pK<sub>aH</sub> of the Two Conjugate Acids (CH<sub>2</sub>N<sub>5</sub><sup>+</sup>) and (HN<sub>6</sub><sup>+</sup>) of Two Hypothetical Molecules the Pentazine (CHN<sub>5</sub>) and the Hexazine (N<sub>6</sub>) of Azabenzene Series: A Chemical Education Perspective

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Abstract Extrapolation of a simple straight-line graph is used to calculate the pK<sub>aH</sub> of two cations (CH<sub>2</sub>N<sub>5</sub><sup>+</sup>) and (HN<sub>6</sub><sup>+</sup>) (eqn. 1 and 2) of two hypothetical molecules pentazine (CHN<sub>5</sub>) and hexazine (N<sub>6</sub>). This is achieved by simply an extrapolation of the locus of the plot of pK<sub>aH</sub> of protonated pyridine, pyridazines, s-triazine and 1,2,4,5-tetrazine versus the number of nitrogen atoms of the cyclic azines. Even well matched pK<sub>aH</sub> values for these two species were found from the extrapolation of the locus of the plot of pK<sub>aH</sub> versus average ionization potential (I<sub>v</sub>/eV) of the neutral azines. This article is useful in graduate research classroom to explain the acid-base properties and to determine the pK<sub>aH</sub> values.

Keywords: pK<sub>aH</sub>, azines

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1. Introduction

A total of 12 azines can be formulated on successive substitution of each sp<sup>2</sup> carbon (= CH –) of benzene by nitrogen atoms (scheme 1). Several reviews appeared in literature about synthesis of these azines [1-5]. One of the two meanings of azines is, in heterocyclic chemistry a class of six-membered aromatic ring compounds. And the other class is N-N linked diimines. The aromatic azines are the compounds containing one nitrogen (pyridine) to six nitrogen atoms (hexazine) [3]. The compounds with one to four nitrogen atoms, pyridine (I), pyridazines (II), (III), (IV), s-triazine (VII) and 1,2,4,5-tetrazine (X) and the pK<sub>aH</sub> of their conjugate acids are known [6,7]. The last two compounds the pentazine (XI, CHN<sub>5</sub>) and the hexazine (XII, N<sub>6</sub>) are two hypothetical molecules [8,9]. They were neither yet synthesized nor yet are pK<sub>aH</sub> values of their cations known. In the present work the estimation of their pK<sub>aH</sub> values is taken up.

2. Methods

All the linear correlations were done using the Kaleida Graph software, Version 4.1 for windows, Reading, PA, USA. The chemical structures are drawn using chemdraw.
3. Results and Discussion

This paper substantiates the determination of $pK_a$ of the two conjugate acids (CH$_2$N$_5^+$) and (HN$_6^+$) of two hypothetical molecules of azabenzone series the pentazine (CHN$_5$) and the hexazine (N$_6$). This is in continuation of our earlier work on the determination of $pK_a$ of pentazole (of N(1)-H acidity) molecule [10] by extrapolation method of the locus of the plot of $pK_a$ versus number of nitrogen atoms and by DFT calculations again a hypothetical molecule not yet synthesized and theoretical determination of $pK_a$s of P(1)-H Phospholes [11]. This is due to the zeal we got from a small note in the Handbook of Heterocyclic Chemistry by Katrizsky et.al [12] in the context of the explanation of the effect of aza substitution on the N(1)-H acidity which shows how the $pK_a$ values of azoles decrease systematically with number of nitrogen atoms.

In the present work we tried the estimation of $pK_{a\text{eff}}$ of the two conjugate acids (CH$_2$N$_5^+$) and (HN$_6^+$) in two different methods. It is noteworthy that for every nitrogen added to the ring system decreases the $pK_{a\text{eff}}$ systematically by 3-4 units ignoring 1,2- and 1,4-pyridazines in the sequence (Table 1). Even using $pK_{a\text{eff}}$ of 1,2- and 1,4-pyridazines with 1,3-pyridazine gives an average $pK_{a\text{eff}}$ of 1.33 (Table 1). This is close to the $pK_{a\text{eff}}$ of 1,3-pyridazine (1.23) which is originally used to see the systematic change of $pK_{a\text{eff}}$ by 3-4 units for every nitrogen added to the ring system. This is due to the high electronegativity of nitrogen which decreases the N-H bond energy and makes the proton to dissociate easily. This makes the neutral base CHN$_5$ and N$_6$ more stable than the cations CH$_2$N$_5^+$ and HN$_6^+$. Hence is the decrease in $pK_{a\text{eff}}$. A plot of $pK_{a\text{eff}}$ versus number of nitrogen atoms yields a good straight line with a correlation coefficient of 0.9872 (Figure 1). On extrapolation of the locus of this plot to number of nitrogen atoms 5 and 6 gave $pK_{a\text{eff}}$ of -9.49 and -13.14 for the two conjugate acids (CH$_2$N$_5^+$) and (HN$_6^+$) respectively. From the Table 1 for every nitrogen added to the ring system the mean ionization potential (I$_v$/eV) increases systematically by a factor of 0.80 eV. Or taking the average I$_v$ (10.43 eV) of 1,2-, 1,3- and 1,4-pyridazines, the systematic change in I$_v$ is 0.88 eV (Table 1). A plot of mean ionization potential (I$_v$/eV) versus number of nitrogen atoms yields a good straight line with a correlation coefficient of 0.9953 (Figure 2). On extrapolation of the locus of this plot to number of nitrogen atoms 5 and 6 gave mean ionization potentials (I$_v$/eV) 12.85 and 13.66 for pentazin (CHN$_5$) and hexazin (N$_6$) respectively. A plot of $pK_{a\text{eff}}$ versus mean ionization potentials (I$_v$/eV) gave a good straight line with a correlation coefficient of 0.9704 (Figure 3). On extrapolation of the locus of this plot to mean ionization potentials of (I$_v$/eV) 12.85 and 13.66 gave $pK_{a\text{eff}}$ of -8.84 and -12.35 for pentazinium cation (CH$_2$N$_5^+$) and hexazinium cation (HN$_6^+$) respectively. The difference of less than one $pK_a$ unit in $pK_{a\text{eff}}$ values obtained in the present work (see rows 7 and 8 and last column of Table 1) from two independent methods is not unexpected. Even large differences were experienced between experimental and theoretical $pK_a$ values of various carbon acids [13]. Probably to our knowledge HN$_6^+$ is the worlds strongest positively charged nitrogen acid.

### Table 1. Mean Ionization Potentials (I$_v$/eV) and $pK_{a\text{eff}}$ values of azines

| Sl. No. | compound | Number of nitrogen atoms | I$_v$ (eV) (neutral molecules) | $pK_{a\text{eff}}$ (protonated species) |
|---------|----------|--------------------------|-------------------------------|----------------------------------------|
| 1       | pyridine | 1                        | 9.60                          | 5.27                                   |
| Sl. No. | compound          | Number of nitrogen atoms | $I_v$ (eV) (neutral molecules) | $pK_a$ (protonated species) |
|--------|-------------------|--------------------------|-------------------------------|---------------------------|
| 2      | 1,2-pyridazine    | 2                        | 10.3                          | 2.24                      |
| 3      | 1,3-pyridazine    | 2                        | 10.5                          | 1.23                      |
|        |                   |                          | Average $I_v$ is 10.43        |                           |
| 4      | 1,4-pyridazine    | 2                        | 10.5                          | 0.51                      |
|        |                   |                          | Average $pK_a$ of the three compounds with two nitrogen atoms in the ring system is 1.33 |
| 5      | s-triazine        | 3                        | 11.3                          | -1.70                     |
| 6      | s-tetrazine       | 4                        | 12.0                          | -6.00                     |
| 7      | pentazine         | 5                        | 12.9                          | -9.49<sup>a</sup>         |
|        |                   |                          |                               | -8.84<sup>d</sup>        |
| 8      | hexazine          | 6                        | 13.7                          | -13.1<sup>b</sup>        |
|        |                   |                          |                               | -12.4<sup>d</sup>        |

<sup>a</sup> from reference [7]
<sup>b</sup> extrapolated values from the plot of $pK_a$ versus number of nitrogen atoms (Figure 1)
<sup>c</sup> extrapolated values from the plot of mean ionization potential versus number of nitrogen atoms (Figure 2)
<sup>d</sup> extrapolated values from the plot of $pK_a$ versus mean ionization potential (Figure 3).

Figure 1. $pK_a$ versus number of nitrogen atoms of azines
The authors don’t have any competing financial interest.

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