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Good correlation between the calculated gas-phase first proton macroaffinities of some triazacycloalkanes ([*X*]aneN$_3$, *X* = 9–12) with their protonation constants in solution

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ABSTRACT

A theoretical study on first protonation step of a series of triazacycloalkanes with general formula {([*X*]aneN$_3$, *X* = 9–12)} (*X* = 9, L222; *X* = 10, L223; *X* = 11, L233; *X* = 12, L333) is reported. The geometry of all ligands and their monoprotonated forms were fully optimized at both the Hartree–Fock and DFT (B3LYP) levels of theory using 6-31+G* basis set. Then the first proton macroaffinities were calculated from the proton microaffinities according to defined equations. It is shown that there are good correlations between the calculated gas-phase first proton macroaffinities of these ligands with their protonation constants in solution.

1. Introduction

Recently we showed that for polybasic molecules the term proton affinity must be replaced with the new terms proton micraffinity, proton macroaffinity and proton overallaffinity [1]. For first time, we showed that there is a good correlation between the calculated gas-phase proton macroaffinities, $\overline{PA}_n$, and corresponding solution-protonation macroconstants (see Eqs. (1) and (2)) for a number of tripodal aliphatic tetraamines.

$$H_{n-1}L^{(n-1)+} + H^+ \rightleftharpoons H_nL^{n+} \tag{1}$$

$$K_n = \frac{[H_nL^{n+}]}{[H_{n-1}L^{(n-1)+}][H^+]} \tag{2}$$

We also investigated the Maxwell–Boltzmann (Eq. (3)) for calculation of probability distribution (x_i) of different protonated species in protonation steps of latter molecules and their bulky analogous [2].

$$x_i = \frac{e^{-\Delta G_i^0/RT}}{\sum_{i=1}^{n} e^{-\Delta G_i^0/RT}} \tag{3}$$

Then we showed that there is good correlations between the gas-phase first proton macroaffinity of Zn(II) complexes of a number of tripodal ligands [3] as well as Cu(II), Ni(II), Zn(II) and Cd(II) complexes of a number of triazacycloalkanes containing 9- through 12-membered rings ([*X*]aneN$_3$, where *X* = 9–12) (see Fig. 1) with their formation constants in solution [4]. Very recently, we showed that the study on proton affinities of polybasic molecules at gas-phase is useful for understanding their structures in solution [5,6]. In this work we want to report the results of our theoretical study on gas-phase first proton macroaffinity of latter macrocyclic ligands. These ligands have been studied extensively in the past 20 years. Several review articles have recently been published on the subject [7–9]. Thermodynamic stability of these ligands has been determined with several methods [9]. Thus following our interest on proton affinities of polybasic ligands we decided to study the correlations between the first proton macroaffinity of these ligands with corresponding protonation macroconstants in solution.

2. Computational methods

The geometries of all species in the gas-phase were fully optimized at both the Hartree–Fock and DFT(B3LYP) [10] levels of theory using the GAUSSIAN 98 [11] set of programs. The standard 6-31+G* basis set was used for all calculations. Vibrational frequency analysis, calculated at the same level of theory, indicate that optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. Calculations were performed on a Pentium-PC computer with 3600 MHz processor. A starting molecular-mechanics structure for the ab initio calculations was obtained using the HYPERCHEM 5.02 program [12].

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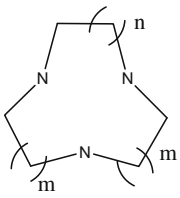

n=m==1 (L222)
n= 2, m=1 (L223)
n=1 m=2 (L233)
n=m=2 (L333)

Fig. 1. Structures of the macrocyclic ligands investigated here along with their common abbreviations.

3. Results and discussion

The proton affinity of a monobasic neutral ligand 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 [13]. 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.

For each polybasic molecule there are several different sites at which protonation can occur; protonation of different sites will release different amounts of energy. We used the term 'microaffinity' for protonation of one special site in a polybasic molecule or corresponding metal complexes [1–6].

The number of proton microaffinities in the first protonation step of the polybasic ligands depends not only upon the number of basic sites but also upon the symmetry of the complexes [14]. The macrocyclic ligands investigated here belong to (A_3) [i.e. L222 and L333], (A_2B) [i.e. L223, and L233] (see Fig. 1) general types, secondary amine sites are donated by A/B. Obviously for monoprotonated form of above general types we have 1 (X) and 2 (X, Y) microspecies, respectively, that differ in the location of proton/charge. Thus it seems the number of proton microaffinities should be 1 and 2, respectively, for latter general types. But as can be seen in the Fig. 2 we can consider several conformers for latter microspecies that differ in the number and/or the location of intramolecular hydrogen bonding. Thus it is clear that the number of proton microaffinities can be increased if the calculations show

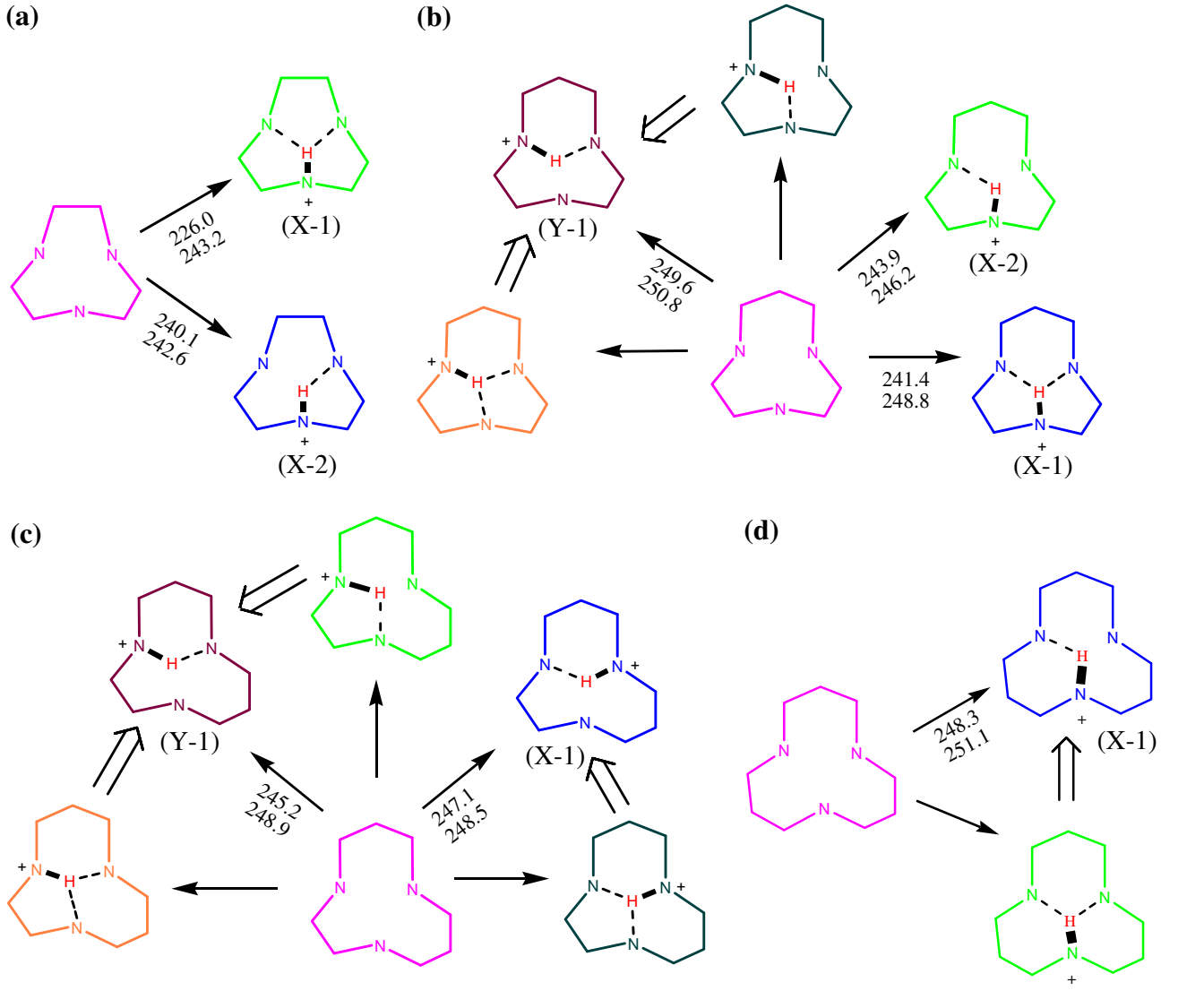

Fig. 2. Illustration of all possible microspecies and their various conformers involved in the first protonation step of L222 (a), L223 (b), L333 (c), and L233 (d) macrocyclic ligands, along with calculated proton microaffinities at B3LYP bold) and HF (plain text) levels of theory. The conversion of unstable conformers to more stable conformers are shown using ⇒ arrow.

that all the conformers are stable and "optimizable" structures. But as it is shown in Fig. 2, upon the optimization process some conformers will be converted to more stable ones. For example in the case of monoprotonated form of symmetrical ligands, $HL222^+$ and $HL333^+$, we can consider two conformers (X-1, X-2) that differ in the number of intramolecular hydrogen bonding. In first conformer the proton is strongly bonded to one nitrogen atom and is weakly connected to the remaining two nitrogen atoms through intramolecular hydrogen bonding. In second conformer the proton is strongly bonded to one nitrogen atom and is weakly connected to only one nitrogen atom through intramolecular hydrogen bonding. As it is shown in the Fig. 2a, in the case of $HL222^+$ both the predicted conformers (X-1 and X-2) were successfully optimized. Thus in latter case two different proton microaffinities were calculated. On the other hand, in the case of $HL333^+$, we could not optimize first conformer because it was converted to second conformer (X-1). Thus one microspecies and one proton microaffinty were confirmed for latter symmetrical ligand.

For monoprotonated form of asymmetric ligands, $HL223^+$ and $HL233^+$, we have two microspecies that differ in the location of the charge/proton. The protonation process for L223 is shown in Fig. 2b. As can be seen, in first microspecies (X) the proton is attached to one secondary amine located between two ethylene arms while in second microspecies (Y) it is located between one ethylene and one propylene arm. For latter microspecies we can consider two and three conformers, respectively, that differ in the number and/or location of intramolecular hydrogen bonding. As it is shown in Fig. 2b from the five considered conformers only three conformers were stable (X-1, X-2 and Y-1). Two conformers from the three considered conformers for species Y were converted to more stable conformer, Y-1, upon the optimization process. Thus we have only three proton microaffinities for latter asymmetrical ligand. The protonation process for L233 is also shown in Fig. 2c. As can be seen, in first microspecies (X) the proton is attached to one secondary amine located between two propylene arms while in second microspecies (Y) it is located between one ethylene and one propylene arm. For latter microspecies we can consider two and three conformers, respectively, that differ in the number and/or location of intramolecular hydrogen bonding. As it is shown in Fig. 2c from the five considered conformers only two conformers were stable (X-1 and Y-1). Other conformers were converted to latter more stable conformers upon the optimization process. Thus we have only two proton microaffinities for latter asymmetrical ligand.

In order to calculate the first proton macroaffinities of present ligands we use here the Eq. (4) which is the simplest form of our previously reported equations and is acceptable equation only for first step of protonation of polybasic molecules [2].

$$\overline{PA_1} = \frac{\sum_{i=1}^{m} PA_i \times S_i}{\sum_{i=1}^{m} S_i} \tag{4}$$

$$PA_i = \frac{\sum_{j=1}^{n} PA_j \times H_j \times X_j}{\sum_{j=1}^{m} H_j \times X_j} \tag{5}$$

In Eq. (4), PA_i is one of the calculated proton microaffinities in step 1 for one microspecies, and S_i denotes the available identical sites to undergo protonation. As it was discussed above for some microspecies there were more than one stable conformers that differ in the number and/or location of intramolecular hydrogen bonding. Thus we established the Eq. (5) for calculation of proton microaffinity of one microspecies from the proton microaffinities of the corresponding conformers. In this equation the PA_j is the proton microaffinities of one conformer, the H_j denotes the number of possible ways for formation of intramolecular hydrogen bonding

Table 1
Calculated zero point energies, total energies, proton microaffinities and first proton macroaffinities (kcal mol^{-1}) of the triazacycloalkanes studied here along with a comparison with corresponding protonation constants in solution.[a]

Species	Protonated site[b]	Micro species	Conformer	*ZPE* (Hartree)	E_0 (Hartree)	PA_j (kcal mol^{-1})	PA_i (kcal mol^{-1})	$\overline{PA_1}$ (kcal mol^{-1})	log K_1
L222				**0.221761**	**−401.670100**			**230.6**	**10.42**
				0.238911	−399.002215			242.7	
$HL222^+$	2,2	X	X-1	**0.237153**	**−402.030201**	**226.0**	**230.6**		
				0.257009	−399.389810	243.2	242.7		
			X-2	**0.238534**	**−402.052737**	**240.1**			
				0.256615	−399.388857	242.6			
L223				**0.252297**	**−440.950954**			**247.1**	**12.02**
				0.270087	−438.000332			249.9	
$HL223^+$	2,2	X	X-1	**0.265660**	**−441.335570**	**241.4**	**242.1**		
				0.287036	−438.396853	248.8	248.1		
			X-2	**0.266888**	**−441.339685**	**243.9**			
				0.287379	−438.392621	246.2			
$HL223^+$	2,3	Y	Y-1	**0.266477**	**−441.348773**	**249.6**	**249.6**		
				0.287155	−438.400002	250.8	250.8		
L233				**0.281096**	**−480.243942**			**245.5**	**11.96**
				0.302009	−477.011893			248.8	
$HL233^+$	3,3	X	X-1	**0.296547**	**−480.637694**	**247.1**	**247.1**		
				0.318998	−477.407886	248.5	248.5		
$HL233^+$	2,3	Y	Y-1	**0.295964**	**−480.634757**	**245.2**	**245.2**		
				0.318449	−477.408544	248.9	248.9		
L333				**0.309111**	**−519.535905**			**248.3**	**12.60**
				0.331879	−516.022636			251.1	
$HL333^+$	3,3	X	X-1	**0.325354**	**−519.931670**	**248.3**	**248.3**		
				0.349801	−516.422741	251.1	251.1		

[a] Calculation were performed at B3LYP (bold)and HF (plain text) using 6-31+G* basis set.
[b] The 2,2; 2,3 or 3,3 are correspond to the protonation of a secondary amine between two ethylene arms, one ethylene and one propylene arm or two propylene arms, respectively.
[c] $E_0 = E_{el} + ZPE$.
[d] From Ref. [9].

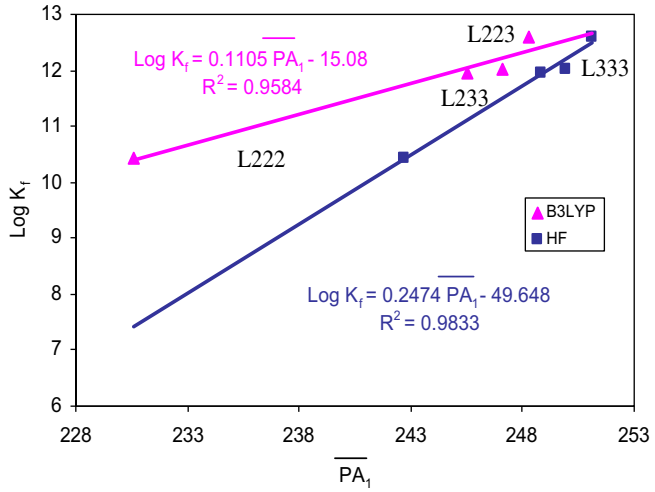

Fig. 3. Correlation of measured log K_1 versus calculated $\overline{PA}_1$ at both the HF and B3LYP levels of theory.

to produce that conformer and x_i is population of the conformer evaluated from the computed Gibbs energies through a Boltzmann distribution.

After calculation of proton microaffinity of all microspecies using the Eq. (5) we calculated the first proton macroaffinity of all triazacycloalkanes discussed here from the Eq. (4) (see Table 1). The results show that the order of basicity of these compounds in the gas-phase, similar to the solution, is as L333 > L223 > L233 > L222 (see Table 1). It is interesting that the basicity for L223 at both the solution and the gas phase is greater than that for L233. The unusual basicity of L223, against the L233, is probably due to difference in the intramolecular hydrogen bonding in latter amines. Note that in the case of L223 there were three stable conformers, while for L233 there were only two stable conformers.We note that the proton macroaffinity of ligands L222 to L333 varies from 230.6 to 248.3 kcal mol^{-1} for B3LYP method and from 242.7 to 251.1 for HF method. Thus, in all cases the HF calculated proton macroaffinities are greater than B3LYP calculated proton macroaffinities.

As it can be seen in Fig. 3 there is good correlations between the calculated proton macroaffinities and corresponding first protonation constants in solution. This correlation once again confirms that there can be a reliable correlation between the gas-phase proton macroaffinity of polybasic molecules and their protonation constants in solution [1,2].

It should be noted that for monoprotonated form of all present ligands we also tried to consider all conformers in which the intramolecular hydrogen bonding does not exist. However, the results showed that the intramolecular hydrogen bonding forms always in latter species.

4. Conclusion

The results of this work once again showed that the reliable theoretical calculation of the gas-phase first proton macroaffinity of polybasic molecules, according to the proton microaffinity analysis is possible. The first proton macroaffinities of triazacycloalkanes with general formula {([*X*]aneN_3, *X* = 9–12)} have good correlations with corresponding protonation constants in solution. The intramolecular hydrogen bonding has an effective role in the structure and the number of microspecies involved in protonation of latter compounds.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2009.07.002.

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