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Hydrogen Bonding and Basicity of Cyclic Imines<sup>1,2</sup>

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Electron donor properties of ethylenimine, azetidine, pyrrolidine, piperidine and the 1-methyl derivatives of each of the foregoing, were measured in two ways: (1) determination of the thermodynamic  $pK_a$  constants from measurements of the  $pH$  of water solutions and (2) determination of hydrogen bonding ability with  $CH_3OD$  by a spectroscopic technique. Both studies agreed that the order of basicity with ring size is  $3 \ll 6 < 4 \leq 5$  for both series of cyclic imines, which is slightly different from the order observed with cyclic ethers. Determination of  $pK_a$  values for the unsubstituted imines at two temperatures enabled calculation of the heats and entropies of dissociation. The values for the latter are considered to indicate the order of basicity with respect to ring size to be  $3 \ll 6 < 4 < 5$ . The variation is consistent with the concept that electron distribution on the atoms in a ring is dependent upon the size of the ring. As has been observed for other cyclic systems, the three-membered ring compounds are unusually poor donors, this property being attributable to their unsaturated or "aromatic" character. They resemble aromatic bases in the ratio of  $pK_a$  to hydrogen bonding ability. In each ring size, introduction of a methyl group on the nitrogen atom causes a decrease in the basicity constant but an increase in the hydrogen bonding ability. The magnitude of these effects seems related to ring size.

The study of the effect of ring size on electron donor properties of cyclic compounds has now been extended to two series of cyclic imines. Previously the hydrogen bonding abilities of cyclic ethers<sup>3</sup> and of lactones<sup>4</sup> were reported to vary according to the ring size. In the cyclic ethers, the 4-membered ring was found to be associated with the best electron donor ability, followed by the 5-, 6- and 3-membered rings in that order, the last being much poorer. In the lactones studied, the reverse order was observed, with the 6-membered ring giving rise to better donor ability than the 5-, which in turn was better than the 4-membered ring. The different order appeared to be due to the site of hydrogen bonding in the lactones being on the carbonyl oxygen rather than the ring oxygen.

The unsubstituted cyclic imines of three to six members were selected as close analogs of the cyclic ethers, but because of possible ambiguity in the data arising from self-association of these imines, the corresponding N-methylamines were studied also. The hydrogen bonding ability was measured spectroscopically as described by Gordy, the frequency shift of the OD band in the infrared spectrum of methanol-*d* solutions being determined.<sup>5</sup> This method has proved to be as reliable as the calorimetric method, using the heat of mixing with chloroform.<sup>3,4,6</sup>

Also determined were the dissociation constants for these compounds in water, as an indication of the electron donor ability in complete transfer of a proton. These basicity constants (which had not been reported previously except for pyrrolidine and piperidine and more recently ethylenimine) serve as a check on the hydrogen bonding data, because of the correlation between these two properties for organic bases of similar structure.<sup>6</sup>

(1) Supported in part by the Petroleum Research Fund of the American Chemical Society.

(2) The material on the dissociation constants of the unsubstituted cyclic imines is taken from the M.S. thesis of L. A. Q., Northwestern University, May, 1952; that on the dissociation constants of the methyl compounds is to be included in the Ph.D. thesis of F. B., Kansas State College.

(3) S. Searles and M. Tamres, *THIS JOURNAL*, **73**, 3704 (1951).

(4) S. Searles, M. Tamres and G. Barrow, *ibid.*, **75**, 71 (1953).

(5) W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

(6) M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, *THIS JOURNAL*, **76**, 3983 (1954).

## Experimental

**Materials.**—The ethylenimine (aziridine), pyrrolidine and piperidine were best grade commercial products,<sup>7</sup> further purified by drying over barium oxide and sodium metal and distilling through a five-plate column under an atmosphere of nitrogen. Physical constants determined were: ethylenimine, b.p. 55–56° (previously reported<sup>8</sup> 55–56°); pyrrolidine, b.p. 85° (748 mm.),  $n_D^{20}$  1.4274 (lit.<sup>9</sup> values b.p. 87.5–88.5°,  $n_D^{20}$  1.4270); piperidine, b.p. 105.5–106° (750 mm.) (lit.<sup>10</sup> b.p. 106°).

Azetidine (trimethylenimine) was prepared by a modification of the method of Howard and Marckwald,<sup>11</sup> b.p. 62.5° (747 mm.),  $n_D^{20}$  1.4229 (lit.<sup>12</sup> values b.p. 62° (730 mm.),  $n_D^{20}$  1.4278). The yield of pure material was 7%. Attempts to make the compound by reaction of 3-bromopropylamine hydrobromide under a variety of conditions resulted in isolation of only allylamine and polymeric material.

1-Methylaziridine was prepared in 30% yield by the Elderfield-Hageman modification<sup>13</sup> of the Wenker synthesis, b.p. 23.5° (739 mm.) (lit.<sup>14</sup> b.p. 27.5° (764 mm.)).

1-Methylazetidine was prepared in the same manner. From 49 g. of 3-methylamino-1-propanol<sup>15</sup> was obtained 3 g. (8%) of an ammoniacal-smelling liquid, b.p. 40° (735 mm.).

*Anal.*<sup>16</sup> Calcd. for  $C_4H_9N$ : C, 67.55; H, 12.76; N, 19.69. Found: C, 67.24; H, 12.54; N, 19.40.

The following derivatives were prepared and recrystallized from benzene. The picrate is rather unstable, polymerizing when recrystallized from alcohol and also on standing a month at room temperature after recrystallization from benzene.

Picrate, m.p. 135–136°. Calcd. for  $C_{10}H_{12}N_4O_7$ : C, 40.0; H, 4.0; N, 18.7. Found: C, 39.6; H, 3.9; N, 18.1.

Picrolonate, m.p. 212–213°. Calcd. for  $C_{14}H_{17}N_5O_6$ : C, 50.1; H, 5.1; N, 20.9. Found: C, 50.0; H, 5.3; N, 20.4.

(7) We thank E. I. du Pont de Nemours & Co. for a gift of pyrrolidine.

(8) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).

(9) S. Gabriel, *ibid.*, **24**, 3234 (1891).

(10) G. Kahlbaum, *Z. physik. Chem.*, **16**, 217 (1895).

(11) C. C. Howard and W. Marckwald, *Ber.*, **32**, 2032 (1899), and thesis of L. A. Q. (ref. 2). An improved preparation of the 1-*p*-toluenesulfonylazetidine consists of adding 1 mole of 15% sodium hydroxide solution over a period of 6 hours to a stirred, refluxing solution of 0.5 mole of *p*-toluenesulfonamide and 0.5 mole of 1-chloro-3-bromopropane in 200 ml. of 95% ethanol, followed by distillation of the alcohol and crystallization (from hot alcohol) of the hard wax that separates from the pot on cooling. A 55% yield of white crystals is obtained, m.p. 112–115° (rather than 120° for the pure compound), which is entirely satisfactory for the reductive cleavage.

(12) L. Ruzicka, G. Salomon and K. E. Meyer, *Helv. Chim. Acta*, **20**, 109 (1937).

(13) R. E. Elderfield and H. A. Hageman, *J. Org. Chem.*, **14**, 622 (1949), who prepared several aziridines and 1-butylazetidine but not 1-methylaziridine or 1-methylazetidine.

(14) W. Marckwald and O. Frobenius, *Ber.*, **34**, 3552 (1901).

(15) S. Searles and V. P. Gregory, *THIS JOURNAL*, **76**, 2789 (1954).

(16) Microanalyses performed by Galbraith Laboratories, Knoxville, Tennessee.

1-Methylpyrrolidine and 1-methylpiperidine were prepared by methylating pyrrolidine and piperidine with formaldehyde and formic acid.<sup>17</sup> Since the infrared spectra of the products had an N-H band, they were treated with sodium hydride until hydrogen evolution ceased and then fractionally distilled from a small amount of lithium aluminum hydride. Physical constants determined were: 1-methylpyrrolidine, b.p. 78–79° (738 mm.),  $n_D^{20}$  1.4250 (lit. b.p. 78.5–79,<sup>18</sup>  $n_D^{20}$  1.4311<sup>19</sup>); 1-methylpiperidine, b.p. 103.5–104° (737 mm.),  $n_D^{20}$  1.4384 (lit. b.p. 105.9° (760 mm.),  $n_D^{20}$  1.4378<sup>20</sup>).

Methanol-*d* was prepared by the method of Redlich and Pordes,<sup>21</sup> b.p. 65° (750 mm.).

**Methods and Apparatus.**—The spectroscopic method used for determining the hydrogen bonding ability of the cyclic imines has been described previously.<sup>3,5</sup> A Beckman model IR-2T spectrometer was used for determining the OD shifts of the unsubstituted cyclic imines, and a Perkin-Elmer model 12B spectrometer was used for the measurements of the methyl compounds. Both instruments were equipped with lithium fluoride prisms, and the monomer OD band in 0.1 molar solution of methanol-*d* in carbon tetrachloride was determined and used as the reference with both instruments.

The centers of the hydrogen bonded OD bands in the 1 molar CH<sub>3</sub>OD solutions were determined after subtracting the absorption of the pure solvent in the same absorption cell, in the manner previously described.<sup>4,6</sup> Duplicate or triplicate runs were made in each case. Due to the broadness of the bands, the estimated precision of locating band centers was about 4 to 6 cm.<sup>-1</sup>.

The ionization constants were determined from pH measurements on aqueous solutions of the imines and their hydrochlorides. A Beckman model G pH meter, equipped with a Beckman 1190–80 glass electrode (the useful range of which extended well beyond pH 11 because of the absence of metal cations) was employed. The meter, which could be read to 0.01 pH unit, was standardized with U. S. Bureau of Standards buffers at pH 4.00, 7.00 and 10.00 (each  $\pm 0.01$ ) at 25° before and after each series of measurements with a particular imine sample. The vessel used was thermostated in a constant temperature water-bath and was fitted with a rubber stopper in which holes were made for the electrodes, the buret, a nitrogen inlet tube and a mechanical stirrer.

The imine was introduced with a micropipet into a measured amount of pure water in the vessel and was titrated with 0.1 *N* hydrochloric acid in a nitrogen atmosphere. In each run pH readings were made before addition of acid, at the end-point (determined by the differential method), and four to ten intermediate points. The titration data were used also to calculate the exact amount of imine introduced. At least two solutions of each imine, with different concentrations in the range  $10^{-3}$  to  $10^{-2}$  molar, were used. The pH values were constant with time, even with the three-membered cyclic imines, indicating that hydrolysis to the corresponding amino-alcohol (which is a much stronger base) was negligible. The statement of Fruton<sup>22</sup> that hydrolysis of the ethylenimine ring is especially rapid in neutral or alkaline solution appears not to be general.

Since the experiments were carried out using moderately dilute solutions, the Debye-Hückel limiting law was applied. Assuming that the activity coefficients of the two univalent ions (H<sup>+</sup> and BH<sup>+</sup>) are equal, the thermodynamic constant,  $K_a = a_B a_{H^+} / a_{BH^+}$ , becomes  $K_a = [B][H^+] / [BH^+]$ . The quantities substituted in this expression were

$$\begin{aligned} [H^+] &= \text{antilog}(-pH) / \gamma_{\pm} \\ [OH^-] &= K_w / \gamma_{\pm} \text{antilog}(-pH) \\ [B] &= C_B - C_{HCl} - [OH] \\ [BH^+] &= C_{HCl} + [OH^-] \end{aligned}$$

where  $C_B$  and  $C_{HCl}$  are the concentration in moles per liter of base and acid, and  $\log \gamma_{\pm} = -0.51 \sqrt{\mu}$ .

(17) H. T. Clarke, B. Gillespie and Z. Weisshaus, *THIS JOURNAL*, **55**, 4571 (1933).

(18) K. Löffler and C. Freytag, *Ber.*, **42**, 3429 (1909).

(19) Y. K. Yurev and F. Shenyan, *J. Gen. Chem. (U.S.S.R.)*, **4**, 1258 (1934); *C. A.*, **29**, 3335 (1935).

(20) H. W. Magnuson and E. R. Schierz, *Univ. Wyoming Pub.*, **7**, 1 (1940); *C. A.*, **34**, 6867 (1940).

(21) O. Redlich and F. Pordes, *Monatsh.*, **67**, 203 (1936).

(22) J. S. Fruton in "Heterocyclic Compounds," ed. by R. C. Elderfield, Vol. I, John Wiley and Sons, New York, N. Y., 1950, p. 71.

The mean values so obtained for  $pK_a$  and  $K_b$  are given in Table I. It may be noted that they agree well with literature values where such exist, considering the variety of investigators and methods involved in determining the earlier values. With the unsubstituted cyclic imines the standard deviations were 0.1–2% of the mean in each case, with the whole range of individual values falling within 3% of the mean (except in one series with piperidine where the range was  $\pm 5\%$  of the mean). With the 1-methyl derivatives the standard deviations were generally 3–5% of the means, with the range of all values within about 10% of the mean in each case.<sup>23</sup>

TABLE I  
HYDROGEN BONDING AND IONIZATION DATA FOR CYCLIC IMINES, (CH<sub>2</sub>)<sub>n</sub>N-R

<i>n</i> + 1	R	OD band in CH <sub>3</sub> OD soln., 25° position, cm. <sup>-1</sup>	Shift, <sup>a</sup> cm. <sup>-1</sup>	$K_b \times 10^4$ (25°)	$pK_a$ (25°)	$pK_a$ (35°)
3	H	2468	221	0.011	8.04 <sup>b</sup>	7.79
4	H	2430	259	20	11.29	11.04
5	H	2427	262	18	11.27 <sup>c</sup>	11.08
6	H	2430	259	16.6	11.22 <sup>d,e,f</sup>	10.92 <sup>c,g</sup>
3	CH <sub>3</sub>	2420	269	0.0072	7.86	
4	CH <sub>3</sub>	2396	293	2.5	10.40	
5	CH <sub>3</sub>	2397	292	2.9	10.46 <sup>c</sup>	
6	CH <sub>3</sub>	2402	287	1.2	10.08	

<sup>a</sup> Referred to the monomer OD band at 2689 cm.<sup>-1</sup> observed in 0.1 molar CH<sub>3</sub>OD in carbon tetrachloride. <sup>b</sup> The  $pK_a$  of ethylenimine (25°) has been reported after this work was completed by W. G. Barb, *J. Chem. Soc.*, 2565 (1955). Using a similar method he obtained a mean value of 7.90. <sup>c</sup> L. C. Craig and R. M. Hixon, *THIS JOURNAL*, **53**, 4367 (1931) reported  $K_b$  values for pyrrolidine and 1-methylpyrrolidine as  $1.3 \times 10^{-3}$  and  $1.5 \times 10^{-4}$ , respectively, but the temperature is not specified. If the temperature was 25°, their  $pK_a$  values are 11.11 and 10.18, respectively. <sup>d</sup> G. Bredig, *Z. physik. Chem.*, **13**, 306 (1894) obtained 11.18 for  $pK_a$  of piperidine at 25° (conductivity method). <sup>e</sup> W. F. K. Jones and G. Solomon, *Trans. Faraday Soc.*, **34**, 1321 (1938), determined  $pK_a$  for piperidine to be 11.06 ( $\mu = 0$ ) at 25° and 10.81 ( $\mu = 0.10$ ) at 35° (e.m.f. method). <sup>f</sup> V. V. Udovenko, L. A. Vvendsenskaya and V. I. Dulova, *Zhur. Obshchei Khim.*, **23**, 2060 (1953); *C. A.*, **48**, 13366 (1954), found  $pK_b$  for piperidine to be 2.80.

## Results and Discussion

The mean values of the hydrogen bonding and ionization constant measurements are listed in Table I. In both the unsubstituted cyclic imines and the N-methyl derivatives, the three-membered ring compounds are definitely the poorest electron donors in hydrogen bonding and the weakest bases toward the proton in water. The larger ring compounds in each series offer a sharp contrast, since they are stronger hydrogen bonding agents, and their ionization constants are greater than those for the corresponding three-membered ring compound by approximately  $10^3$ .

Considering the experimental precision, one cannot differentiate between the hydrogen bonding ability of the unsubstituted 4-, 5- and 6-membered imines, but the ionization constant of the last, piperidine, is significantly smaller than that of the other two, both at 25° and at 35°. The ionization constants for pyrrolidine and azetidine are the

(23) A graphical summary of the data, showing range of individual values, standard deviations and mean values for different series of determinations has been deposited as Document number 4844 with the A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A photoprint or microfilm copy may be secured by remitting \$1.25 in advance by check or money order payable to the Chief of the Service.

same within experimental error at 25°, but at 35° pyrrolidine appears to be very slightly the stronger base.

Substitution of a methyl group on the nitrogen atom of each unsubstituted cyclic imine produces qualitatively the same effect, namely, increased hydrogen bonding ability and decreased basicity in water. There is also a greater spread in these properties for the 4-, 5- and 6-membered ring N-methyl compounds, with the result that the order with respect to size is more clearly  $3 \ll 6 < 4 \leq 5$ .

The effect of ring size on electron donor ability in cyclic imines thus is somewhat different from that found in the cyclic ethers, where the order was  $3 \ll 6 < 5 < 4$ . It seems most probable that the difference is due to a different effect of ring size on distribution of electrons about the ring atoms for the two types of compounds. The preliminary results of proton magnetic spectra studies<sup>24</sup> showed that in the cyclic ethers the electron density of the hydrogens on the alpha carbon atoms varied with ring size in the order  $3 > 6 = 5 > 4$ , but in the cyclic imines the order was  $3 > 6 = 4 > 5$ .

A quantitative comparison of the hydrogen bonding ability and basicity in water for the individual compounds leads to some interesting conclusions. The correlation between the shift of the OD band in methanol-*d* solutions and the  $pK_a$  has been examined for pyridine and related compounds and for non-cyclic aliphatic amines.<sup>6</sup> An excellent linear relation was found for the former compounds, while the data for the primary and secondary amines fitted another linear relation. The values found here for azetidine, pyrrolidine and piperidine fall very close to this second line, but that for ethylenimine does not. Its basicity in water is too low relative to its hydrogen bonding ability for the compound to be included in the general relation for the aliphatic amines, but not low enough to fit the relation for pyridine and related compounds. Thus a single relation seems to be general for such amines and imines, regardless of ring size, except for the three-membered ring.

It seems significant that none of the points obtained by plotting the  $pK_a$  values against the OD shifts for the 4-, 5- and 6-membered 1-methyl cyclic imines was on the line obtained for aliphatic amines. Actually, these points fell rather close to the line for the pyridine derivatives, as also does that for triethylamine. This might raise speculation as to whether the linear relation is general for nitrogen bases having no hydrogen on the nitrogen; the tertiary amines, however, may be subject to relatively large steric and solvation effects which could cause deviations. Tri-*n*-butylamine, for which there is good reason to suspect hydrogen bonding to be sterically hindered, does not fall on the line. It is noteworthy that 1-methylaziridine deviates from the line in the direction of too low a basicity for the hydrogen bonding ability.

From the concept of the hydrogen bond as an electron density probe,<sup>6</sup> it is seen that the aziridines have the lowest electron density on nitrogen, but that it is not as low as the  $pK_a$  would indicate.

(24) H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, *THIS JOURNAL*, **76**, 4242 (1954).

The status is thus somewhat similar to that of the pyridine bases and suggests partial aromatic character for the aziridines.

The reason why aromatic bases might be expected to show a relatively low ratio of basicity constant to hydrogen bonding ability is that the unshared electrons on the nitrogen are delocalized, due to contribution to the resonance of the ring. They are thus less available for covalent bond formation with a proton. This has been mentioned previously with respect to pyridine,<sup>6</sup> which is aromatic, and there are reasons to believe that aziridines may be somewhat similar.

The unsaturated nature of the aziridine ring has been indicated by the elegant work of Cromwell and collaborators,<sup>25,26</sup> in connection with conjugation with unsaturated groups, which shows that an unshared pair of electrons on nitrogen can be drawn into resonance involving the three-membered ring. Delocalization of the electrons from the nitrogen may result also from contribution of resonance structures similar to those postulated for ethylene oxide.<sup>27</sup> Therefore, we attribute the low basicity of the aziridines to partial aromatic character.

A very interesting study of the basicity of the unsubstituted cyclic imines toward trimethylboron has been reported by Brown and Gerstein.<sup>28</sup> It is very appropriate to compare their results with ours, since the two studies differ principally in the nature of the electron acceptor substances.

They found the basicity varied with ring size in the order  $3 < 6 < 5 < 4$  and attributed these results to the counteracting effects of "I-strain" for the small rings and "F-strain" for the larger rings. "I-strain" might seem a reasonable explanation for the low  $K_b$  values and hydrogen bonding ability of the aziridines, but it cannot be the full explanation. For these systems, steric factors are relatively unimportant in hydrogen bonding and in interaction with a proton, so that "I-strain" here would not be significantly counteracted by F-strain. "I-strain" alone would predict the basicity order  $3 < 4 < 5 < 6$  in interactions with all reagents. The fact that this order is not observed makes plausible the explanation that the electron distribution around the heteroatom in the ring varies with ring size. There is the possibility, of course, that in interaction with the bulky trimethylboron "F-strain" may overshadow differences in intrinsic basicity for the 4-, 5- and 6-membered rings and thus alter the basicity order.

It is very interesting that substitution of methyl for hydrogen in every case weakens the basic strength in water, regardless of ring size. Exactly the same effect is observed in open-chain acyclic amines, and there have been two explanations advanced for the phenomenon: (1) the additional group causes increased crowding (or "B-strain")

(25) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952); N. H. Cromwell, *et al.*, *THIS JOURNAL*, **73**, 1044, 5929 (1951).

(26) There is also evidence for the unsaturated nature of cyclopropane rings: J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030, 5034 (1951); M. T. Rogers, *ibid.*, **69**, 2544 (1947); R. P. Mariella and R. Raube, *ibid.*, **74**, 518 (1952).

(27) S. Searles, M. Tamres and E. R. Lippincott, *ibid.*, **75**, 2775 (1953).

(28) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950).

particularly in the substituted ammonium ion, thus destabilizing the latter relative to the free amine,<sup>29</sup> and (2) the additional alkyl group on the nitrogen decreases the solvation of the ammonium ion and hence its stability.<sup>30,31</sup> The present results definitely favor the second explanation, as it is difficult to see how there can be much crowding about the nitrogen in these cyclic imines, particularly those with small rings.

The degree to which  $K_b$  is lowered by introduction of an N-methyl group, however, appears dependent on ring size, decreasing with decreasing ring size. The variation might be attributed either to operation of some B-strain in the larger rings, or to greater ease of solvation of a tertiary ammonium ion as two of the groups are pulled back. The effect of ring size on the magnitude of the hydrogen bonding ability increase associated with introduction of an N-methyl, appears in the reverse order, though the differences in the 4-, 5- and 6-membered rings are within the experimental error. The much larger increase in the 3-membered ring probably is due to greater self-association of ethyl-enimine which is more acidic than the other cyclic imines.

It is possible to determine the thermodynamic constants for the ionization of the simple imines, since data were obtained at two temperatures. These constants are listed in Table II. The

TABLE II  
THERMODYNAMIC FUNCTIONS FOR IONIZATION OF CYCLIC IMINES,  $(CH_2)_nNH$

$n + 1$	$\Delta F_{25}^\circ$ , kcal.	$\Delta H^\circ$ , kcal.	$-\Delta S^\circ$ , e.u.
3	11.0	10.5	2
4	15.4	10.5	16
5	15.4	8.0	25
6	15.3	12.6 <sup>a</sup>	9

<sup>a</sup> Wynne-Jones and Salomon, ref. *e* in Table I, determined a value of 12.9 kcal. for this constant.

(29) H. C. Brown, M. D. Taylor, M. Gerstein and H. Bartholomay, *THIS JOURNAL*, **66**, 431, 435 (1944).

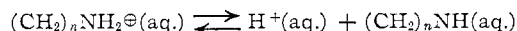
(30) R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1286 (1949); A. F. Trotman-Dickenson, *ibid.*, 1293 (1949).

(31) R. G. Pearson and F. V. Williams, *THIS JOURNAL*, **76**, 258 (1954).

$\Delta H^\circ$  and  $\Delta S^\circ$  values (particularly the latter) are reliable to not more than whole numbers because of the possibility of cumulative errors.

The heats of ionization are of the same order of magnitude for all the compounds, but wide variations are observed in the entropies. In studying the entropy of ionization of various carboxylic and inorganic acids, Pitzer<sup>32</sup> has concluded that differences are due mainly to differences in hydration entropies of the ions produced. The latter have been shown by Latimer and his co-workers<sup>33</sup> to be due principally to the electrostatic effect of the charge on the water dipoles. Pitzer was successful in applying this idea to explain why the weakest acids had the largest values for  $-\Delta S^\circ$ .

In applying the idea to the present case, namely,



one notes that the base with lowest electron density on nitrogen will give a conjugate acid in which the proton is least effectively screened. Such an ion will be most effective in orienting the water molecules in its vicinity, and its conjugate base will be least effective. Therefore, ionization of the ethyl-enimmonium ion, the strongest acid of the conjugate acids of this series of imines, should have the smallest negative change in  $\Delta S^\circ$ . On the other hand, the weakest conjugate acid, derived from the strongest base, should have the greatest negative change in  $\Delta S^\circ$ . The entropy data thus are consistent with the conclusion that for these cyclic imines the order of basicity is  $3 \ll 6 < 4 < 5$ .

It is of interest that Wynne-Jones and Salomon<sup>34</sup> have determined the ionization constants and the heats of ionization of several cyclic imines with larger rings: 6-, 9-, 15- and 18-membered. The data are not directly comparable with ours because of the use of a different solvent, but they indicated that each further increase in ring size causes small but probably significant decreases in both the basicity and the heat of ionization.

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(32) K. S. Pitzer, *ibid.*, **59**, 2365 (1937).

(33) W. M. Latimer, *Chem. Revs.*, **18**, 349 (1936).

(34) Reference *e*, Table I.