World Journal of Chemical Education, 2022, Vol. 10, No. 3, 105-109
Available online at http://pubs.sciepub.com/wjce/10/3/3
Published by Science and Education Publishing
DOI:10.12691/wjce-10-3-3

pK_{aH} of the Two Conjugate Acids ($CH_2N_5^+$) and (HN_6^+) of Two Hypothetical Molecules the Pentazine (CHN_5) and the Hexazine (N_6) of Azabenzene Series: A Chemical Education Perspective

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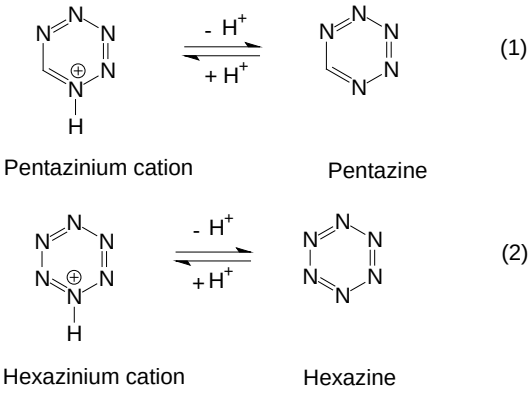
Received June 20, 2022; Revised July 25, 2022; Accepted August 03, 2022

Abstract Extrapolation of a simple straight-line graph is used to calculate the pK_{aH} of two cations ($CH_2N_5^+$) and (HN_6^+) (eqn. 1 and 2) of two hypothetical molecules pentazine (CHN_5) and hexazine (N_6). This is achieved by simply an extrapolation of the locus of the plot of pK_{aH} 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_{aH} values for these two species were found from the extrapolation of the locus of the plot of pK_{aH} versus average ionization potential (I_v/eV) of the neutral azines. This article is useful in graduate research classroom to explain the acid-base properties and to determine the pK_{aH} values.



Keywords: *p$K_{aH;}$ azines*

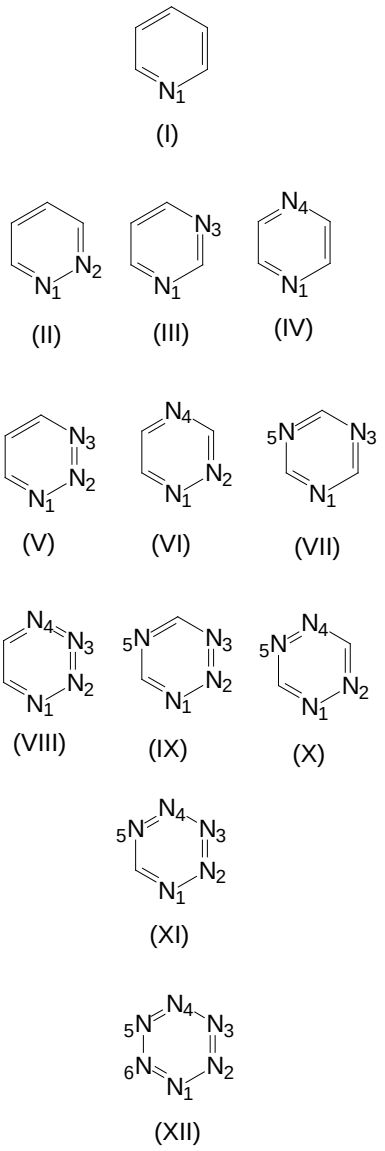
Cite This Article: R. Sanjeev, R. Ravi, D. A. Padmavathi, and V. Jagannadham, "pK_{aH} of the Two Conjugate Acids ($CH_2N_5^+$) and (HN_6^+) of Two Hypothetical Molecules the Pentazine (CHN_5) and the Hexazine (N_6) of Azabenzene Series: A Chemical Education Perspective." *World Journal of Chemical Education*, vol. 10, no. 3 (2022): 105-109. doi: 10.12691/wjce-10-3-3.

1. Introduction

A total of 12 azines can be formulated on successive substitution of each sp2 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_{aH} of their conjugate acids are known [6,7]. The last two compounds the pentazine (XI, CHN_5) and the hexazine (XII, N_6) are two hypothetical molecules [8,9]. They were neither yet synthesized nor yet are pK_{aH} values of their cations known. In the present work the estimation of their pK_{aH} 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.



Scheme 1.

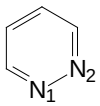
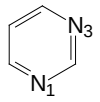
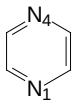
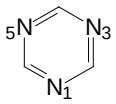
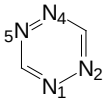
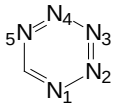
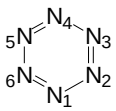
3. Results and Discussion

This paper substantiates the determination of pK_{aH} of the two conjugate acids ($CH_2N_5^+$) and (HN_6^+) of two hypothetical molecules of azabenzene 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_as of P(1)-H Phospholes [11]. This is due to the zeal we got from a small note in the Hand Book 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_{aH} of the two conjugate acids ($CH_2N_5^+$) and (HN_6^+) in two different methods. It is noteworthy that for every nitrogen added to the ring system decreases the pK_{aH} systematically by 3-4 units ignoring 1,2- and 1,4-pyridazines in the sequence (Table 1). Even using pK_{aH} of 1,2- and 1,4-pyridazines with 1,3-pyridazine gives an average pK_{aH} of 1.33 (Table 1). This is close to the pK_{aH} of 1,3-pyridazine (1.23) which is originally used to see the systematic change of pK_{aH} 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 $CH_2N_5^+$ and HN_6^+. Hence is the decrease in pK_{aH}. A plot of pK_{aH} 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_{aH} of -9.49 and -13.14 for the two conjugate acids ($CH_2N_5^+$) 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_{aH} 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_{aH} of -8.84 and -12.35 for pentazinium cation ($CH_2N_5^+$) and hexazinium cation (HN_6^+) respectively. The difference of less than one pK_{aH} unit in pK_{aH} 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_{aH} values of azines[a]

Sl. No.	compound	Number of nitrogen atoms	I_v (eV) (neutral molecules)	pK_{aH} (protonated species)
1	 pyridine	1	9.60	5.27

Sl. No.	compound	Number of nitrogen atoms	I_v (eV) (neutral molecules)		pK_{aH} (protonated species)	
2	 1,2-pyridazine	2	10.3	Average I_v is 10.43	2.24	Average pK_{aH} of the three compounds with two nitrogen atoms in the ring system is 1.33
3	 1,3-pyridazine	2	10.5		1.23	
4	 1,4-pyridazine	2	10.5		0.51	
5	 s-triazine	3	11.3		-1.70	
6	 s-tetrazine	4	12.0		-6.00	
7	 pentazine	5	12.9[c]		-9.49[b]	
					-8.84[d]	
8	 hexazine	6	13.7[c]		-13.1[b]	
					-12.4[d]	

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

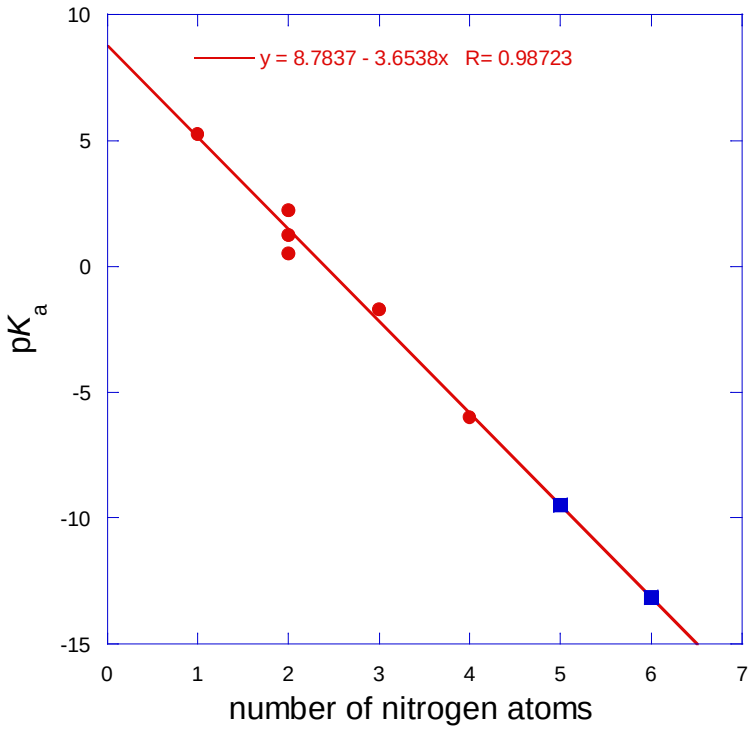


Figure 1. pK_a versus number of nitrogen atoms of azines

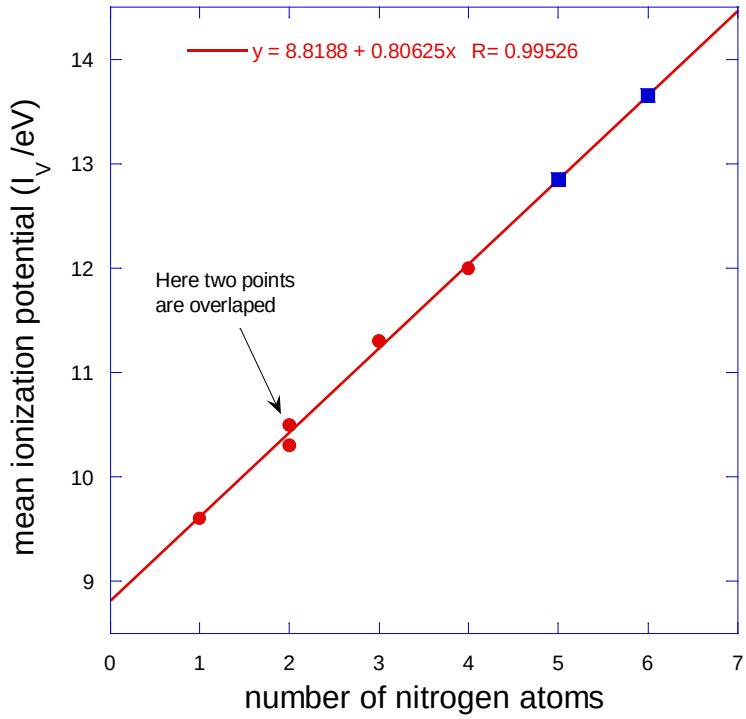


Figure 2. Plot of mean ionization potential (I_V/eV) versus number of nitrogen atoms in the azines

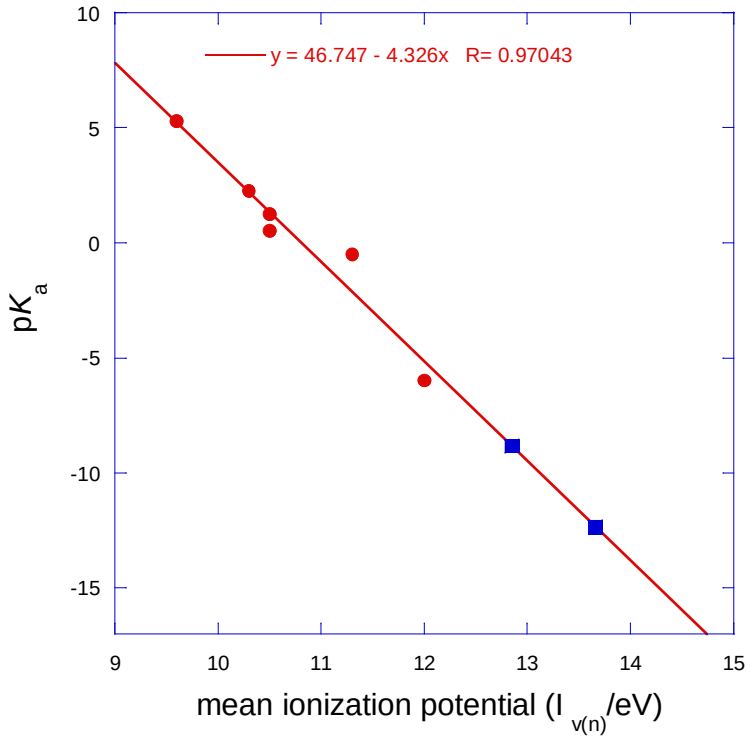


Figure 3. Plot of pK_a versus mean ionization potential ($I_{V(n)}$/eV)

Notes

The authors don't have any competing financial interest.

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