

Common Dimer - Responsible for the Trends in pK_{aH} s of Both Pyridazinium Cations and Di-cations: An Educational Perspective

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Abstract A species formed by dimerization from monoprotonated 1,2-pyridazine i.e., 1,2-pyridazinium cation that was optimized by DFT calculations is identified as a common dimer to explain the systematic changes in the pK_{aH} s of both Pyridazinium cations and Pyridazinium di-cations.

Keywords: Pyridazinium cation dimer, pK_{aH} s, 1,2-pyridazine, 1,3-pyridazine, 1,4-pyridazine

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1. Introduction

The acid-base properties of the three 1,2-, 1,3- and 1,4-pyridazines and their cations are well studied by DFT calculations by our group [1]. In the present work, we have taken up the study of the trends in pK_{aH} s of both Pyridazinium cations and Pyridazinium di-cations. A common dimeric species is identified to explain the systematic changes in the pK_{aH} s of Pyridazinium cations and Pyridazinium di-cations. The present study constitutes an excellent one-hour classroom lecture for graduate students and young researchers.

2. Methods

All the chemical structures are drawn using ChemDraw. The pK_{aH} values of the monoprotonated and di-protonated conjugate acids of the three pyridazines are from reference [2].

3. Discussion

The structures of the three pyridazines, equilibrium dissociation of their conjugate acids of both cations and di-cations with pK_{aH} values are given in Table 1. Looking at the pK_{aH} of these compounds, position of the second nitrogen changes the pK_{aH} of the conjugate acids of mono-protonated species systematically. They decrease nearly by a factor of half each time (Table 1) [2].

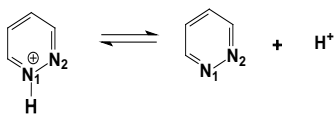
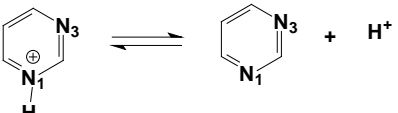
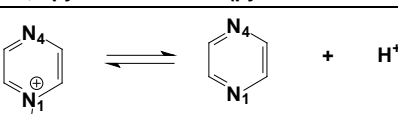
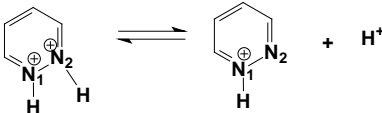
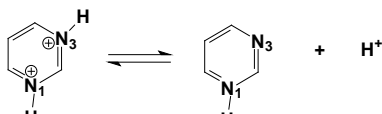
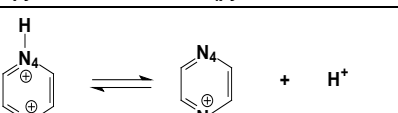
It is known that there will be a small loss of basic strength or gain of acidic strength upon introduction of second nitrogen in nitrogen containing compounds. This is

due to high electronegativity of nitrogen and doesn't tend to easily donate its lone pair of electrons which is a characteristic property of a Lewis base. The fact that the pK_a of NH_3 falls from 9.3 to 8.5 in hydrazine ($NH_2=NH_2$) is a glaring example [3]. However, the loss of base strength upon introduction of second nitrogen in six membered heterocycles like pyridazines is appreciable. Again, pyridine is an example whose pK_{aH} is 5.23 [4] falls to 2.24 in 1,2-pyridazine. This is primarily due to the high electronegativity of nitrogen and weakens the base strength. And another striking factor is that pyridazinium ion with two adjacent nitrogens can form hydrogen-bonded dimer as shown in Figure 1 (structure X). The dimeric form is optimized and well established from our DFT studies [1]. This dimeric form makes the pyridazinium ion more stable than the neutral parent pyridazine or mono-protonated pyridazine hence cannot lose the proton easily. Consequently, the species becomes a weak acid. This in turn results in higher pK_{aH} . This kind of dimer formation is not possible for 1,3- and 1,4-pyridazine.

The di-protonated species however became even stronger acid than the mono-protonated species with high negative pK_{aH} values (Table 1) [2]. This is due to loss of electron accepting capacity of second nitrogen on protonation and the di-protonated species becomes less stable and more acidic compared to the mono-protonated species. The two positive charges on two adjacent nitrogens in 1,2-pyridazinium di-cation may experience strong mutual repulsion. This makes the di-cation less stable compared to the mono-cation and tend to lose a proton easily. Therefore, the di-cation becomes a stronger acid with lower pK_{aH} . In the case of di-cations of 1,3 and 1,4-pyridazines there will be an increase in distance between two positive charges and may attenuate the repulsive forces. Thus, making these di-cations little

weaker acids with higher pK_{aH} compared to the di-cation of 1,2-pyridazene (Table 1).

Table 1. Dissociation Equilibriums of pyridazanium cations and di-cations

Monoprotonated Cations		
Sl. No.	Dissociation Equilibrium	pK_{aH}
1	 <p>1,2-pyridazanium ion</p>	2.24
2	 <p>1,3-pyridazanium ion (pyrimidinium ion)</p>	1.23
3	 <p>1,4-pyridazanium ion (pyrazenium ion)</p>	0.51
Di-protonated cations		
4	 <p>1,2-pyridazanium dication</p>	-7.10
5	 <p>1,3-pyridazanium dication (pyrimidinium dication)</p>	-6.30
6	 <p>1,4-pyridazanium dication (pyrazenium dication)</p>	-6.60

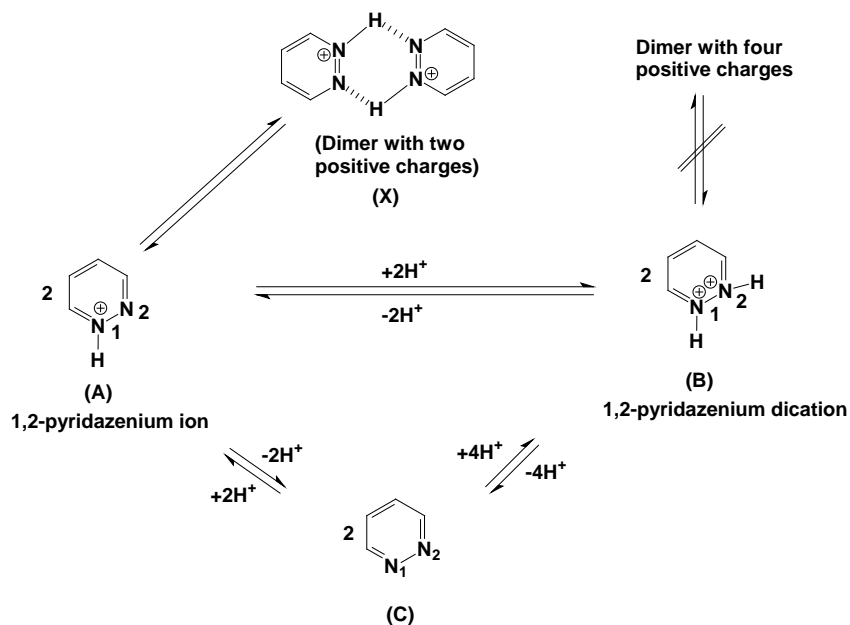


Figure 1.

The common dimer (Figure 1, **X**) that is responsible for explaining the higher acidic property (lower pK_{aH}) of 1,2-pyridazinium cation and di-cation compared to their other structural analogues of 1,3- and 1,4-pyridazinium cations (Table 1). From our earlier work on DFT studies on the structure **X** [1] of Figure 1 that the species is well characterized in terms of the difference in the H-bond energy of the monomer cation and dimer cation which is found to be -6.50 kcal/mole. And as such the 1,2-pyridazinium di-cation (structure **B**, Figure 1) cannot form any kind of dimer like the one **X**, due to lack of free nitrogen. It can only lose two protons to give 1,2-pyridazinium cation (structure **A**, Figure 1) which in turn can form the dimer **X**.

4. Conclusions

Theoretically well characterized structure **X** is the common dimer for both the 1,2-pyridazinium cation and di-cation to explain the changes in pK_{aH} .

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