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Computational Prediction of pK_{aH} of Conjugate Acids Pentazinium ($CH_2N_5^+$) and Hexazinium (HN_6^+) of the Two Hypothetical Molecules Pentazine and Hexazine

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Abstract In our earlier article we had determined the pK_{aH} of the two conjugate acids Pentazinium ($CH_2N_5^+$) and Hexazinium (HN_6^+) of the two hypothetical molecules Pentazine (CHN_5) and Hexazine (N_6) respectively; this we had done by exploiting Katritzky graphical method. In this article we have reinforced our determination of pK_{aH} of the two conjugate acids Pentazinium ($CH_2N_5^+$) and Hexazinium (HN_6^+) by DFT calculations. These DFT calculations can easily be carried out by Graduate students. This would be a good exercise/project-based learning activity for Graduate students to run the SMD_{sSAS} model calculations

Keywords: *p$K_{aH,}$ Pentazinium, Hexazinium, DFT & SMD_{sSAS}*

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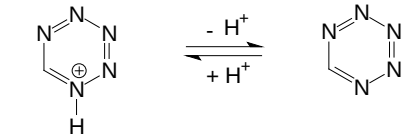
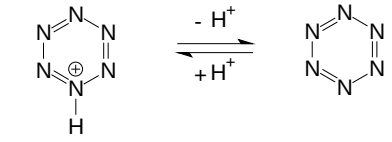
1. Introduction

In our earlier article [1], we had taken the 8 aromatic azines (Table 1) out of which the last two are hypothetical molecules Pentazine and Hexazine and have not been synthesized. The pK_{aH} of the first six protonated species were available in the literature [2,3,4]. For the last two members of azine series that is Pentazinium (Equation 1) and Hexazinium (Equation 2) the pK_{aH} was determined using two Graphical plots. Out of the two graphical plots, the first one (Plot1) was that of p$K_{aH,}$ versus number of Nitrogen atoms of aromatic azines, that is, Katritzky graphical method [5].

The plot 1 was extrapolated to 5th (Pentazinium) and 6th (Hexazinium) Nitrogen atoms; thus, yielding p$K_{aH,}$ of Pentazinium and Hexazinium. In this article, as already mentioned in the abstract we have reinforced the determination of pK_{aH} of Pentazinium and Hexazinium by DFT calculations. These simple computational calculations can easily be carried out by Graduate students. It can be given as project-based learning activity. After carrying out the these DFT calculations, the Graduate students, will be able to run the SMD_{ssas} (SOLVENT MODEL DENSITY$_{scaled\ solvent\text{-}accessible\ surface}$) model calculations.



Pentazinium cation Pentazine (1)



Hexazinium cation Hexazine (2)

2. Methods

Gaussian 09 [6] software was used to carry out all the theoretical calculations. The pK_{aH} values were determined using SMD_{sSAS} (scaled solvent-accessible surface) model. The geometries were optimized at the M06-2X/6-31+(d,p) level. The optimization and frequency calculations were performed simultaneously. The method for the determination of pK_{aH} is the same as that described in Lian et al. [7]. The nonspecific form of Equation 1 and Equation 2 is given by Equation 3 [7]:

$$AH^+(aq) \xrightarrow{\Delta G^*aq} AH(aq) + H^+(aq) \quad (3)$$

where $AH^+(aq)$ is either Pentazinium cation or Hexazinium cation. AH(aq) is either Pentazine or Hexazine. The free energies of $AH^+(aq)$ and AH(aq) are obtained from the optimized (opt + freq) structures using M06-2X functional and 6-31+(d,p) basis set.

The pK_{aH} of cation AH^+ is calculated according to Eqn 4:

$$pK_{aH} = \Delta G^*_{aq}/2.303RT \quad (4)$$

The free energy in the 1 M standard state, ΔG^*_{aq},, was calculated directly from the aqueous Gibbs free energies of the acid and conjugate base using Eqn 5:

$$\Delta G^*_{aq} = G^*_{aq}(AH) + G^*_{aq}(H^+) - G^*_{aq}(AH^+) \quad (5)$$

The gas-phase standard phase correction term, $G^{o\rightarrow *}$ for both acid and conjugate base, cancel in this equation. The standard state aqueous free energy of proton, $G^*_{aq}(H^+)$, was calculated using Eqn 6:

$$G^*_{aq}(H^+) = G^o_g(H^+) + \Delta G^*_{aq,solv}(H^+) + \Delta G^{o\rightarrow *} \quad (6)$$

In the above equation $G^o_g(H^+)$ = –6.29 kcal mol^{-1} and the experimentally measured hydration free energy $\Delta G^*_{aq,solv}(H^+)$ = –265.9 kcal mol^{-1} was taken from the literature [8,9,10,11,12]. $\Delta G^{o\rightarrow *}$ is the gas-phase standard correction and is used to convert from 1 atm ideal gas standard state to 1 M standard state, where superscripts o and * indicate 1 atm and 1 M standard states, respectively: $\Delta G^{o\rightarrow *} = RT$ ln 24.26 = 1.89 kcal mol^{-1} at 298 K [13]. Therefore, substituting in equation 6,

$G^*_{aq}(H^+)$ = (-6.29) + (-265.9) + (1.89)

= -270.3 kcal mol^{-1}

This $G^*_{aq}(H^+)$ = -270.3 kcal mol^{-1} is substituted in equation 5, along with $G^*_{aq}(AH)$ and $G^*_{aq}(AH^+)$.

The synopsis of the above method is to find the free energy of $G^*_{aq}(AH^+)$ i.e. say Pentazinium ion, $G^*_{aq}(AH)$ say Pentazine and taking the $G^*_{aq}(H^+)$ as -270.3 kcal mol^{-1} we get ΔG^*_{aq}. This ΔG^*_{aq} is substituted in equation 4 to get the pK_{aH}.

3. Discussion

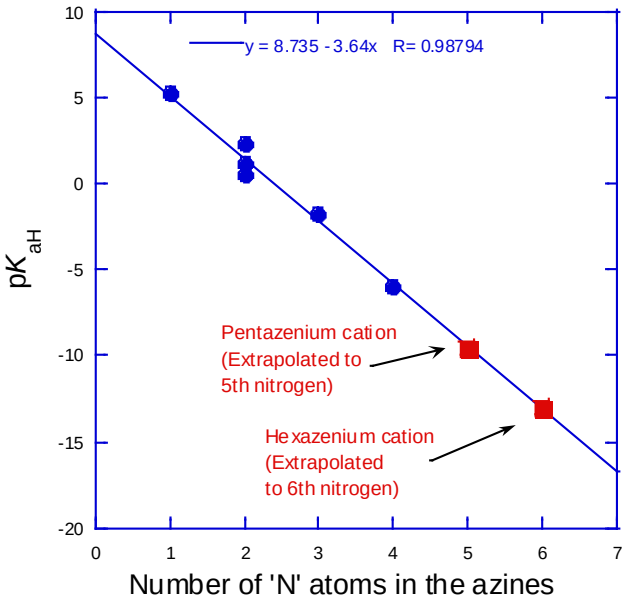
Lian et al [7] mentioned that in the continuum model, the cavity formed by the solute-solvent boundary is one of the most important factors for accuracy of the model. He conveyed that the essence of SMD_{sSAS} (scaled solvent-accessible surface) approach is to improve the accuracy of the SMD (solvent model density) continuum model by optimizing the solute-solvent boundary. In the SMD_{sSAS} model a scaling factor α is introduced to tune the size of the cavity, thereby improving the solute-solvent interaction. Thus, the factor α is extremely crucial in SMD_{sSAS} model. One can refer to reference [7] for further details regarding the merits of SMD_{sSAS} model. In his article Lina et al [7] proved that SMD_{sSAS} method gave the most accurate pK_a values of carboxylic acids, amines and thiols. Liean et al had taken the α value of 0.485 (for elements H, C and N). In the present article we have used SMD_{sSAS} model for the accurate determination of pK_{aH} of aromatic azines (Table 1). Since our compounds contained H, C & N atoms we took a cue from Lian et al [7] article (he reported the α value of 0.485 for H, C and N atoms) to choose the crucial α value. The crucial α value was further tuned to get the accurate value of pK_{aH} values (Table 1). To make it lucid and comprehensible to Graduate students, the following input file of Pentazinium ion is depicted (the bottom of the input file has the crucial alpha value, which has been tuned to 0.447 for Pentazinium ion).

```
%chk=mol.chk
%lindaworkers=cnode1362.cm.cluster
# opt freq m062x/6-31+g(d,p) scrf=(solvent=water, read) pop=nbo geom=connectivity

Pentazinium ion
1 1
N
N            1          B1
C            1    1.28750605    2    119.32188762
N            2          B2    1          A1    3          D1
N     3          B3    1          A2    2     0.00000000
H     3     B4   1   120.59325302    2    180.00000000
N     5     B5   3        A3              1          D2
H     1     B6   3        A4              5          D3

 B1        1.40002009
 B2        1.23803184
 B3        1.46404372
 B4        1.07000000
 B5        1.23231199
 B6        1.00000000
 A1      120.66752010
 A2      118.81349395
 A3      119.14599004
 A4      120.33905619
 D1       -0.00000000
 D2       -0.00000000
 D3     -180.00000000

 1 2 1.0 3 2.0 8 1.0
 2 4 2.0
 3 5 1.0 6 1.0
 4 7 1.0
 5 7 2.0
 6
 7
 8

 surface=sas
 alpha=0.447
```

The crucial SMD_{sSAS} α (alpha) value = 0.447 is for Pentazinium ion. SMD_{sSAS} α (alpha) values of all the compound are given in Table 1. The pK_{aH} values of the first six members (Table 1) are available in the literature and we got almost the same pK_{aH} values. The pK_{aH} of protonated hypothetical molecules Hexazine and Pentazine were not reported in the literature. We reported pK_{aH} of protonated Hexazine and Pentazine (Plot1) by Katritzky graphical method [1]. In the present study by SMD_{sSAS} method we got almost the same (Table 1) for protonated Pentazine -9.56 (~0.74% error) and Hexazine -13.06 (~0.4% error). Thus, we can conclude that pK_{aH} of protonated Hexazine and Pentazine are reasonably correct. Further, we can also infer that SMD_{sSAS} is a reasonably good method to determine the pK_{aH} values for this azine series.

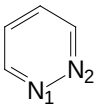
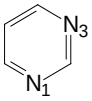
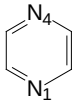
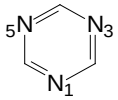
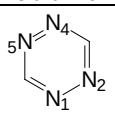
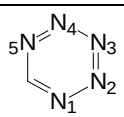
LEARNING OUTCOMES

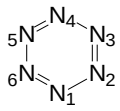
1). Students would be able to find the pK_{aH} values by Katrizky graphical method (to be more correct, this method was reported in our earlier article [1])
2). Students would have mastered the prediction of pK_{aH} values by SMD_{sSAS} solvent model.
3). We want the graduate students to figure out the correct method to find the crucial alpha value and understand the significance of alpha from reference [7].



Plot 1. pK_{aH} versus Number of N atoms of Azines

Table 1. Aromatic azines with their corresponding data

Serial No.	Compound	Number of nitrogen atoms	pK_{aH} (Literature value)	SMD_{sSAS} α value	pK_{aH} by SMD_{sSAS}	% Error of pK_{aH} relative to Literature value
1	 pyridine	1	5.27 [2]	0.482	5.20	1.32
2	 1,2-pyridazine	2	2.24 [3]	0.480	2.25	0.44
3	 1,3-pyridazine	2	1.23 [3]	0.483	1.18	4.06
4	 1,4-pyridazine	2	0.51 [3]	0.483	0.56	9.80
5	 s-triazine	3	-1.70 [4]	0.469	-1.75	2.94
6	 s-tetrazine	4	-6.00 [4]	0.455	-5.990	0.16
7	 pentazine	5	-9.49 [1]	0.447	-9.56	0.73

8	 hexazine	6	-13.1[1]	0.422	-13.06	0.30

4. Conclusion

The pK_{aH} of the two cations (eqn. 1 and 2) Pentazinium ($CH_2N_5^+$) and Hexazinium (HN_6^+) of the two hypothetical molecules Pentazine (CHN_5) and Hexazine (N_6) were determined by our group with the help of Katritzky plot [1]; they turned out to be -9.49 and -13.1 respectively. In this article we determined the same by DFT calculations; we got -9.56 for Pentazinium and -13.06 for Hexazinium, bolstering our pK_{aH} determinations. The fact that we are getting the same pK_{aH} values by both the methods, that is Katritzky graphical method and SMD_{sSAS} method, we can infer that our values are reasonably correct. Further, we can also infer that SMD_{sSAS} is a reasonably good method to determine the pK_{aH} values for this azine series. After successfully finding the pK_{aH} of all the compounds (Table1), the Graduate students would have mastered the SMD_{sSAS} model calculations. Thus, it is a good exercise/project-based learning activity to master the SMD_{sSAS} model calculations.

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Conflict of Interest Statement

The authors declare no conflicts of interest

Availability of Data and Material

All the electronic data related to this article is provided in the supplementary material.

Author Contributions

Equal contribution from all the four authors.

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