from 120 to 160°. Vacuum distillation yielded 5.8 g (55%) of hydrosilylation products with bp 140-142° (2 mm), n_D^{20} 1.5595, and d_4^{20} 0.9841. Found: C 75.1; H 8.9, N 5.6%; MR_D 89.13. $C_{17}H_{25}NSi$. Calculated: C 75.4; H 9.3; N 5.2%; MR_D 89.25.

All of the remaining trialkyl-, triethoxy-, and dimethylsiloxysilylquinolines were similarly obtained. Their physicochemical constants and the results of analysis are presented in Table 1.

Hydrosilylation of 2-Vinylquinoline with Ethyldichlorosilane. A 6.2-g (0.04 mole) sample of 2-vinylquinoline was added dropwise to a mixture of 5 g (0.04 mole) of ethyldichlorosilane, 0.3 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol, 0.1 g of hydroquinone, and 10 ml of dry dioxane, and the mixture was refluxed for 10 h. The solvent was then removed by distillation, and the residue was vacuum distilled at 150-155° (1 mm) to give 5.1 g (45%) of hydrosilylation products as a yellow oil that hydrolyzed readily in air. The structures and isomeric composition (α to β ratio 25 : 75) of the reaction products were established from the PMR spectra.

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PROTONATION OF 1,5-NAPHTHYRIDINE DERIVATIVES

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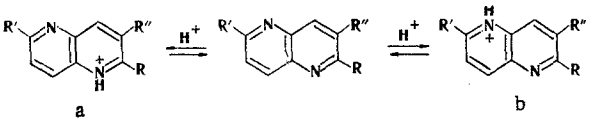
UDC 547.834.2

The direction of protonation (1-N or 5-N) or 2-, 2,3-, and 2,6-substituted derivatives of 1,5-naphthyridine was determined on the basis of the basicity constants.

Mono- and disubstituted 1,5-naphthyridine derivatives ($R \neq R' \neq R''$) contain two nonequivalent basic centers – the 1-N and 5-N nitrogen atoms – the monocations formed by protonation of which may have structure a or b.



a b

I R=R′=R″=H; II R=NH$_2$, R′=R″=H; III R=CH$_3$, R′=R″=H; IV R=Cl, R′=R″=H; V R=NHCOCH$_3$, R′=R″=H; VI R=OCH$_3$, R′=R″=H; VII R=OH, R′=R″=H; VIII R=SH, R′=R″=H; IX R=R′=H, R″=NO$_2$; X R=OH, R′=H, R″=NO$_2$; XI R=OCH$_3$, R′=Cl, R″=H; XII R=N(CH$_3$)$_2$, R′=Cl, R″=H

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TABLE 1. Effect of Substituents on the Basicities in Pyridines, Quinolines, and 1,5-Naphthyridines

Substituent	$\Delta pK = pK_R - pK_H$		
	1,5-naphthyridine derivat.	quinoline derivatives*	pyridine derivatives*
2-NH_2	2,76	2,40	1,63
6-NH_2		0,69	
2-CH_3	0,50	0,47	0,74
6-CH_3		−0,02	
2-Cl	−1,25		−4,45
6-Cl		−1,32	
2-$NHCOCH_3$	−0,41		−1,14
2-OCH_3	0,72	−1,77	−1,95
6-OCH_3		0,12	
2-OH (oxo)	−0,71	−5,35	−4,53
6-OH		0,23	
2-SH (thione)	−1,14	−6,38	−6,30
6-SH		−0,99	
3-NO_2	−2,28	−3,89	−4,42
7-NO_2		−2,50	

*The pK_a values were taken from [6].

TABLE 2. Experimental and Calculated Basicity Constants of 1,5-Naphthyridine Derivatives

1,5-Naphthyridine and its deriv.	Exptl. pK_a	Calc. pK_1	Calc. pK_5
I*	2,91		
II†	5,67	5,33	3,62
III	3,41	3,5	2,93
IV	1,66	−1,75	1,61
V	2,50	1,32	2,20
VI	3,63	1,14	3,03
VII	2,21	−2,46	3,1
VIII	1,77	−3,46	1,91
IX†	0,63	−0,98	0,48
X	0,26	−6,35	0,67
XI	0,47	−0,16	−1,67
XII	5,18	4,74	−1,04

* The pK_a value was taken from [8].
† These pK_a values were taken from [9].

TABLE 3. Constants Used in This Study

Substituent	σ_2	σ_6
NH_2	−0,41	−0,12
CH_3	−0,10	−0,003
Cl	0,79	0,22
$NHCOCH_3$	0,27	0,12
OCH_3	0,30	−0,02
OH	0,91	−0,04
SH	1,08	0,17

To study the effect of substituents on the basicities of the compounds and the position of the protonation center we measured the electrolytic dissociation constants of some 2-, 2,3-, and 2,6-substituted derivatives (I-XII) of 1,5-naphthyridine. The results are presented along with the necessary literature data and the calculated values in Tables 1-3. The introduction of electron-donor substituents in the 1,5-naphthyridine molecule gives rise to an increase in the basicity, whereas the introduction of electron-acceptor substituents lowers the basicity. In addition, the investigated compounds can be divided into two groups with respect to the character of the effect of the substituents on the basicity. The first group includes 2-amino- and 2-methyl-1,5-naphthyridines (II, III). In this case a change in the basicity, which is characterized by the expression $\Delta pK = pK_R - pK_H$, for 1,5-naphthyridine is close to the ΔpK values of the corresponding 2-substituted quinolines and pyridines but differs markedly from the ΔpK_a values of 6-substituted quinoline derivatives (see Table 1). Since the ring nitrogen atom of 2-aminoquinoline and 2-aminopyridine is protonated [1, 11], it is apparent that the indicated naphthyridines also add a proton to the 1-N atom. Brown, Mitchell, and Plasz [2], who determined the basicities of 1,5-naphthyridine (pK_a = 3.05) and its 2-amino derivative (pK_a = 5.73), compared the ΔpK_a value obtained (1.86) with the analogous values in the pyridine and quinoline series and also arrived at the conclusion that 2-amino-1,5-naphthyridine undergoes primary protonation at 1-N.

The second group of compounds includes 1,5-naphthyridines with substituents that have −I and −C effects (NO_2) or predominant −I and variable +C effects (Cl, OCH_3, OH, and $NHCOCH_3$). The change in the basicity

that occurs when a substituent is introduced in this case is much less pronounced than in the case of the corresponding pyridine and quinoline derivatives (Table 1). For example, the electron-acceptor effect of a 2-acetamido group in 1,5-naphthyridine ($\Delta pK = -0.41$) on the basicity is weaker by a factor of 2.8 than in pyridine ($\Delta pK = -1.14$). The ΔpK value in the case of 2-chloro-1,5-naphthyridine (−1.25) is lower by a factor of ~3.6 than the analogous value for 2-chloropyridine (−4.45). At the same time, 2-chloro-1,5-naphthyridine ($\Delta pK = -1.25$) and 6-chloroquinoline experience practically identical changes in their basicities. Protonation of the compounds of the second group evidently occurs at 5-N, which is far away from the substituent, and the observed weakening of the effect of the substituent is associated with the increase in the mutual distance between it and the most basic center.

The relative proton-acceptor capacities of the 1-N and 5-N basic centers in the various derivatives can be estimated from the approximate calculated values corresponding to their basicity constants. The addition of the proton will take place at the center that gives the largest pK_a value.

The ionization constants for protonation at 1-N (pK_1) and 5-N (pK_5) were calculated for all of the investigated compounds by the method in [3]. The Hammett equation in the form

$$pK_a = 5.25 - 5.90\Sigma\sigma, \quad (1)$$

$$pK_a = 4.94 - 5.90\Sigma\sigma \quad (2)$$

for pyridines (1) and quinolines (2) can be used for the calculation of the basicity constants of 2-substituted derivatives of pyridine and quinoline when special values of the σ_2 substituent constants are used. The σ_2 constants were obtained from Eqs. (1) and (2) from the corresponding experimental pK_a values. The σ_2 substituent constants obtained in this way for the pyridine and quinoline series have rather close values, and the pK_a values of quinoline derivatives can, where necessary, be calculated on the basis of the σ_2 constants for the pyridine series.

The method described above has been extended [4] to other two-ring systems, and it has been shown that Eq. (2) can also be used to predict the pK_a values when the substituent and the basic center are located in different aromatic rings. The σ_6 and σ_7 constants in this case should be calculated from expressions (3) and (4) proposed in [5]:

$$\sigma_6 = 0.58\sigma_m, \quad (3)$$

$$\sigma_7 = 0.35\sigma_m + 0.35\sigma_p, \quad (4)$$

The Hammett equation that we used for the approximate calculations of the pK_1 and pK_5 values for the naphthyridine series has the form

$$pK_a = 2.91 - 5.9\Sigma\sigma. \quad (5)$$

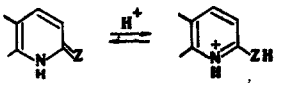
The ρ value was assumed to be 5.9, as in the case of the pyridine and quinoline series.

The σ_2 substituent constants were calculated from Eq. (2) from the pK_a values of the corresponding quinoline derivatives. The σ_2 values corresponding to the pyridine series [Eq. (2)] were used for the 2-Cl and 2-$NHCOCH_3$ groups; the σ_6 values for 6-$N(CH_3)_2$, 6-Cl, and 6-$NHCOCH_3$ were determined from Eq. (3). All of the necessary pK_a values of the quinolines and pyridines were taken from [6].

The pK_1 and pK_5 values obtained in this way are presented in Table 2, and the σ_2 and σ_6 values are presented in Table 3.

It was found that the pK_1 values are larger than the pK_5 values for compounds with electron-donor substituents in the 2 position of the naphthyridine ring (II, III) and that there is a correspondence between the experimental values of the basicity constants and the values calculated for the 1-N center, i.e., the site of addition of a proton is the nitrogen atom in the 1 position. The calculated pK_5 values are larger than the pK_1 values for naphthyridines with electron-acceptor substituents (IV-IX), whereas the experimental basicity constants are close to the pK_5 values but differ markedly from the pK_1 values. This constitutes evidence in favor of protonation of IV-IX at 5-N, and the nitrogen atom of the second ring consequently serves as the most basic center in this case.

Particular attention should be paid to the 2-hydroxy and 2-mercapto derivatives. It is known that 2-hydroxy and 2-mercapto compounds in the pyridine and quinoline series exist in the oxo or thiono forms and are protonated at the oxygen or sulfur atoms [7].



Z = O, S

2-Oxo- and 2-mercapto-1,5-naphthyridines VII and VIII should have similar structures, and a second possible cationoid center in the molecules of this compound, in addition to the 5-N center, is the oxygen or sulfur atom, respectively, of the oxo or mercapto groupings.

Our data show that these 1,5-naphthyridine derivatives are protonated at the 5-N atom, which is far away from the substituent. This follows from the closeness of the experimental basicity constants and pK_5 values calculated for the addition of a proton to the nitrogen atom in the 5 position. At the same time, one observes a very large difference (4.5-5.2 orders of magnitude) between the experimental values of the constants and the calculated pK_1 values in the case of protonation of the exocyclic heteroatom.

Thus the proton-acceptor capacity of the nitrogen atom in the 5 position of 1,5-naphthyridine is found to be higher than that of oxygen in the 2-oxo group or of sulfur in the 2-thiono group.

A similar examination of 2,6-disubstituted 1,5-naphthyridine derivatives XI and XII shows that, as expected, protonation occurs at the nitrogen atom of the ring that contains an electron-donor substituent or the less electron-accepting of the two substituents.

Correlation of the basicity constants with the σ substituent constants was examined for all of the investigated compounds. In selecting the σ constants we took into account the above-established mutual orientation of the substituent and the protonation center.

The equation that we obtained has the form

$$pK_a = 3.04 - 6.13\Sigma\sigma,\ r = 0.98,\ s = 0.35.$$

If an attempt at correlation is made for all of the compounds only with the σ_2 or σ_6 values, one observes practically no correlation (r = 0.4-0.8; s = 1-1.7). This fact once again confirms the correctness of the above conclusions regarding the site of protonation in the investigated compounds.

EXPERIMENTAL

Potentiometric and spectral methods were used in the determination of the basicity constants for 10^{-3} M (potentiometric method) or 10^{-4}-10^{-5} M (spectral method) aqueous alcohol solutions of the compounds. The pH values were measured with a PNM-26 pH meter; the titrant was added by means of a Radiometer ABU-13 microburet (Denmark). The UV spectra were recorded with a Hitachi EPS-3 spectrophotometer (Japan). The H_0 values for solutions with known acid concentrations were taken from [10]. The reproducibility of the results was no less than ± 0.06 pK_a units. The synthesis of the investigated compounds was published in [12-14].

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