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Theoretical studies on proton affinities of H_2N–$(CH_2)_n$–NH_2 (n = 2–10) diamines at gas phase. Good correlation with protonation constants in solution

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ABSTRACT

A theoretical study on complete protonation of a series of diamine molecules with general formula H_2N–$(CH_2)_n$–NH_2 (n = 2–10, L2–L10) has been reported. The gas-phase protonation energies were computed using density functional theory (DFT) calculations. The standard 6-31G* and 6-311++G** basis sets were used in all calculations. Three species, L, HL^+ and H_2L^{2+} can be considered in protonation steps of diamine molecules. Among these, the HL^+ is involved in both the first, $L + H^+ \rightarrow HL^+$, and second, $HL^+ + H^+ \rightarrow H_2L^{2+}$, steps. Two different structures were considered for latter species: (I) a linear-like structure (II) a cyclic structure due to intramolecular hydrogen bonding. The trends for variations of calculated PA_1 in the series of these molecules, is very similar to that of their measured protonation constants when we consider the linear structure for all species. Furthermore, for latter structures there are good correlations between the calculated proton macroaffinities in the gas-phase with corresponding protonation constants in solution. The latter observation has led us to predict the stepwise protonation constants for L7 and L9.

1. Introduction

Recently, according to a theoretical study on proton affinity of some tripodal tetraamines, we introduced three new defined gas-phase proton affinities for polybasic molecules: proton microaffinity, proton macroaffinity and proton overallaffinity [1]. The proton microaffinity corresponds to protonation of a special site on a polybasic molecule [1–4]. The number of proton microaffinities, similar to number of protonation microconstants, depends not only upon the number of basic sites but also upon the symmetry of the molecule [5]. The proton macroaffinity corresponds to a weighted mean of various proton microaffinities in each step of the protonation of a polybasic molecule. The number of proton macroaffinities for one polybasic molecule depends on the number of basic sites. The proton overallaffinty is also corresponds to full protonation of a polybasic molecule. The proton overallaffinity can be calculated in two different ways. It can be defined as the negative of the electronic energy difference between L (a polybasic molecule) and its fully protonated form, H_2L^{2+}, together with a correction for difference in zero point energies. In latter case, we show the proton overallaffinity as PA_{ov}. In second way, it can be defined as summation of the calculated proton macroaffinities for the polybasic molecule. In this case, we show it as $\overline{PA}_{ov}$. Obviously, as a consequence of Hess's law, for one polybasic molecule the $\overline{PA}_{ov}$ must be the same as or very close to PA_{ov}, if the proton macroaffinities, $\overline{PA}_n$, are calculated in a correct way.

In this work, we report the results of our theoretical studies on full protonation of a series of diamine molecules with general formula H_2N–$(CH_2)_n$–NH_2 (n = 2–10). The first protonation step of a number of latter compounds at gas phase have been already investigated [6–12]. Herein, for first time, we report a theoretical study on both protonation steps of all above molecules at gas phase. The diamines with 2–10 methylene groups are selected because their protonation constants, except for n = 7 and 9, at different ionic strengths are available. Thus, we can study the correlation of our gas-phase proton affinities with corresponding protonation constants in solution. The chain like structure of the aliphatic diamines permits us to easily consider or ignore the intramolecular hydrogen-bond formation in the monoprotonated species (HL^+). Hence, we can consider a cyclic structure and/or a linear-like structure for latter species. A literature review shows that in all previous studies on gas-phase proton affinities of aliphatic diamines the intramolecular hydrogen-bonding is considered in HL^+ species [6–10]. In present study, we consider both the cyclic and the linear structures for HL^+ species. Obviously, the amount of proton affinity depends on the stability of the structures considered for species involved in porotonation process. The different structures are correspond to different proton affinities. Thus, according to study on the correlation of our different calculated proton affinities with corresponding protonation constants in solution we can guess whether the cyclic or the linear-like structure must be considered for diamine molecules in solution.

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In addition, we also wish to know whether and how much the formation of intramolecular hydrogen-bonding affects the values of proton micro-, macro- and overallaffinities of diamine molecules.

2. Computational methods

The geometries of all species with 2–10 methylene groups in the gas phase were fully optimized at DFT (B3LYP) [13] level of theory using the Gaussian 03 set of programs [14]. The standard 6-31G* basis set was used for all calculations. The standard 6-311++G** was also used for further calculations on resulting structures of latter calculations. Vibrational frequency analyses, calculated at the same level of theory, indicate that all optimized structures in the gas phase are at the stationary points corresponding to local minima without any imaginary frequency. A starting PM3 structure for ab initio calculations in the gas phase was obtained using the HyperChem 5.02 program [15].

3. Results and discussion

The proton affinity of a monobasic neutral ligand (related to the acidity) at 0 K is defined as the negative of the electronic energy difference between HL^+ and L together with a correction for difference in zero point energies. To convert the 0 K value to 298 K, one has to include thermal corrections for the translational, rotational and vibrational energies and a correction for the change in the number of molecules assuming ideal gas behavior [16]. Defined in these ways, the proton affinity of L is a positive number; the more positive the number, the greater is the energy gained by the system upon association of H^+ with L.

Obviously for each polybasic molecule there may be several ways for protonation depending on which site is protonated. Protonation of different sites will release different amounts of energy which are correspond to different proton microaffinities [1–4]. In the case of present A_2-type diamines two available basic sites are equal and in the first step of protonation, $L + H^+ \rightarrow HL^+$, two related proton microaffinities are equal, PA_1. In the second protonation step, $HL^+ + H^+ \rightarrow H_2L^{2+}$, there is also another proton microaffinity, PA_2. Indeed, in this especial case of symmetry each proton microaffinity corresponds to one proton macroaffinity (i.e. $PA_1 = \overline{PA}_1$ and $PA_2 = \overline{PA}_2$). Thus in this paper we use PA_1 and PA_2 instead of $\overline{PA}_1$ and $\overline{PA}_2$ for first and second proton macroaffinities, respectively. On the other hand, as it is illustrated in Fig. 1, for present diamine molecules the intramolecular hydrogen bonding can be considered or ignored in monoprotonated, HL^+, species. Thus two different structures for monoprotonated species should be considered: (I) a linear-like structure; (II) a cyclic structure in which the proton is covalently bound to one of the amino groups and is hydrogen-bonded to other amino group (see Fig. 1). Obviously, the latter structures have different stabilities/energies and formation of each structure from initial neutral molecule will release different amounts of energies (i.e. different proton microaffinities). The formation of H_2L^{2+} from the latter two different structures corresponds also to different amounts of proton microaffinities. Thus the values of calculated PA_1 and PA_2 depend on the structure of the HL^+. It should be noted that in this research we have chosen the most stable conformers for both the linear-like and cyclic structures [6–10].

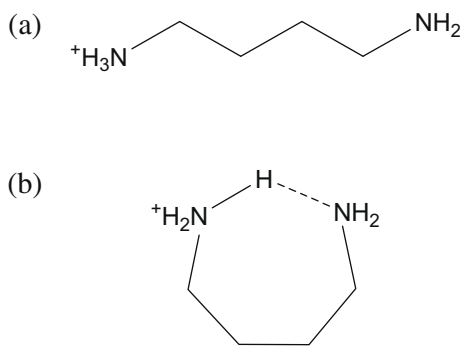

Fig. 1. Illustration of linear-like (a) and cyclic (b) structures for monoprotonated form of diamines (herein L4).

We note that the formation of intramolecular hydrogen bonding within the fully protonated species, H_2L^{2+}, is impossible because both the nitrogen atoms are protonated. It has been theoretically/experimentally shown that two protonated amino groups in a molecule tend to be located as far as possible from each other [17–20]. Thus it is clear that the most stable conformer for latter species is a linear-like structure.

The most stable conformer for a number of neutral diamines has been already studied in the gas phase. While some authors have chosen the linear-like structure as most stable structure [9,10], others have considered a cyclic structure for their diamines [6–8]. Obviously the intramolecular hydrogen bonding in a neutral diamine, L, is not comparable with that in a protonated species, HL^+. Thus, at first, we give our main attention to the HL^+ to see whether the cyclic and/or the linear-like structure can be considered for these species in solution. If the results showed that a linear-like structure must be considered for HL^+ species, then we can be sure that a similar linear-like structure will be adopted by the neutral species.

The gas-phase proton microaffinities which are directly correspond to the proton macroaffinies of these molecules calculated are given in Table 1. The values of proton overallaffinities, PA_{ov} which are completely same with $\overline{PA}_{ov}$ values (see Section 1) are also shown in the latter Table.

The results show that the calculated values for first proton macroaffinities, PA_1, of present diamine molecules are very close to each other. On the other hand, the calculated values for second proton macroaffinities, PA_2, are considerably different (specially when we compare the PA_2 of one molecule containing a small number of methylene groups with that of other molecules). For all molecules, the PA_1 is always greater than PA_2 but the difference in their values will be decreased with increasing the number of methylene groups.

Now, let us to compare the calculated proton macroaffinities for linear-like and cyclic structures. We note that the protonation process including the linear structures has smaller values for PA_1 and greater values for PA_2 than that including cyclic structures. The reason is clear, the formation of intramolecular hydrogen bonding in first protonation step increases the value of PA_1 while its dissociation upon the protonation in second step decreases the value of PA_2. Thus the intramolecular hydrogen bonding in monoprotonated species affects the PA_1 and PA_2 values of these molecules, but it have no effect on their proton overallaffinities (see Table 1 and Fig. 2).

Fortunately, the protontion constants for aliphatic diamines with 2–10 methylene groups (L2–L10), except for $n = 7$ and 9, at different ionic strengths have been determined [21]. It has been shown that the order of the first protonation constants for latter diamines usually is L2 < L3 < L4 < L5 < L6 < L8 < L10. It is interesting that we can see a same trend for first proton macroaffinities of these molecules only if we consider a linear-like structure for HL^+ species. The data in the Table 1 show that the variations of PA_1 values associated to the cyclic structures at both the gas phase and the solution are different with those associated to the linear structures. Thus only the proton macroaffinities associated to the linear structures have a reliable correlation with corresponding