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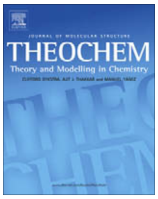

Good correlation between the calculated gas-phase first proton macroaffinities of some triazacycloalkanes ([X]aneN_3, X = 9–12) with their protonation constants in solution

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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 microaffinity, 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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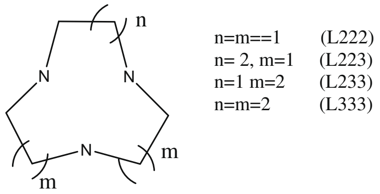

Fig. 1. Structures of the macrocyclic ligands investigated here along with their common abbreviations.

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

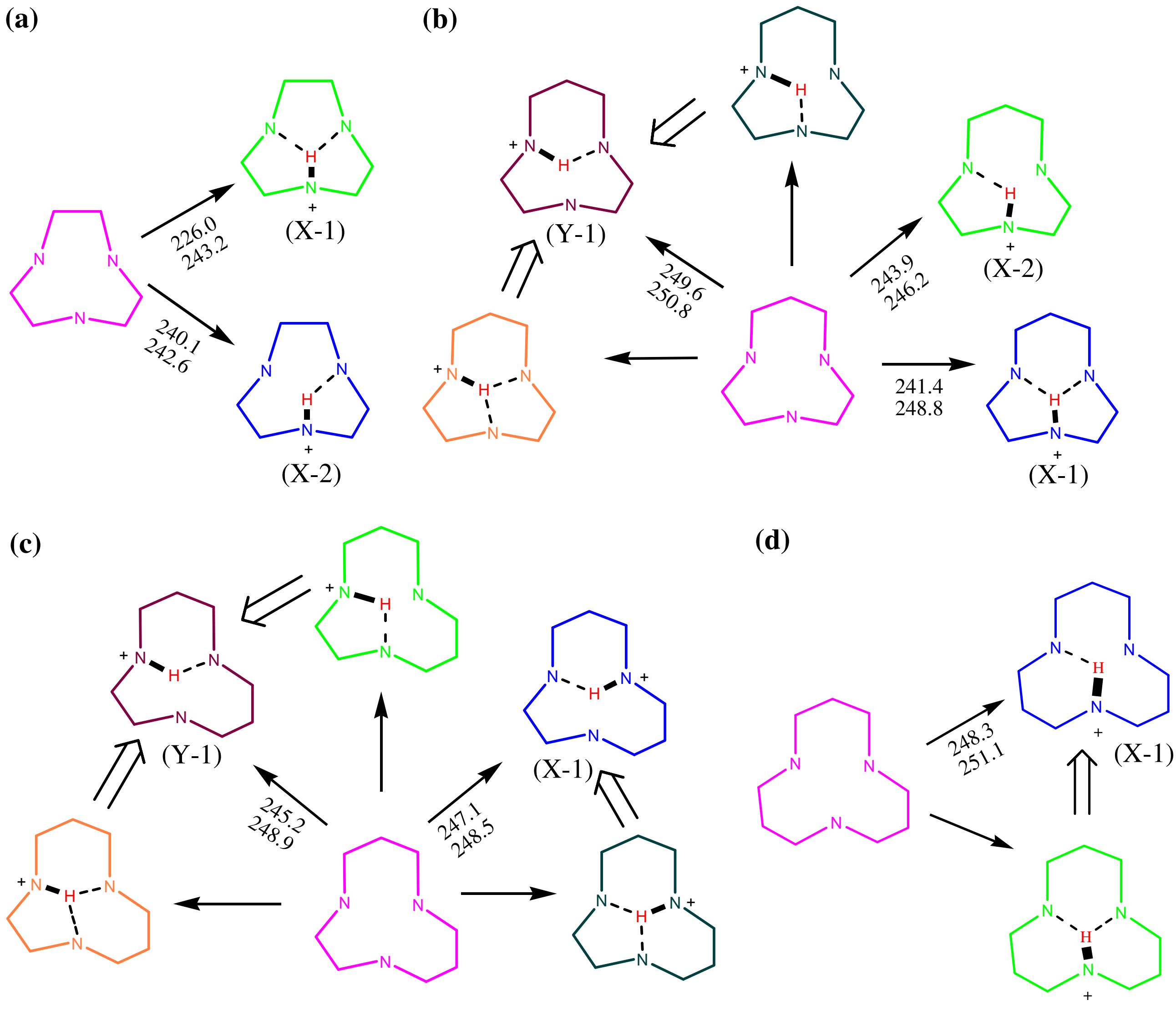

Fig. 2. Illustration of all possible microspecies and their various conformers involved in the first protonation step of L222 (a), L223 (b), L333 (c), and L233 (d) macrocyclic ligands, along with calculated proton microaffinities at B3LYP bold) and HF (plain text) levels of theory. The conversion of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