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Comparison of the Acidities and Basicities of Amino-Substituted Nitrogen Heterocycles

Ross Stewart* and Madeleine G. Harris

Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1W5

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Seventeen amino-substituted heterocycles, including pyridines, pyrimidines, cytosines, isocytosines, and adenines, have been compared with respect to acidity (pK_{HA}, deprotonation at amino) and basicity (pK_{BH^+}, protonation at ring nitrogen). Unlike the analogous deaza compounds, in which protonation and deprotonation occur at the same site, there is no correlation between pK_{HA} and pK_{BH^+}. The pK_{BH^+} for amino protonation of some of these compounds can be calculated, however, and in these cases the points fall very near the line for the deaza compounds. The displacement from this line can be regarded as a measure of the difference in basicity of the amino nitrogen atom and an aza nitrogen atom in the heterocycle in question.

The basic nature of organic amines is well known (eq 1), their acidic character much less so (eq 2).

$$RNH_3^+ \rightleftharpoons H^+ + RNH_2 \quad (1)$$

$$K_{BH^+} = [H^+][RNH_2]/[RNH_3^+]$$

$$RNH_2 \rightleftharpoons H^+ + RNH^- \quad (2)$$

$$K_{HA} = [H^+][RNH^-]/[RNH_2]$$

Recent studies of the ionization of aminoarenes[1] and aminoheterocycles[2] in basic aqueous dimethyl sulfoxide have provided us with a considerable number of pK_{HA} values (standard state, water) and we herein examine the relationship between proton gain (pK_{BH^+}) and proton loss (pK_{HA}) in such compounds.

Listed in Tables I and II are the available data for those aminoheterocycles in which a primary amino substituent NH_2 is the *acidic* center and for which both pK_{BH^+} and pK_{HA} are known. In most amino substituted nitrogen heterocycles the most *basic* center in the molecule is not the amino group but rather a ring nitrogen atom,[3] and this is so for all the heterocyclic compounds listed in the tables.

Previous work had shown that for most anilines and diphenylamines there is a linear relation between pK_{BH^+} and pK_{HA}, with the acidity, as represented by pK_{HA}, being more sensitive to substitution than basicity, as represented by pK_{BH^+}.[4] (The slope of a plot of pK_{HA} against pK_{BH^+} is 1.3.) The exceptions to this generality are those anilines and diphenylamines containing nitro groups at the ortho or para positions. The presence of one such group causes a large increase in acidity with the effect of additional nitro groups being much less. The change in *basicity*, however, is quite regular as successive nitro groups are introduced to the ortho and para positions. The net result is that a plot of pK_{HA} against pK_{BH^+} for anilines and diphenylamines has a discontinuity and a change of slope near the place where ortho and para nitroamines appear. There are two other commonly encountered -R groups in organic chemistry, cyano and carbonyl. The former does not appear to behave like nitro in the above respect, whereas there is some indication that the latter does. (Compare the effects of multiple substitution of these groups on methane acidity.[5])

We have plotted in Figure 1 the most recently published values of pK, many of which have been obtained by extrapolative techniques.[1a] It can be seen that for compounds in which the locus of protonation and deprotonation is the amino group (anilines, filled circles) there is a fairly regular, though nonlinear, relationship.

The most acidic and least basic compound in Figure 1 is 2,4,6-trinitroaniline, whose pK_{BH^+} and pK_{HA} values are in some doubt. It is half-protonated in 96% H_2SO_4[6] and earlier literature values are more negative than that[7] used here. Its response to base, likewise, is ambiguous, since there is evidence that it forms Meisenheimer complexes by addition of base, which accompanies or precedes proton loss.[8] Any attempt to accommodate these uncertainties by displacing the point in Figure 1 would have the effect of *increasing* the degree of curvature of the line.

The amino-substituted heterocycles (open triangles) all fall well off the line in Figure 1, and in the expected direction. That is, if the amino group is not the favored site of protonation then another location (invariably a ring nitrogen atom in conjugation with the amino group) must have a more positive pK_{BH^+} and such compounds will deviate in the direction shown. Furthermore, for several of these compounds, the aminopyridines and aminopyrimidines, the pK_{BH^+} for amino protonation can be calculated using the Hammett equation.[9] When this is done and the points included in the figure (filled triangles) it is found that these compounds now fall near the line determined by the anilines. The shifts in position of these

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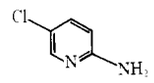
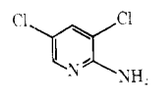
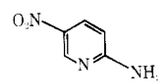
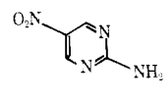
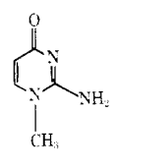
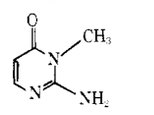
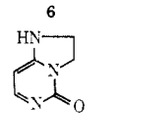
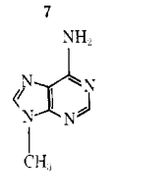
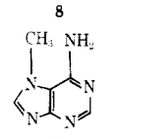
Table I. The pK_{HA} and pK_{BH^+} Values of Amino Heterocycles[a] in Water at 25 °C

compd[b]	registry no.	pK_{BH^+} (ref)	pK_{HA}[c]
 1	1072-98-6	4.71 (22)	21.8
 2	4214-74-8	2.67 (23)	20.8
 3	4214-76-0	2.80 (24)	15.8
 4	3078-77-6	0.3 (25)	14.7
 5	2080-17-3	4.0 (26)	14.3
 6	2417-17-6	4.2 (26)	14.3
 7	63934-46-3	7.0 (27)	12.5
 8	700-00-5	3.3[d] (28)	16.7
 9	935-69-3	3.6[d] (28)	14.7

[a] Additional pK data in Table II. [b] (1) 2-amino-5-chloropyridine; (2) 2-amino-3,5-dichloropyridine; (3) 2-amino-5-nitropyridine; (4) 2-amino-5-nitropyrimidine; (5) 1-methylisocytosine; (6) 3-methylisocytosine; (7) 2,3-dihydro-1*H*-5-oxoimidazo[1,2-c]pyrimidine; (8) 9-methyladenine; (9) 7-methyladenine. [c] Reference 2. [d] Room temperature, 50% DMF – 50% water.

compounds are shown by dotted horizontal lines in the figure.

The horizontal deviation in Figure 1 for the amino heterocycles may be taken as an estimate of the difference in basicity between the amino group and the ring nitrogen atom that is the favored site. The largest deviations are found for 3-methylcytosine (**17**) and the closely related compound **7**. The latter is the only nonprimary amine considered herein; it has been included because it provides some confirmation of the extent of deviation of the cytosine.

The question arises as to whether the acidities and basicities of the amino groups in cytosines and isocytosines should conform to the relationship shown in the figure. That is, does the horizontal deviation for **17**, some 13 pK units, give an estimate of the difference in basicity between the 4-amino group and the 1-aza group in this compound? Since cytosines are not truly aromatic such an analysis may well overestimate this quantity, but, bearing in mind the similar resonance effects exerted by a 3-carbonyl group in an aminocytosine and a 4-nitro group in an aniline, the results in Figure 1 suggest that the basicity of the amino group in 3-methylcytosine is very low, indeed.[10]

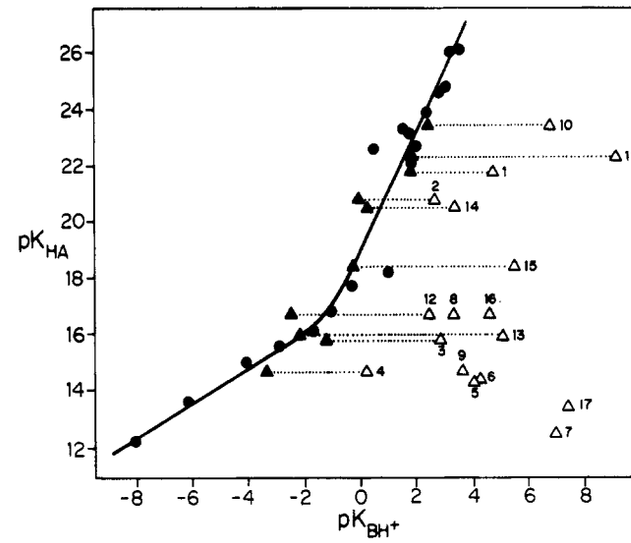
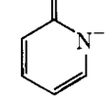
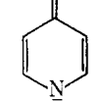


Figure 1. Plot of pK_{HA} against pK_{BH^+} for anilines (closed circles) and amino heterocycles (open triangles). Calculated points for protonation at the amino group of the latter are given by closed triangles. The numbering corresponds to that in Tables I and II. The anilines, in order of increasing pK_{HA}, with pK_{HA} and pK_{BH^+} values listed in parentheses, are 2,4,6-$(NO_2)_3$ (12.2, −8.1); 2,4-$(NO_2)_2$-6-Br (13.6, −6.2); 2,4$(NO_2)_2$ (15.0, −4.1); 4-NO_2-2,6-$(Cl)_2$ (15.6, −2.9); 4-NO_2-2,5-$(Cl)_2$ (16.1, −1.7); 2-NO_2-4-Cl (16.8, −1.1); 2-NO_2 (17.7, −0.3); 4-NO_2 (18.2, 1.0); 2,3-$(Cl)_2$ (22.1, 1.8); 2,6-$(Cl_2)_2$ (22.6, 0.4); 2,4-$(Cl)_2$ (22.7, 2.0); 4-CN (23.2, 1.7); 2,5-$(Cl)_2$ (23.3, 1.5); 3,5-$(Cl_2)_2$ (23.9, 2.4); 3-CN (24.6, 2.8); 3,4-$(Cl)_2$ (24.8, 3.0); 3-CF_3 (26.0, 3.2); 3-Cl (26.1, 3.5).

One is on firmer ground in comparing ΔpK ($pK_{HA} - pK_{BH^+}$) for compounds in which the amino group is attached to an aromatic ring. Albert et al.[11] suggested some time ago that the high basicity of 4-aminopyridines is due to resonance in the neutral molecule requiring considerable charge separation, whereas that in the cation involves, of course, no separation of charge at all. The lower basicity of 2-aminopyridine is plausibly explained, then, on the basis of a smaller degree of charge separation in the resonance hybrid of the neutral compound. Since the aza group's electron-withdrawing character appears to be chiefly due to induction rather than resonance[12] the importance of the canonical structures **10′** and **11′** is uncertain. Nonetheless, the conclusion that the proximity of the aza and amino groups in the 2 compound stabilizes its neutral form more than that of its 4 isomer seems sound, since we find that 2-aza compounds are also less *acidic* than their 4-aza isomers (Table II). Indeed, for the isomeric cytosines **16** and **17** there is independent evidence showing that the neutral compounds differ in stability by approximately the amount required to produce the ΔpK differences shown in Table II.[13,2b]

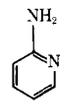
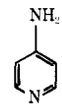
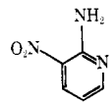
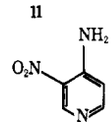
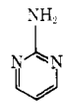
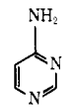
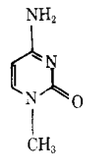
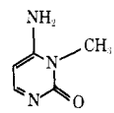


10′



11′

Table II. Effect of the Position of the Aza Group on the Acidity and Basicity of 2- and 4-Aza Amino Heterocycles[a]

2-aza compds				4-aza compds				ΔpK_{HA}	ΔpK_{BH^+}
	registry no.	pK_{HA}[b]	pK_{BH^+}[c]		registry no.	pK_{HA}[b]	pK_{BH^+}[c]	$(pK_{HA}^{2\text{-aza}} - pK_{HA}^{4\text{-aza}})$	$(pK_{BH^+}^{2\text{-aza}} - pK_{BH^+}^{4\text{-aza}})$
 10	504-29-0	23.5	6.71	 11	504-24-5	22.3	9.15	1.2	−2.44
 12	4214-75-9	16.7	2.42	 13	1681-37-4	15.9	5.05	0.8	−2.63
 14	109-12-6	20.5	3.41	 15	591-54-8	18.4	5.58	2.1	−2.17
 16	1122-47-0	16.7	4.55	 17	4776-08-3	13.4	7.38	3.3	−2.83
							av	1.9	−2.52

[a] (10) 2-Aminopyridine; (11) 4-aminopyridine; (12) 2-amino-3-nitropyridine; (13) 4-amino-3-nitropyridine; (14) 2-aminopyrimidine; (15) 4-aminopyrimidine; (16) 1-methylcytosine; (17) 3-methylcytosine. [b] Reference 2. [c] References: compounds 10–13, ref 24; 14, and 15, ref 11b; 16 and 17, ref 27.

Calculations

The basicity of the amino group in each of the ten aminopyridines and aminopyrimidines was calculated using the Hammett equation $\log K/K_0 = \rho\sigma$ where ρ has been taken as the value for aniline 2.91.[14] For those compounds in which the 2 position (to the amino group) is either unoccupied or contains an aza substituent the calculations were done in the usual way. (The 2-aza group is known to be a well-behaved substituent.[9a,15]) The value of $\log K_0$ was taken as 4.58[14] and the following σ constants were used: $\sigma_{2N} = 0.75$ $\sigma_{4N} = 0.96$, $\sigma_{4Cl} = 0.23$, and $\sigma_{4NO_2} = 1.24$.[14] The aza substituent constants are those of Deady and Shanks et al.[15a] derived from their studies of the basic hydrolysis of methyl pyridinecarboxylates, a reaction in which no formal charge appears on the aza group. That good correlations have been obtained in the present and earlier work[2a] using these values supports the notion that these groups operate mainly by induction.

For compounds containing a non-aza group in the 2 position to the amino group the appropriate 2-substituted aniline was taken as the parent compound in the Hammett equation, the following $\log K_0$ values being used: 2,4-dichloroaniline, −2.0;[16] 2-nitroaniline, +0.30.[6] Thus, the amino group basicity in **2** is given by $(\log K) + 2.0 = 2.91 \times 0.75$, which gives for $pK_{BH^+(amino)}$ a value of −0.2.

The data for the anilines come from ref 1a (average of values obtained by the two extrapolative methods used therein), 4, 7, and 16–19. (See the caption for Figure 1 for numerical values.) A few of the pK_{BH^+} values shown in Tables I and II differ slightly from those given in the attached references because a correction has been made to convert them from 20 to 25 °C. The correction is small, −0.13 units, and is an estimate based on the results of Essery and Schofield.[20]

The ionization process that occurs in aqueous dimethyl sulfoxide between hydroxide ion and amino heterocycles appears to be proton transfer, not hydroxide addition, although the latter reaction, which tends to be time dependent, is known to take place with a number of heterocyclic compounds lacking amino groups.[21] The pattern of spectral changes accompanying ionization in base of the compounds in Tables I and II is consistent with simple proton loss, although the possibility of adduct formation cannot be unequivocally ruled out.

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Friedel–Crafts Chemistry. A Mechanistic Study of the Reaction of 3-Chloro-4′-fluoro-2-methylpropiophenone with $AlCl_3$ and $AlCl_3$–CH_3NO_2

Seemon H. Pines* and Alan W. Douglas

Merck Sharp & Dohme Research Laboratories, Rahway, New Jersey 07065

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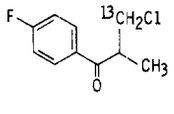
The mechanism of reaction of 3-chloro-4′-fluoro-2-methylpropiophenone (**1**) with $AlCl_3$ has been studied using both ^2H- and ^{13}C-labeled substrate. Analysis of kinetic isotope effects and of label location in the products as revealed in ^2H and ^{13}C NMR spectra allows definition of the major pathways involved. In cyclization to the 2-methylindanone **2**, an isotope rate effect supports ionization concerted with C_2–H migration as the rate-determining step. The skeletally rearranged products **3** and **4** form via initial methyl migration and not acyl migration. When the $AlCl_3$–CH_3NO_2 system is used as catalyst, no rearrangements transpire, and formation of **2** proceeds below the thermal threshold required with neat $AlCl_3$. This reaction occurs via enolization as a result of the protic nature of $AlCl_3$–CH_3NO_2 solutions. This same system possesses oxidizing power, and chloride is oxidized to chlorine which, in the enolizing medium, converts **2** to its α-chloro analogue **6**. When chloride concentration is low, competitive oxidation of **2** to isocoumarin **7** is also observed.

Reaction of 3-chloro-4′-fluoro-2-methylpropiophenone (**1**) with $AlCl_3$ was recently reported to give three products: 5-fluoro-2-methyl-1-indanone (**2**), 5-fluoro-3-methyl-1-indanone (**3**), and 2-(4′-fluorophenyl)-1-oxoniacyclopent-1-enyl cation (**4**).[2] Formation of each product was pictured, with some reservations, as having proceeded through carbenium ions which differed fundamentally from those cited in cyclialkylation of phenylalkyl halides[3] by the presence of a carbonyl group linking the aliphatic and aromatic moieties.

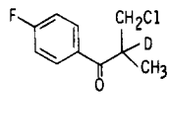
We have continued study of this reaction, and wish now to report the results of experiments using (a) both ^{13}C- and ^2H-labeled **1** and (b) nitromethane as solvent. The label studies amplify our understanding of some of the mechanistic pathways involved; the presence of nitromethane alters the outcome of the reaction entirely.

Results

Carbon-13 labeled **1** (C-1) was made via methoxymethylation[4] with $H^{13}CHO$; C_2-deuterated **1** (D-1) came from the addition of deuterium chloride to 4′-fluoromethacrylophenone (**5**).



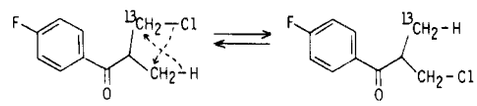
C-1



D-1

Products **2**, **3**, **4**, and "unreacted" starting material observed after reaction of C-1 with 2–3 equiv of $AlCl_3$ at 100 °C, neat, showed that scrambling had occurred in two and only two positions, as shown in Figure 1. Because this scrambling was also observed with C-1 at 70 °C, where *no* carbon–carbon bond reorganization could be discerned, the result was attributed to the equivalent of a 1,3-hydride shift in **1** as depicted in Scheme I.[5] (The C_2-attached H was not involved, as will be evident below from results with D-1.)

Scheme I[a]



[a] For clarity, complexation of $AlCl_3$ is not shown in this or the other schemes.

The reaction of D-1 was, overall, slower than unlabeled **1** under identical conditions. Dissection of the relative rates of the individual processes supported C_2–H (or C_2–D) bond breaking as rate determining in the formation of unrearranged indanone **2**, with $k_H/k_D = 2.5$. Negligible rate differences were seen in formation of **3** or **4**. Deuterium in CH_2D and CHD groups of **2**, **3**, and **4** was located by ^{13}C NMR spectroscopy. Integration of the signals for ^2H-split vs. solely ^1H-bearing singlet ^{13}C signals provided a semiquantitative distribution. Proton NMR showed no detectable loss nor scrambling of ^2H in the recovered D-1. Overall ^2H content in each product was also assessed by mass spectroscopy; attempts to assign its distribution in **2** and **3**, methyl group vs. indanone ring, by means of mass fragmentography[6] were not in accord with the ^{13}C NMR results.

Mechanistic suggestions are proposed on the basis of the rates and products; unfortunately, the loss of some of the deuterium, and some of its incorporation into the aromatic nucleus as ultimately shown by ^2H NMR, precludes total definition of the reactions.

Reaction of 1 M solutions of **1** in nitromethane containing 2 equiv of $AlCl_3$ occurred slowly as low at 70 °C to produce **2** without detectable formation of **3** or **4**. The medium, however, supported further reaction of **2** along two parallel paths to its α-chlorinated derivative **6** and to the isocoumarin **7** (Scheme II). The isocoumarin was not observed when the experiment was conducted in sealed tubes. These unexpected transformations are ascribed to the nature of the modified catalytic system.

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