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Short communication

Complete gas-phase proton microaffinity analysis of five linear tetraamines containing two ethylenediamine residues

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ABSTRACT

Density functional theory (DFT) and ab initio (Hartree–Fock) calculations employing the 6-31G** basis set were used to determine gas-phase proton microaffinities ($PA_{n,i}$) of five linear tetraamines with general formula $NH_2(CH_2)_2NH(CH_2)_nNH(CH_2)_2NH_2$ (where n = 2, 3, 4, 5 and 6). The corresponding proton macroaffinities ($\overline{PA}_n$) were calculated according to our recently established method with and without considering Boltzmann distribution of microspecies. The results showed that there are good correlations between the calculated proton macroaffinities, $\overline{PA}_n$, and proton overallaffinities, $\log \overline{PA}_{ov}$, of these tetraamines in the gas phase with corresponding protonation macroconstants, $\log K_n$, and overall protonation constants, $\log \beta_4$, in solution, respectively.

1. Introduction

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 [1–7]. 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.

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. Therefore the term "proton affinity" for protonation of a special site on a polybasic molecule can be replaced by term "proton micraffinity", which we recently used for gas-phase protonation of polybasic molecules [8–14]. We also applied two other types of defined gas-phase proton affinities for such molecules: proton macraffinity and proton overallaffinity. The proton macroaffinity is a weighted mean of various proton microaffinities involved in each step of protonation of a polybasic molecule and corresponds to its protonation macroconstant in solution. We introduced an equation, Eq. (1), for calculation of proton macroaffinities, $\overline{PA}_n$, of polybasic molecules with any type of symmetry [8–10].

$$\overline{PA}_n = \frac{\sum_{j=1}^{l}\sum_{i=1}^{m} PA_{n,i} \times R_{n,j} \times S_{n,j}}{\sum_{j=1}^{l}\sum_{i=1}^{m} R_{n,j} \times S_{n,j}} \quad (1)$$

where

$$R_{n,j} = \sum_{j=1}^{K} R_{n-1,j} \times S_{n-1,j}$$

This formula shows that each proton macroaffinity, $\overline{PA}_n$, not only depends on the related proton microaffinities, $PA_{n,i,}$ and the relative abundance of corresponding microspecies, $R_{n,j,}$ but also on the available identical sites that undergo protonation, $S_{n,i.}$ Obviously the relative abundance of the initial neutral molecule, $R_{1,1}$, is 1, and that of any other species depends on both the relative abundance of previous species, $R_{n-1,j}$, and the available identical sites on them, $S_{n-1,j,}$ which are involved in its formation.

The proton overall affinity, PA_{ov}, is also defined as the negative of the electronic energy difference between L and its fully protonated form (herein $H_4L_4^+$) together with a correction for difference in zero point energies. According to Hess's law the summation of the calculated proton macroaffinities for one polybasic molecule ($\overline{PA}_{ov}$; see Eq. (2)) must be the same as or very close to its PA_{ov}.

$$\overline{PA}_{ov} = \sum_{n=1}^{m} \overline{PA}_n \quad (2)$$

In our previous works, we have shown that there is a good correlation between the calculated gas-phase proton macroaffinities and the corresponding solution-protonation macroconstants (K_n; see Eqs. (3) and (4)) for a number of tripodal tetraamines [8,9]. Furthermore, the correlation between the calculated $\text{Log}\,\overline{PA}_{ov}$ and measured $\log \beta_4$ (see Eq. (5)) was really excellent for the latter tetraamines.

$$H_{n-1}L^{(n-1)+} + H^+ \longleftrightarrow H_nL^{n+} \quad (3)$$

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$$K_n = \frac{[H_n L^{n+}]}{[H_{n-1} L^{(n-1)+}][H^+]} \quad (4)$$

$$\beta_n = K_1 K_2 \ldots K_n \quad (5)$$

We also have been interested in studying the proton affinity of metal complexes and their correlation with the protonation and formation constants in solution, respectively [13,14].

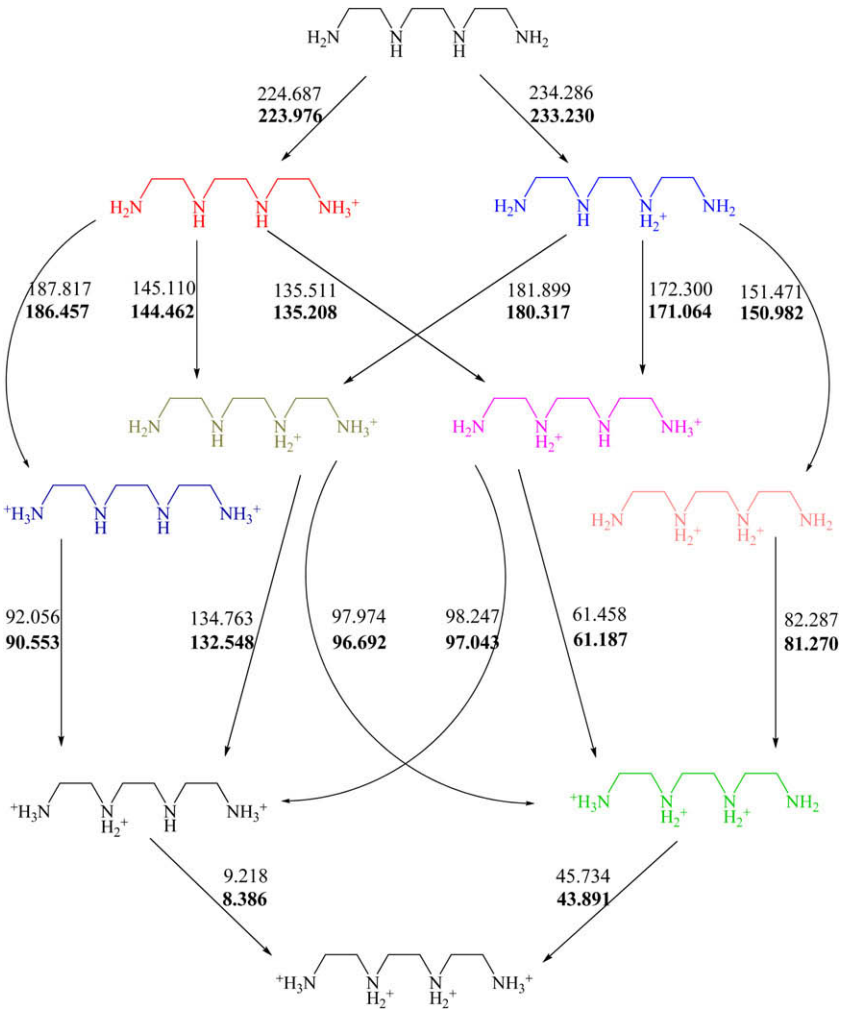
In this work we want to show that there is also good correlation between the calculated proton macroaffinities of five linear tetraamines with general formula $NH_2(CH_2)_2NH(CH_2)_nNH(CH_2)_2NH_2$ (where n = 2, L222; n = 3, L232; n = 4, L242; n = 5, L252; and n = 6, L262), with corresponding protonation macroconstants in solution.

2. Computational method

The geometries of all species in the gas-phase were fully optimized at both the Hartree–Fock and DFT(B3LYP) [15] levels of theory using the GAUSSIAN 98 set of programs [16]. The standard 6-31G** as well as 6-31+G* basis sets were used for all calculations. The results of 6-31G** calculations are given here and those for 6-31+G* calculations are give in the Supporting Information. 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 3000 MHz processor. A starting molecular-mechanics structure for the ab initio calculations was obtained using the HYPERCHEM 5.02 program [17].

3. Results and discussion

Recently, we showed that in the successive protonation of a linear aliphatic tetraamine, spermine, we can consider several conformers for each microspecies that differ in the number and/or the location of intramolecular hydrogen bonding [12]. We also calculated the most stable conformers as well as the most abundant conformers for each microspecies. It was shown that the most abundant conformers all have linear like structures, without intramolecular hydrogen bonding, and all the most stable conformers, except one, show intramolecular hydrogen bonding in their structure. We showed that with considering the most abundant conformers (i.e. the linear like structures) an excellent correlation can be observed between the calculated macroaffinities of spermine with corresponding protonation macroconstants in solution. Similarly, recently we showed that only the gas-phase proton affinities of trans like structures (without intramolecular hydrogen bonding) of a number of diamine molecules have good correlation with corresponding protonation macroconstants in solution [10]. Thus in this work we studied only the linear like structures, without intramolecular hydrogen bonding, for all microspecies of the compounds investigated here.



Scheme 1. Illustration of all possible paths for protonation of ligand L222, along with calculated $PA_{n,i}$ (kcal/mol). The data obtained at the HF/6-31G** level are given as plain text, those for the B3LYP/6-31G** level are in bold.

Table 1
Comparison of gas-phase proton macroaffinities (kcal/mol), $\overline{PA}_n$, and proton overallaffinities, $\overline{PA}_{ov}$, for linear tetraamines.[a]

	L222	L232	L242	L252	L262
$\overline{PA}_1$	229.48 **228.60**	229.95 **229.01**	229.99 **229.05**	230.14 **229.21**	230.18 **229.22**
$\overline{PA}_2$	162.35 **161.41**	168.36 **167.22**	172.88 **171.76**	176.39 **175.22**	179.21 **178.10**
$\overline{PA}_3$	94.46 **93.21**	106.65 **105.35**	115.72 **114.30**	122.70 **121.32**	128.24 **126.85**
$\overline{PA}_4$	27.47 **26.13**	45.45 **43.93**	58.818 **57.33**	69.26 **67.75**	77.47 **76.00**
$\overline{PA}_{ov}$	513.78 **509.37**	550.43 **545.54**	577.49 **572.45**	598.51 **593.51**	615.11 **610.19**
PA_{ov}	513.78 **509.37**	550.43 **545.54**	577.49 **572.45**	598.51 **593.51**	615.11 **610.19**

[a] The data obtained at the HF/6-31G** level are given as plain text, those for the B3LYP/6-31G** level are in bold.

In the case of tetraamines investigated here, with two secondary nitrogen atoms and two primary ones as it has been previously mentioned about spermine [12], the $S_{n,i}$ is equal for all microspecies in each step (2 for first step and 1 for other steps). Thus we can remove the $S_{n,i}$ from the Eq. (1) and use the following simplified equation:

$$\overline{PA}_n = \frac{\sum_{j=1}^{l}\sum_{i-1}^{m} PA_{n,i} \times R_{n,j}}{\sum_{j=1}^{l} R_{n,j}} \tag{6}$$

where

$$R_{n,j} = \sum_{j=1}^{K} R_{n-1,j}$$

The number of proton microaffinities in the complete protonation of polybasic molecules depends not only upon the number of basic sites but also upon the symmetry of the molecule. The linear tetraamines investigated here belong to the general type A_2B_2. It has been mathematically shown that for the protonation of such molecules in solution there are 10 different microspecies as well as 16 microconstants [18]. The successive protonation steps of a typical example of linear tetramines studied here are shown in Scheme 1. In this scheme the different microspecies for each tetraamine are illustrated as different colours, and proton microaffinities are calculated according to the energies of related microspecies (see Supporting Information).

Therefore, we considered all possible proton affinities (proton microaffinities, $PA_{n,i}$), and calculated proton macroaffinity ($\overline{PA}_n$) for each step (see Scheme 1 and Table 1). As can be seen in Fig. 1, there are good correlations between the calculated log $\overline{PA}_n$ in the gas phase and corresponding measured log K_n in solution for all four successive protonation steps of L222, L232, L242, L252 and L262 [19]. Also, the results show that, as expected, the proton macroaffinities of all ligands step by step decrease as $\overline{PA}_1 > \overline{PA}_2 > \overline{PA}_3 > \overline{PA}_4$.

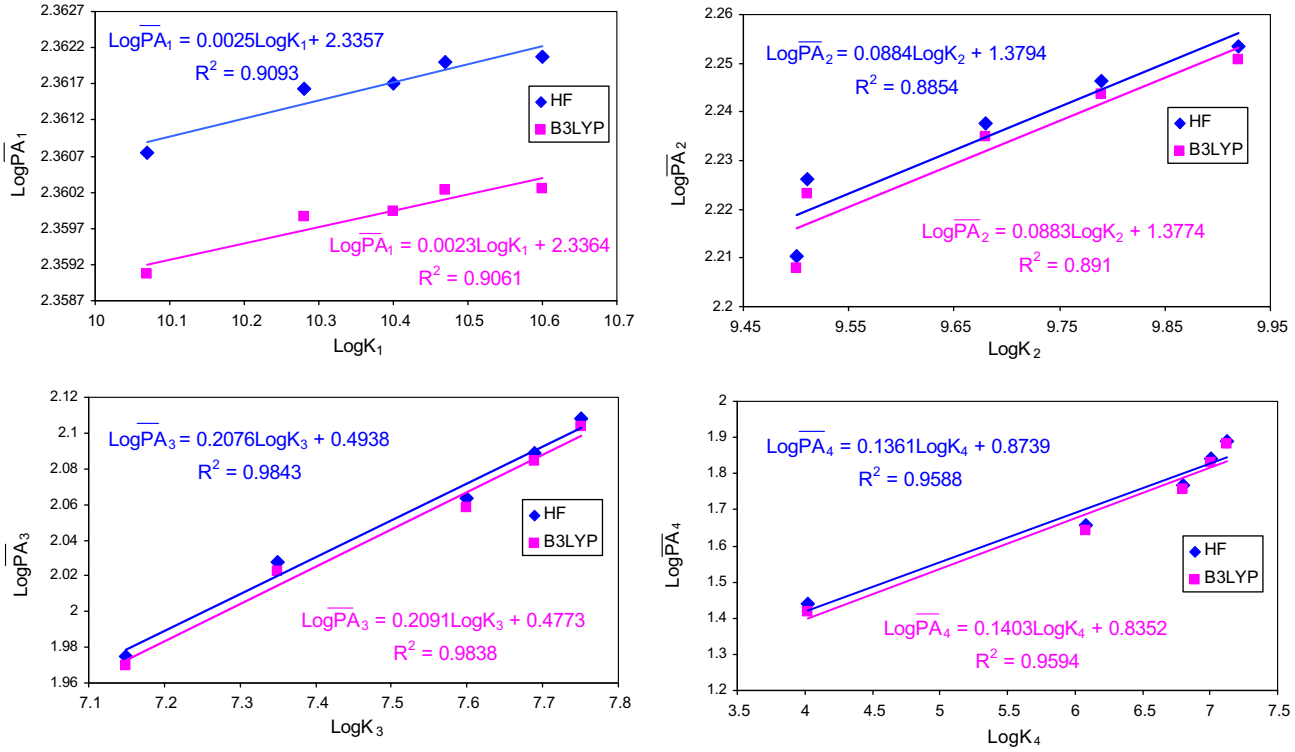


Fig. 1. Log K_n versus calculated Log $\overline{PA}_n$ for all four steps of complete protonation of the L222, L232, L242, L252 and L262 linear tetraamines at both HF and B3LYP levels of theory using 6-31G** basis set.

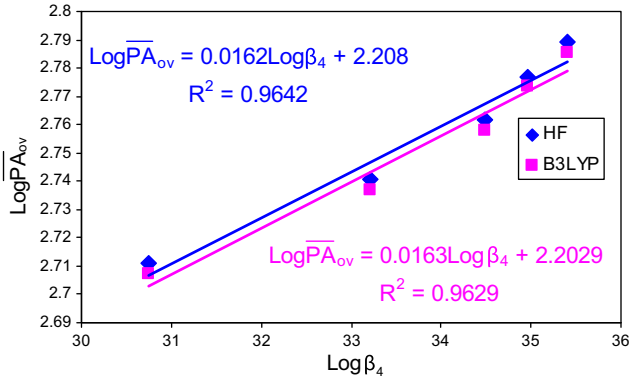


Fig. 2. Log β_4 versus calculated Log$\overline{PA}_{ov}$ using Eq. (6) at both HF and B3LYP levels of theory using 6-31G** basis set for L222, L232, L242, L252 and L262 linear tetraamines.

The variations of calculated log $\overline{PA}_n$ in the series of these polybasic molecules is very similar to that of their log K_n (Figs. S7 and S8). Over the four steps of protonation the summation of the proton macroaffinities gives the order of basicity as: L262 > L252 > L242 > L232 > L222.

Obviously this is the expected trend for the basicity of these molecules (increasing basicity with increasing number of methylene groups), as has been previously observed for the protonation constants of these ligands, L262 > L252 > L242 > L232 > L222 (Table S24) [19]. Also the summation of the calculated proton macroaffinities, $\overline{PA}_n$, for each of the linear tetraamines investigated here, $\overline{PA}_{ov}$, are the same as or very close to the proton overallaffinities, PA_{ov} for related molecules (Table 1). Furthermore, as can be seen in Fig. 2, the correlation between the calculated Log$\overline{PA}_{ov}$ and measured log β_4 (see Eqs. (3)–(5)) is really good. This correlation confirms our definition of the proton overallaffinity.

After computation of proton macroaffinities, from Eq. (6) we have also used the Eqs. (7) and (8) to calculate the proton macroaffinities, $\overline{PA}_n$.

$$\overline{PA}_n = \frac{\sum_{i=1}^{n} PA_{n,i} \times X_i}{\sum_{i=1}^{n} X_i} \tag{7}$$

$$\overline{PA}_n = \frac{\sum_{j=1}^{l}\sum_{i-1}^{m} PA_{n,i} \times R_{n,j} \times X_i}{\sum_{j=1}^{l} R_{n,j}} \tag{8}$$

where

$$X_i = \frac{e^{-\Delta G_i^0/RT}}{\sum_{i=1}^{n} e^{-\Delta G_i^0/RT}} \tag{9}$$

In the latter two equations, in contrast to Eq. (1), the population of the various species (xi) is considered; this is evaluated from the computed Gibbs energies through a Boltzmann distribution according to Eq. (9). While in the case of Eq. (7) the proton macroaffinities are calculated mainly according to a Boltzmann distribution, in Eq. (8) the latter distribution is added to Eq. (6). The correlation of log K_n and calculated log $\overline{PA}_n$ for all four steps of complete protonation of the L222, L232, L242, L252 and L262 was studied (see Supporting Information, Figs. S2 and S3). The result showed that, using only Eq. (6), the correlations are very good for all four successive protonation steps.

4. Conclusions

The results of this work show that the reliable theoretical calculation of the gas-phase proton macroaffinities and proton overallaffinities of linear tetraamine ligands according to the complete proton microaffinity analysis is potentially possible. Once again it was shown that there can be a good correlation between the proton macroaffinity of a series of polybasic molecules in the gas phase and corresponding protonation macroconstants in solution.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2010.04.019.

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