addition of a Water to the Complexes

n	$D(\text{N}\cdots\text{H})$	$d(\text{H}-\text{O})$	$\nu(\text{H}-\text{O})$	ΔD	Δd	$\Delta\nu$
1	1.8672	0.9921	3289.7			
2	1.7736	1.0080	3006.9	-0.0936	0.0159	-282.8
3	1.6892	1.0239	2724.5	-0.0844	0.0159	-282.4
4	1.6605	1.0298	2622.9	-0.0288	0.0060	-101.6
5	1.6699	1.0275	2670.9	0.0094	-0.0023	48.0
6	1.6601	1.0304	2616.7	-0.0098	0.0029	-54.2
7	1.6351	1.0380	2504.6	-0.0250	0.0076	-112.2

systems. The geometries of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bonds obtained at the PW91/6-311++G(3df,3pd) level of theory are presented in Figures 1–4. From Table 1, one can observe, except for $n = 5$, the following tendencies as the number of water molecules increases: an elongation of the proton donating bond ($\text{H}-\text{O}$), a red shift of the vibrational frequencies of $\text{H}-\text{O}$, and a shortening of the $\text{N}\cdots\text{H}$ intermolecular distance. According to the work of Grabowski et al. and Albrecht et al.,^{59–62} these tendencies clearly show the increasing strength of the H-bond as the number of water molecules increases (except for $n = 5$).

As shown in Table 1, for the changes in ΔD , Δd , and $\Delta\nu$ that occur following the addition of a new water molecule, we observe that the vibrational frequencies of the proton donating bond ($\text{H}-\text{O}$) have a large red shift and the $\text{N}\cdots\text{H}$ distances decrease. We note that there are few changes to the length of the proton donating bond ($\text{H}-\text{O}$). In addition, one can observe that these three parameters change consistently and that the changes are much greater at $n = 2$ or 3. This may occur because clusters with $n = 1$ and $n = 2$ water molecules cannot form tetrameric or pentameric rings. Therefore, large geometrical rearrangements must occur at $n = 2$ and $n = 3$ as the additional water molecules are incorporated into the cyclic structure. This view is consistent with the common structural feature mentioned above.

Relative to $n = 4$, the strength of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bond decreases for $n = 5$. This is indicated by an increase in the $\text{N}\cdots\text{H}$ intermolecular distance, a shortening of the proton

donating bond length ($\text{H}-\text{O}$), and a blue shift of the $\text{H}-\text{O}$ vibrational frequency. This result can be directly related to the dramatic structural change at $n = 5$ in which the three-dimensional configuration becomes the most stable structure.

Relationship between the Geometrical and Topological Parameters. To further clarify the nature of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bond between methylamine and water in the global minima, the characteristics at the BCPs of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ bonds were analyzed using the AIM methodology.^{54,55,63–70} Numerous studies have found this approach to be very useful to estimate the strength of hydrogen bonding.^{71–76}

Parameters such as the electron density (ρ) at the proton-acceptor BCP and its Laplacian ($\nabla^2\rho$) often correlate with the H-bond energy. Other parameters have also been shown to correlate with this energy, including the proton-acceptor distance and the proton donating bond length. Numerous correlations and dependencies between the parameters derived from AIM^{54,67} and other parameters of the analyzed systems were found.^{72,73,77–82} Such relationships are often well-defined, particularly for homogeneous samples.⁸²

Figure 5 shows the relationship between the $\text{N}\cdots\text{H}$ distance and the electron density at the $\text{N}\cdots\text{H}$ hydrogen bond BCP for

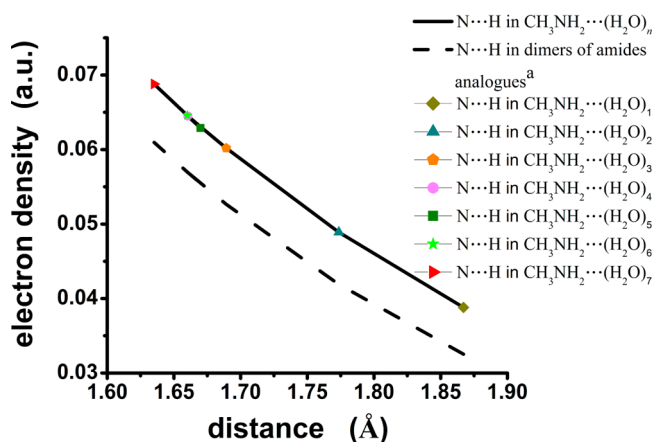


Figure 5. Dependence between the atom–atom distance of $\text{H}\cdots\text{N}(\text{N}-\text{H})$ (in Å) and the electron density at the corresponding BCP (in au). The solid line corresponds to the N,H pair of interacting atoms in the methylamine hydrates. The different symbols reveal the conditions of different sizes. The dashed line corresponds to the N, H pair of interacting atoms in the dimers of the amide derivatives, which has a function between the $\text{N}\cdots\text{H}$ distance and the electron density, i.e., $y = 5.124e^{-2.71x}$. ^aReference 73.

the global minima of methylamine hydrates in our study, as well as the dimers of amide analogs published previously.⁷³ One can observe that the trends of these two systems are in good agreement and that, within a certain distance, the electron density of $\text{N}\cdots\text{H}$ in the methylamine hydrates is larger than the electron density in the amide analog dimers. This result indicates that the electron density at the BCP depends not only on the distance of the two atoms forming the hydrogen bond but also on the molecular systems. In other words, identical types of hydrogen bonds with identical distances between the constituent atoms in different molecular systems may possess different electron densities at the BCPs. In addition, the reason the electron density of $\text{N}\cdots\text{H}$ in the methylamine hydrates is larger than the amide analog dimers may be relevant for ligands that interact with amino groups (NH_2). That is, the electronegativity of the methyl group in methylamine is weaker

than that of the carbonyl group in the amide analog dimers. Thus, the electronegativity of the nitrogen atom in the NH_2 in methylamine is larger, which causes the electron density at the BCP of the $\text{N}\cdots\text{H}$ hydrogen bond in the methylamine hydrates to be larger.

Further, as shown by the trend of the solid line in Figure 5, the electron density increases as the $\text{N}\cdots\text{H}$ distance decreases. The electron density at the BCP is usually a good indicator of the strength of the interaction; that is, a larger electron density, ρ , indicates a stronger hydrogen bond.⁷² As shown in Table 1, there is a one-to-one correspondence between the $\text{N}\cdots\text{H}$ distance and the number of water molecules in the cluster. Further, except for $n = 5$, the distance of the $\text{N}\cdots\text{H}$ hydrogen bond decreases as the number of water molecules decreases.

The trend of the solid line also reflects the exponential dependence between the size of the cluster and the interaction between methylamine and the water molecules. Except for $n = 5$, the strength of the $\text{N}\cdots\text{H}$ hydrogen bond in the $\text{CH}_3\text{NH}_2\cdots(\text{H}_2\text{O})_n$ ($n = 1-7$) clusters increases exponentially as the size of the cluster increases. This is consistent with the conclusion of our analysis of the geometrical parameters.

In addition, according to the function of the amide analog dimers⁷³ and the difference of these two systems, we can estimate the relationship between the $\text{N}\cdots\text{H}$ distance and the electron density at the $\text{N}\cdots\text{H}$ hydrogen bond BCP of methylamine hydrates to be

$$y = 5.124e^{-2.71x} + 0.0075 \quad (1)$$

where x denotes the $\text{N}\cdots\text{H}$ distance and y denotes the electron density. As shown in Figure 5, although the conclusions from our results mentioned above fluctuate at $n = 5$, this function still applies for this special case as well. In fact, the compatibility of this function for $n = 5$ verifies its wider applicability to some extent. According to the function for the amide analog dimers,⁷³ this relationship may also extend to the interactions of covalent bonds ($\text{N}-\text{H}$) and transition states for methylamines hydrates. However, it is necessary to verify the relationship explicitly with additional theoretical and experimental investigations.

Analysis of the Topological Parameters. Topological parameters derived from Bader theory can indicate the type of interaction. There are well-known relationships between energetic topological parameters and the Laplacian of the electron density at the critical point (expressed in atomic units, eq 2, virial equation, and eq 3)

$$\frac{1}{4}\nabla^2\rho = 2G_C + V_C \quad (2)$$

$$H_C = V_C + G_C \quad (3)$$

where G_C , V_C , and H_C are the kinetic, potential, and total electron energy densities at the critical point, respectively. G_C is a positive value, whereas V_C is a negative one. One can see that if the modulus of the potential energy outweighs 2 times the kinetic energy, then the Laplacian is negative (eq 2). This outcome implies a covalent type of interaction. However, there are interactions where the modulus of the potential energy outweighs the kinetic energy one time; in such a case, the Laplacian is positive, but H_C is negative (eq 3). Rozas et al. classified hydrogen bonds on the basis of $\nabla^2\rho$ and H_C values.⁷⁰ Weak and medium strength hydrogen bonds show both positive $\nabla^2\rho$ and H_C values. For strong H-bonds, $\nabla^2\rho$ is positive and H_C is negative. For very strong hydrogen bonds,

$\nabla^2\rho$ and H_C values are negative. The values of the topological parameters of the $\text{N}\cdots\text{H}$ hydrogen bonds between amino groups and water molecules for all the global minima are listed in Table 2. One can see that all the $\text{N}\cdots\text{H}$ H-bonds in our study can be classified as strong.

Table 2. Topological Parameters at Intermolecular Bond Critical Points of the $\text{N}\cdots\text{H}$ Hydrogen Bonds of the Global Minima at the PW91/6-311++G(3df,3pd) Level of Theory

n	ρ	G_C	V_C	H_C	$\nabla^2\rho$	$ V_C /G_C$
1	0.0388	0.0246	-0.0305	-0.0059	0.0747	1.24
2	0.0489	0.0300	-0.0419	-0.0119	0.0726	1.40
3	0.0602	0.0345	-0.0545	-0.0200	0.0580	1.58
4	0.0645	0.0362	-0.0593	-0.0231	0.0522	1.64
5	0.0629	0.0358	-0.0578	-0.0220	0.0552	1.61
6	0.0646	0.0362	-0.0595	-0.0233	0.0517	1.64
7	0.0688	0.0376	-0.0641	-0.0265	0.0447	1.70

Further, on the basis of the trends of the topological parameters listed in Table 2 (i.e., the increase of ρ and G_C and a decrease of V_C and H_C), we can also conclude that, except for $n = 5$, there is an increase in the strength of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ interaction as the number of water molecules in the cluster increases.

In conclusion, from the analysis of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bonds, we find that the strength of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bond can be classified as strong and the hydrogen bond is the main intermolecular interaction that increases as the number of water molecules increases in the global minima of the methylamine hydrates. This is true, except for the complex with five water molecules ($n = 5$), where the minimum energy structure changes from a cyclical configuration to a three-dimensional configuration, causing the topological parameters to fluctuate slightly. Nevertheless, the results for most of the complexes indicate that the contribution of the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bonds to the stability of clusters increases as the size of the hydrates increases.

As the conclusions above, for the system consisting of one methylamine molecule and up to seven waters the interactions between the amino groups and water molecules can be classified as strong hydrogen bonds. Further, the strength of the intermolecular interactions $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ increases as the size of the hydrated clusters increase. Because the amino group (NH_2) is also a constituent of proteins and responsible for many properties of biopolymers, the condition of $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bonds in methylamine hydration clusters also reflects the mechanism of the interaction between the proteins and water molecules in organisms to some extent. Thus, these results are meaningful for biological processes.

IV. CONCLUSION

In this paper, the stable structures of $\text{CH}_3\text{NH}_2\cdots(\text{H}_2\text{O})_n$ ($n = 1-7$) clusters were obtained by the BH algorithm coupled with the PW91/6-311++G(3df,3pd) level of theory. An analysis of structures and energetics showed that the stable geometries arise from a fusion of tetrameric or pentameric rings except for those with $n = 1$ and 2, which possess too few molecules. By the geometrical and topological parameters analysis, we found that the $\text{H}_2\text{N}\cdots\text{H}-\text{O}$ hydrogen bonds of the global minima are all strong hydrogen bonds and their strengths increase as the sizes of clusters increase except for $n = 5$ where there is a slight fluctuation. This work may shed light on the form mechanism

of methylamine existing in organisms and the hydration structures of larger molecules containing amino functional groups and their interaction with the water molecules nearby.

■ ASSOCIATED CONTENT

■ Supporting Information

Details about the comparison of the optimization methods are presented in section A. All the PW91/6-311++G(3df,3pd) optimized Cartesian coordinates and DF-MP2-F12 single point energies for each isomer are presented in section B. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

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