QUANTITATIVE DETERMINATION OF THE ELECTRONIC EFFECTS OF PYRIDYL GROUPS

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The series of σ constants of 2-, 3-, and 4-pyridyl groups was calculated on the basis of data from the ^{1}H, ^{13}C, and ^{19}F NMR spectra of isomeric aminophenyl-, phenyl-, and fluorophenylpyridines. The literature σ constants and the values found in the research were analyzed.

In the study of heterocyclic compounds researchers frequently find it necessary to use σ constants of one kind or another by means of which the reactivities and certain physical properties of the corresponding functional derivatives can be quantitatively characterized. In series of six-membered nitrogen-containing heterocyclic systems a rather extensive number of studies have been devoted to the determination of the σ constants in the pyridine series, and most of the constants described in the literature are capable of characterizing the electronic effects of aza groups as endocyclic substituents in the benzene ring [1]. The amount of data pertaining to the effects of the pyridyl groups themselves is much smaller. The values of the series of σ constants of 2-, 3-, and 4-pyridyl groups taken from literature sources are presented in Table 1.

A comparison of the values of the same constants determined by different methods not only demonstrates their significant deviation but also in some cases casts doubt on the very possibility of their use even within the framework of a rough approximation. The reason for the large deviations of the individual values of the σ constants of the pyridyl groups from the average values is the use in a number of studies for their determination of insensitive or statistically unreliable correlation ratios, as well as the marked influence of solvation effects in taking measurements in solvents with different natures. Thus the polarographic reduction of nitrophenylpyridines in ethanol [2] gives definitely elevated values of the constants due to the effect of specific solvation at the nitrogen atom of the pyridine ring [compare with the σ_p values of the protonated pyridyl groups 2-Py$\overset{+}{N}$H (0.75) and 4-Py$\overset{+}{N}$H (0.65) [11]], although the same method with dimethyl sulfoxide (DMSO) as the solvent leads to σ_I values that agree quite well with the inductive constants that were determined by means of the NMR spectra (Table 1). The polarographic reduction of pyridylazobenzenes proves to be unsuitable because of significant variations of the experimentally found values of the constants of the pyridyl groups as a function of the medium [for example, in DMSO and dimethylformamide (DMF)]. The utilization of the dependences [9] of the frequencies of the symmetrical and asymmetrical stretching vibrations of the NO_2 group in substituted nitrobenzenes on the Hammett substituent constants gives a set of markedly different σ_m and σ_p values for the 3-pyridyl group (Table 1). It should also be noted that the σ_p constants presented in [12] for pyridyl groups (0.55 for 2-Py, 0.58 for 3-Py, and 0.81 for 4-Py) quantitatively describe an effect that reflects interaction of the pyridyl groups with the aromatic system and is transmitted through the exocyclic nitrogen atom in N-substituted anilines (the so-called "bonded" substituent effect), and these constants are not examined in Table 1 because of their particular specificity.

Within the framework of our research to evaluate the reactivities of azine derivatives it seemed necessary to determine and refine the σ constants of pyridyl groups by a sufficiently reliable method. We have previously calculated the constants of sym-triazinyl and pyrimidinyl groups [13-16] on the basis of the chemical shifts of the carbon and fluorine nuclei in the ^{13}C and ^{19}F NMR spectra of phenyl- and fluorophenylpyrimidines, as well as the chemical shifts of the protons of the amino group in the ^{1}H NMR spectra of aminophenyl derivatives of

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TABLE 1. σ Constants of Pyridyl Groups[a]

Constant	Pyridyl group, R			Method of determination
	2-Py	3-Py	4-Py	
σ_I	0,144	0,185	0,207	$E_{1/2}$ $RC_6H_4NO_2$ in DMSO [2]
	[0,593]	[0,704]	[0,754]	$E_{1/2}$ $RC_6H_4NO_2$ in EtOH [2]
	[0,210]		[0,426]	$E_{1/2}$ $RC_6H_4N{=}NC_6H_5$ in DMSO [3]
	0,11	0,22	0,24	^1H NMR $RCH{=}CH_2$ [4]
	0,12	0,15	0,18	^{13}C NMR $C_6H_5CH_2R$ in DMSO [5]
	0,10			^{19}F NMR RC_6H_4F in CH_2Cl_2 [6]
	0,08	0,22	0,18	^1H NMR $RC_6H_4NH_2$ in DMSO[b]
	0,10	0,20	0,23	^{13}C NMR C_6H_5R in DMSO[b]
	0,11	0,18	0,19	^{19}F NMR RC_6H_4F in DMSO[b]
σ_I (av)	0,11 ± 0,03	0,19 ± 0,04	0,21 ± 0,03	
σ_R^0	0,042	−0,005	−0,004	$E_{1/2}$ $RC_6H_4NO_2$ in DMSO [2]
	[0,108]	[−0,039]	[0,016]	$E_{1/2}$ $RC_6H_4NO_2$ in EtOH [2]
	[0,254]		[−0,034]	$E_{1/2}$ $RC_6H_4N{=}NC_6H_5$ in DMSO [3]
	0,00			^{19}F NMR RC_6H_4F in CH_2Cl_2 [6]
	0,01			see [7]
	0,01	−0,05	−0,01	^{13}C NMR C_6H_5R in DMSO[b]
	−0,01	−0,07	−0,01	^{19}F NMR RC_6H_4F in DMSO[b]
σ_R^0 (av.)	0,01 ± 0,03	−0,04 ± ± 0,03	−0,01 ± ± 0,01	
σ_R	0,27	0,03	0,26	^1H NMR $RC_6H_4NH_2$ in DMSO[b]
σ_m	0,160	0,183	0,206	$E_{1/2}$ $RC_6H_4NO_2$ in DMSO [2]
	[0,552]	[0,691]	[0,760]	$E_{1/2}$ $RC_6H_4NO_2$ in EtOH [2]
	[0,307]		[0,413]	$E_{1/2}$ $RC_6H_4N{=}NC_6H_5$ in DMSO [3]
	[0,33]			pK_a RC_6H_4COOH in H_2O [8]
	[0,355]	[0,000]	[0,376]	$\nu_s NO_2$ $RC_6H_4NO_2$ in $CHCl_3$ [9]
	[0,324]	[0,485]	[0,324]	$\nu_{as} NO_2$ $RC_6H_4NO_2$ in $CHCl_3$ [9]
	0,17	0,23	0,27	^1H NMR $RC_6H_4NH_2$ in DMSO[b]
σ_p	[0,206]	[0,206]	[0,233]	$E_{1/2}$ $RC_6H_4NO_2$ in DMSO [2]
	[0,691]	[0,760]	[0,875]	$E_{1/2}$ $RC_6H_4NO_2$ in EtOH [2]
	[0,495]	[0,471]	[0,448]	$E_{1/2}$ $RC_6H_4N{=}NC_6H_5$ in DMSO [3]
	[0,17]			pK_a RC_6H_4COOH in H_2O [8]
	[0,300]	[0,300]	[0,360]	$\nu_s NO_2$ $RC_6H_4NO_2$ in $CHCl_3$ [9]
	[0,249]	[0,163]	[0,332]	$\nu_{as} NO_2$ $RC_6H_4NO_2$ in $CHCl_3$ [9]
	[0,2]			^{13}C NMR 2-RPy [10]
	0,35	0,25	0,44	^1H NMR $RC_6H_4NH_2$ in DMSO[b]

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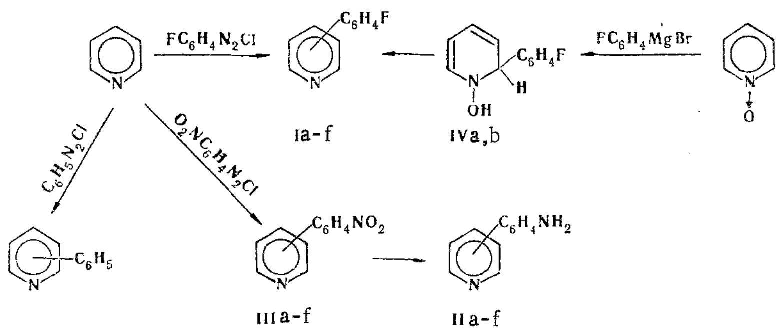
[a] Unreliable values are given in brackets and were disregarded in the calculation of the average values. [b] This study.

sym-triazine and pyrimidine, by means of the corresponding correlation expressions that link the chemical shifts of the indicated nuclei with the σ constants of the substitutents in the benzene ring. The same method was used in the present research to calculate the constants of the pyridyl groups.

The isomeric phenylpyridines, m- and p-fluorophenylpyridines (I), and m- and p-aminophenylpyridines (II) were synthesized via the following schemes:



On the basis of the corresponding substituted anilines we carried out the radical arylation of pyridine [17] via the Gomberg reaction. The individual isomers of phenylpyridine and arylpyridines I and III were isolated from the mixtures obtained, which consist of products of mono- and diarylation of pyridine, by preparative thin-layer chromatography (TLC). The yields of isomeric monoarylpyridines vary markedly as a function of the nature of the arylating agent (the overall yields range from 6 to 53%), but the isomer ratios correspond to the principles previously noted in [17]. In addition, 2-fluorophenylpyridines (Ia, b) were obtained by the method in [6] by the reaction of pyridine N-oxide with isomeric fluorophenylmagnesium bromides and subsequent dehydration of the 2-fluorophenyl derivatives of N-hydroxy-1,2-dihydropyridine (IV). Amino derivatives II were obtained in high yields by catalytic hydrogenation of nitro derivatives III by the method in [11]. The NMR spectra of the compounds obtained are presented in Tables 2 and 3.

The assignments of the signals in the ^{13}C NMR spectra of the phenylpyridines (Table 3) to the carbon atoms of the phenyl groups were made in analogy with the assignments in the spectra of phenylpyrimidines [16] with allowance for the relative intensities of the signals. The remaining signals were assigned to the carbon atoms of the pyridine ring on the basis of quantitative data on the effect of the phenyl group as a substituent on the ^{13}C chemical shifts in the benzene and pyrimidine rings in the case of biphenyl [18] and phenylpyrimidines [16]. For comparison, the ^{13}C chemical shifts of unsubstituted pyridine, which we determined for a dilute solution in DMSO, are presented in Table 3.

The σ_I and σ_R° constants of the pyridyl groups were calculated from correlation Eqs. (1) and (2) (taken from [16]) on the basis of the chemical shifts of the m- and p-carbon atoms of the phenyl groups

$$\sigma_I = 0.019 + 0.308\Delta\delta C_m + 0.011\Delta\delta C_p, \tag{1}$$

$$\sigma_R^0 = 0.001 - 0.062\Delta\delta C_m + 0.044\Delta\delta C_p \tag{2}$$

in the ^{13}C NMR spectra of phenylpyridines ($\Delta\delta' C_m$ and $\Delta\delta' C_p$ in Table 3) calculated relative to the signal of unsubstituted benzene (128.27 ppm) with allowance for corrections (0.15 ppm for C_m and 0.10 ppm for C_p) for the effect of the magnetic anisotropy of the pyridine ring. These corrections were previously calculated for the analogous C_m and C_p positions in biphenyl [18] and were used in the case under consideration under the assumptions of, first, approximately identical values of the induced ring currents in the benzene and pyridine rings [19] and, second, the closeness of the geometrical parameters of the biphenyl and phenylpyridine molecules. For the latter the angle between the planes of the benzene and pyridine rings was assumed to be 35-40° [20]. The calculated values of the constants are presented in Table 1.

The same σ_I and σ_R° constants were calculated on the basis of the ^{19}F chemical shifts of m- and p-fluorophenyl derivatives Ia-f scaled to the signal of unsubstituted fluorobenzene (-49.66 ppm) by means of the well-known correlation equation of Taft and co-workers [21].

To calculate the σ_I and σ_R (σ_R^-) constants of the pyridyl groups we used the previously found expressions [14] that link the chemical shifts of the protons of the amino groups in series of m-substituted anilines with the σ_I^- and σ_R^- substituent constants and the chemical shifts of the protons of the amino groups in series of p-substituted anilines with the σ_I^- and σ_R^- substituent constants; corrections (0.03 ppm for m-NH_2 and 0.02 ppm for p-NH_2) for the magnetic anisotropy of the pyridine ring were introduced into the chemical shifts of the protons of the NH_2 groups of aminophenylpyridines IIa-f scaled to the signal of unsubstituted aniline (4.90 ppm). These corrections were calculated by the method in [22] under the same assumptions as those used in the calculation of the corresponding corrections for the carbon atoms of the phenyl group.

Preliminary calculations of the σ_R and σ_R^- resonance constants from these correlation equations with fixed values of inductive constants σ_I found from the ^{19}F NMR spectra showed that the two resonance constants are very close for each of the three pyridyl groups. Assuming that $\sigma_R = \sigma_R^-$, the expressions presented in [14] can therefore be converted to Eqs. (3) and (4), from which we calculated (independently of the ^{19}F NMR method) the σ_I and σ_R constants.

$$\sigma_I = 0.008 - 1.332\Delta\delta NH_2\text{-}m + 0.427\Delta\delta NH_2\text{-}p, \tag{3}$$

$$\sigma_R = -0.002 + 1.200\Delta\delta NH_2\text{-}m - 1.129\Delta\delta NH_2\text{-}p \tag{4}$$

TABLE 2. ^1H and ^{19}F NMR Spectra of Arylpyridines I and II in Dimethyl Sulfoxide (DMSO)

Compound	Aryl group	Chemical shift,[a] δ, ppm									
		2-H	3-H	4-H	5-H	6-H	$—C_6H_4—$	NH_2	$\Delta\delta NH_2$[b]	F	$\Delta\delta F$[c]
Ia	2-(m-FC_6H_4)	—	(7,18—8,08 m)			8,63—8,79 m	7,18—8,08 m			−49,85	−0,19
Ib	2-(p-FC_6H_4)	—	7,83—8,34 m		7,15—7,53 m	8,62—8,78 m	7,30 dd; 8,17 dd			−49,43	0,23
Ic	3-(m-FC_6H_4)	8,96 d	—	8,11 ddd	(7,05—7,80m)	8,63 dd	7,05—7,80 m			−50,37	−0,71
Id	3-(p-FC_6H_4)	8,87 dd	—	8,05 ddd	7,47 dd	8,58 dd	7,30 dd; 7,78 dd			−48,26	1,40
Ie	4-(m-FC_6H_4)	8,68 dd	7,72 dd	—	7,72 dd	8,68 dd	7,10—7,81 m			−50,42	−0,76
If	4-(p-FC_6H_4)	8,66 dd	7,68 dd	—	7,68 dd	8,66 dd	7,33 dd; 7,87 dd			−49,98	−0,32
IIa	2-(m-$H_2NC_6H_4$)	—	7,73—7,89 m		(7,27)	8,63 ddd	6,56—7,47 m	5,13	−0,20		
IIb	2-(p-$H_2NC_6H_4$)	—	7,68—7,85 m		7,14 dd	8,57 ddd	6,68 d; 7,84 d	5,37	−0,45		
IIc	3-(m-$H_2NC_6H_4$)	8,83 dd	—	7,96 ddd	7,43 ddd	8,56 dd	6,56—7,31 m	5,18	−0,25		
IId	3-(p-$H_2NC_6H_4$)	8,82 dd	—	7,93 ddd	7,37 dd	8,44 dd	6,71 d; 7,45 d	5,21	−0,29		
IIe	4-(m-$H_2NC_6H_4$)	8,64 dd	7,58 dd	—	7,58 dd	8,64 dd	6,59—7,36 m	5,24	−0,31		
IIf	4-(p-$H_2NC_6H_4$)	8,51 dd	7,56 dd	—	7,56 dd	8,51 dd	6,70 d; 7,55 d	5,48	−0,56		

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[a] In the pyridine ring $J_{2,3}$ and $J_{5,6}$ = 4-5 Hz, $J_{2,4}$ and $J_{4,6}$ = 1.5-2.3 Hz, $J_{2,5}$ and $J_{3,6}$ = 1-2 Hz ($J_{2,5}$ < 1 Hz in the spectrum of IId), and $J_{3,4}$ and $J_{4,5}$ = 8.0-8.7 Hz. In the p-disubstituted benzene ring $^3J_{H,F}$ = 9.0 Hz and $^4J_{H,F}$ = 5.5 Hz. [b] Relative to the signal of aniline (4.90 ppm) in DMSO, the negative values correspond to a shift to weak field. [c] Relative to the signal of fluorobenzene (−49.66 ppm) in DMSO, the negative values correspond to a shift to weak field.

TABLE 3. ^{13}C NMR Spectra of Phenylpyridines in Dimethyl Sulfoxide (DMSO)

Compound	Chemical shift, δ, ppm									$\Delta\delta$,[a] ppm		$\Delta\delta'$,[b] ppm	
	2-C	3-C	4-C	5-C	6-C	C_i	C_o	C_m	C_p	C_m	C_p	C_m	C_p
Pyridine	149,53	123,74	135,99	123,74	149,53								
2-Phenylpyridine	156,00	120,13	137,07	122,50	149,47	138,68	126,44	128,65	128,92	0,38	0,65	0,23	0,55
3-Phenylpyridine	147,58	135,50	133,99	123,74	148,39	137,01	126,76	129,03	128,00	0,76	−0,27	0,61	−0,37
4-Phenylpyridine	150,12	121,10	146,94	121,10	150,12	137,12	127,71	129,08	129,08	0,81	0,81	0,66	0,71

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[a] Relative to the signal of benzene (128.27 ppm) in DMSO, the positive values correspond to a shift to weak field. [b] With allowance for the magnetic anisotropy of the pyridine ring.

The inductive and mesomeric constants of the three pyridyl groups calculated by the three methods (Table 1) are in fairly good agreement with the most reliable literature values. The deviations of the individual constants from their average values generally do not exceed 0.03. The Hammett σ_m and σ_p constants of the pyridyl groups were evaluated from the ^1H NMR spectra of pyridylanilines under the assumption that $\sigma_m = \sigma_I = 1/3\sigma_R$ and $\sigma_p = \sigma_I + \sigma_R$, which is completely valid for series of substituted anilines [14]; in this case one may note the closeness of the σ_m values that we found and the literature values and the difference in the σ_p values. The depressed values of the σ_p constants (and, to a much smaller extent, the σ_m constants), which are presented in [2] for all three pyridyl groups, are probably due to the smaller effect of the resonance component on the half-wave potential in the polarographic reduction of nitrobenzenes, in analogy to what occurs in isolated reaction series. This is also indicated by calculations [2] of the σ_I^- and σ_R^0 constants on the basis of the σ_m and σ_p values.

The σ constants of the pyridyl groups that we found can be used along with certain literature values to evaluate the reactivities and spectral characteristics of derivatives of the pyridine series.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra of 4% solutions of the compounds in dry DMSO were recorded with a Varian 56/60 A spectrometer at 60 and 56.4 MHz, respectively, at 37°C with the $^{13}C—H$ satellite of DMSO (221 Hz from the signal of tetramethylsilane) and C_6F_6 as the internal standards. The ^{13}C NMR spectra of 4% solutions of the compounds in DMSO were recorded at 28°C under pulse conditions with a Brucker HX-90 spectrometer (22.63 MHz); the pulse was 15 μsec

(60°C), the lag between pulses was 10 sec, the sweep width was 5000 Hz, the number of scans was 300, and the internal standard was tetramethylsilane. The solution was treated with 5% d_6-DMSO to stabilize the resonance conditions. The R_f values were determined on Silufol UV-254 plates [elution with $CHCl_3$—ether (1.5:2)].

2-(m-Fluorophenyl)pyridine (Ia) and 2-(p-Fluorophenyl)pyridine (Ib). These compounds were obtained by the method in [6] by the reaction of pyridine N-oxide with the corresponding fluorophenylmagnesium bromides and subsequent dehydration of N-hydroxy-1,2-dihydropyridine derivatives IVa, b by the action of acetic anhydride. Meta isomer Ia, with bp 125-130°C (6.7 hPa) [bp 101-105°C (1.3 hPa) [6]], was obtained in 11% yield. Para isomer Ib, with bp 103-105°C (2.7 hPa) [bp 105-108°C (1.3 hPa) [6]], was obtained in 17% yield.

(m-Fluorophenyl)pyridines (Ia, c, e). A solution of the diazonium salt [prepared from 28 g (0.25 mole) of m-fluoroaniline in 88 ml of concentrated HCl and 18 g (0.26 mole) of $NaNO_2$ in 30 ml of water] was added dropwise in the course of an hour at 40°C to 220 ml (2.7 moles) of pyridine, after which the mixture was stirred at 100°C for 1 h. It was then cooled and poured into 1 liter of water, and the aqueous mixture was made alkaline to pH 9 by the addition of concentrated NH_4OH and extracted with ether. The ether and pyridine were removed by distillation, and the residue was distilled at 110-126°C (2.5-4 hPa) to give 21.1 g (48%) of a mixture. The mixture was separated by thin-layer chromatography (TLC) on silica gel (0.1-0.14 mm fraction) containing SFN-1 indicator in a $CHCl_3$—ether system (1.5:2). Effective separation was achieved at a plate length of 0.6-0.7 m and an adsorbent layer thickness of 2-3 mm. The optimal amount of mixture to be separated was determined experimentally. The zones on the chromatogram were detected in UV light. The individual compounds were eluted from the collected zones with ethanol, the eluate was evaporated, and the residue was distilled *in vacuo*. The yield of Ia, with bp 126-128°C (9 hPa) and R_f 0.88, was 8.0 g (18%) (this product was identical to the product obtained by the method in [6]). Isomer Ic, with bp 121-123°C (5 HPa) and R_f 0.40, was 4.5 g (10%). Found, %: C 76.4; H 4.8; F 11.2; N 8.1. $C_{11}H_8FN$. Calculated, %: C 76.3; H 4.7; F 11.0; N 8.1. Isomer Ie, with bp 132-134°C (12 hPa) and R_f 0.30, was 2.9 g (6%). Found, %: C 76.5; H 4.6; F 10.9; N 8.0. $C_{11}H_8FN$. Calculated, %: C 76.3; H 4.7; F 11.0; N 8.1.

p-(Fluorophenyl)pyridines (Ib, d, f). The similar reaction of 155 ml (1.9 mmole) of pyridine and 18 g (0.16 mole) of p-fluoroaniline gave 11 g (38%) of a mixture of isomers, separation of which yielded the individual compounds. The yield of isomer Ib, with bp 118-119°C (8 hPa), mp 39-40.5°C (from hexane), and R_f 0.77, was 0.78 g (3%) (this product was identical to the product obtained by the method in [6]). The yield of Id, with bp 122-123°C (9 hPa), mp 27-29°C (from hexane), and R_f 0.33, was 0.48 g (2%). Found, %: C 76.7; H 4.8; F 10.6; N 8.3. $C_{11}H_8FN$. Calculated, %: 76.3; H 4.7; F 11.0; N 8.1. The yield of isomer If, with bp 118-119°C (8 hPa), mp 47-48.5°C (from hexane), and R_f 0.17, was 0.23 g (1%). Found, %: C 76.6; H 4.7; F 10.8; N 8.0. $C_{11}H_8FN$. Calculated, %: C 76.3; H 4.7; F 11.0; N 8.1.

Phenylpyridines. These compounds were obtained by the action of benzenediazonium chloride on pyridine by the method in [17]; the overall yield was 40% after distillation at 136-138°C (10 hPa). The mixture was separated into the individual isomers by TLC as described above: 2-phenylpyridine (R_f 0.96) was obtained in 8% yield, 3-phenylpyridine (R_f 0.72) was obtained in 2% yield, and 4-phenylpyridine (R_f 0.63) was obtained in 3.5% yield. The constants of the compounds obtained were in agreement with the constants presented in the literature.

(m-Nitrophenyl)pyridines (IIIa, c, e). These compounds were obtained by the action of m-nitrobenzenediazonium chloride on pyridine by the method in [17]; the overall yield was 50% after distillation at 162-170°C (0.07-0.2 hPa). Separation was carried out as described above, except that $CHCl_3$—ethyl acetate (1:1) was used as the mobile phase in TLC. The individual compounds were eluted from the collected zones with ethanol, the eluate was evaporated, and the residue was crystallized from petroleum ether (bp 70-100°C) and sublimed *in vacuo*. Compounds IIIa (R_f 0.72), IIIc (R_f 0.19), and IIIe (R_f 0.17) were obtained in 8%, 5%, and 2% yields, respectively.

(p-Nitrophenyl)pyridines (IIIb, d, f). These compounds were obtained in 71% overall yield by a method similar to that used to prepare the meta isomers. After separation by TLC, isomers IIIb and IIIf were crystallized from petroleum ether (bp 70-100°C) and were sublimed *in vacuo*; IIId was crystallized from CCl_4—petroleum ether (1:1) and sublimed *in vacuo*. Compounds IIIb (Rf 0.69), IIId (R_f 0.19), and IIIf (R_f 0.13) were obtained in 29%, 19%, and 5%, respectively. Their constants were in agreement with the constants presented in the literature.

(Aminophenyl)pyridines (IIa-f). These compounds were obtained by the method in [11] by hydrogenation of nitro derivatives IIIa-f in ethanol in the presence of 10% Pd/C. The catalyst was removed by filtration, the filtrate was evaporated, and the residue was crystallized [IId from 70% ethanol, IIe from benzene–petroleum ether (3:1), and IIf from ethanol] and sublimed *in vacuo*. In the case of isomer IIa the filtrate was evaporated, the residue was extracted with ether, the ether was removed by distillation, and the residue was distilled at 160-163°C (8 hPa). Compound IIb was extracted with ether, the extract was evaporated, and the residue was crystallized from petroleum ether and sublimed *in vacuo*. Compound IIc was extracted with a boiling mixture of $CHCl_3$ and petroleum ether (1:1), the extract was concentrated and cooled, and the precipitate was separated and sublimed *in vacuo*. The products were obtained in 70-98% yields. The constants of the compounds obtained were in agreement with the constants presented in literature.

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