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The  $^{13}\text{C}$  NMR, UV AND IR SPECTRA  
OF 2-FLUOROPYRIDINE METHYL DERIVATIVES

$^{13}\text{C}$  NMR, UV and IR spectra of methyl derivatives of 2-fluoropyridine have been recorded. The influence of the substituents on the spectral characteristics of the compounds has been discussed. The electronic spectra have been calculated by a modified INDO method. Transition energies, intensities and assignments are compared with UV spectra.

## INTRODUCTION

$^1\text{H}$  NMR spectra of methyl derivatives of 2-fluoropyridine were analyzed [1]. The signs and magnitudes of the long-range spin-spin coupling constants between the methyl protons and the ring protons and fluorine are consistent with a model in which the nitrogen atom polarizes the  $\sigma$ -electron system but leaves the  $\pi$ -electron contribution to the coupling constants relatively unchanged.

There are dramatic changes in the ring proton-fluorine couplings whereas the couplings involving the methyl protons differ very little from those in the corresponding toluene derivatives. Thus, the coupling over six bands between fluorine and methyl protons is  $1,25 \pm 0,03$  Hz in 2-fluoro-5-methylpyridine compared to  $1,15 \pm 0,02$  Hz in *p*-fluorotoluene.

Lichter and Wasylishen [2] measured  $^{13}\text{C}$  NMR and carbon-fluorine coupling constants of 2-, 3-, 4-fluoropyridine and fluoropyridinium ions. With the exception of C(2) in the 2-fluoro compounds, chemical shifts were derived additively from those of the corresponding carbons in pyridine, pyridinium ion and fluorobenzene. The value  $^1J_{\text{CF}}$  in 2-fluoropyridine is algebraically more positive than  $^1J_{\text{CF}}$  in 3- and 4-fluoropyridine in consistence with a positive contribution associated with the presence of approximate ion pair orbital. Protonation induces an increase in the one-bond couplings of 2- and 4-fluoropyridine while that of 3-fluoropyridine is unaffected. Many of the detailed trends exhibited by the coupling constants are in parallel to values of  $J_{\text{CH}}$  in pyridine and fluorobenzene as well as some other heterocycles, although only rough overall correlation exists.

A better correlation exists between corresponding values in the fluoronitrobenzenes vs. the fluoropyridinium ions. Most of the experimental coupling trends are reproduced by values calculated using finite perturbation theory in the INDO MO approximation assuming only the Fermi contact mechanism.

Infrared spectra in the potassium bromide were presented for 2-fluoro- and 2-chloropyridine [3]. 2-Substituted pyridines in the infrared spectra are characterized by two relatively intensive bands near 600 and 400  $\text{cm}^{-1}$ . The vapour-phase contours of the far infrared bands of 2-fluoro- and 2-chloropyridine indicate that the bands at 600 and 400  $\text{cm}^{-1}$  arise, respectively, from in-plane and out-of-plane vibration.

Absorption data of the aromatic CH-valence vibrations of monosubstituted pyridine derivatives are different according to whether the measurements are carried out for the liquid or in  $\text{CCl}_4$  solution. In the liquid phase, not only the individual bands but also centre of gravity of the bands are shifted to longer wavelengths, while the intensities are generally larger than those measured in  $\text{CCl}_4$  solution. The differences between the intensities in the liquid phase and  $\text{CCl}_4$  solution increase with increasing electron withdrawal by the substituents. This indicates an increase in the intermolecular interaction [4].

Intensity measurements of the CH-stretching vibrations of 2-fluoropyridine show that also for pyridine derivatives there exists a functional relation between intensities and the Taft substituent parameters  $\sigma_1$  [5]. The interpretation of these facts leads to conclusion concerning the polarity of the C—H bond moments of the investigated pyridine derivatives. The influence of the heteroatom N on the C—H bond moments are discussed [5].

The IR and Raman spectra of 2-fluoropyridine were reported and interpreted [6]. Details of their assignment and those of other halopyridines were discussed. The characteristics of the fluorine atom, its size, which is bioisosteric with both the hydrogen atom and the hydroxyl group, its unique electronic properties, provide biological properties of aromatic fluorides [7]. Thus, Ar—F bonds appear in a broad variety of molecules having the enormous activity as antibiotics, anti-folate, sedatives, estrogen receptor imaging agents etc. [4]. Therefore, it was worthwhile to investigate in detail the electronic structure of methyl derivatives of 2-fluoropyridine to gain understanding of the mechanism of the biological activity of these compounds. Earlier published works [1—7] did not include  $^{13}\text{C}$  NMR, IR and electronic spectra of methyl derivatives of 2-fluoropyridine.

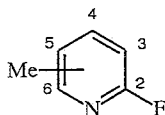
#### EXPERIMENTAL

2-Fluoropicolines used in the study were synthesized by the method previously described [8, 9]. The  $^{13}\text{C}$  NMR spectra were recorded on a Tesla B589A spectrometer at 25.742 MHz. Typical conditions were: spectral width 7600 Hz, 8K data points, pulse angle  $90^\circ$  (13  $\mu\text{s}$ ) and repetition time of 2s. These conditions resulted in a digital resolution of 1.22 Hz (i. e., 0.05 ppm). All spectra were proton decoupled. Samples were ca. 10% in  $\text{CDCl}_3$  as solvent, and the centers of the  $\text{CDCl}_3$  peaks (77.11 ppm) were used as an internal reference.

The UV absorption spectra were recorded by means of a UV-vis (Zeiss, Jena) spectrometer (alcohol solution, concentration  $\approx 10^{-4}$  M, cell thickness 0.097 cm) [9]. Calculations of the electronic spectra and electronic structure of 2-fluoropicolines were performed within the framework of the modified all-valence electron INDO method [10] using some of its modifications [11—13] and including 100 single excited configuration interaction procedure. The ground state geometry of the species was optimized using the semiempirical AM1 method [14].

#### RESULTS AND DISCUSSION

Carbon-13 chemical shifts for 2-fluoropyridine and its methyl derivatives are given in Table 1. Each carbon in all compounds was assigned by comparison the measured shift with that calculated on the assumption that the fluorine substituent effect in fluorobenzene relative to benzene [15] could be added to the shift of the given carbon in pyridine. The better accordance between calculated and experimental chemical shifts were obtained when the effect of fluorine was taken from  $^{13}\text{C}$  NMR of 2-fluoropyridine [2]. For each compound satisfactory correlations were obtained ( $0.992 \div 1$ , Figure 1). The measured and calculated chemical shifts are compared in Figure 2 where  $r = 0.996$  (Table 2 and 3). The correlation in Figure 1 demonstrates that fluorine substituent effects are additive over a fairly large set of ring positions (only in the case if substituent effect were taken from  $^{13}\text{C}$  NMR of 2-fluoropyridine [2]). The largest donations might be expected in those cases where extensive conjugative interaction between fluorine



Me position: 1 -; 2 3-; 3 4-; ; 5 5-; 6 6-

Table 1

<sup>13</sup>C NMR chemical shifts of 2-fluoropyridine and its methyl derivatives

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C-CH <sub>3</sub>
2-Fluoro-pyridine	165.07 [164.60] (185.0)	109.74 [110.50] (111.0)	140.88 [141.80] (137.4)	121.09 [122.10] (119.4)	147.69 [148.30] (151.6)	
2-Fluoro-3-methylpyridine	163.57 [165.30] (185.7)	122.12 [119.40] (119.9)	141.45 [142.50] (138.1)	119.30 [122.00] (119.3)	144.40 [145.40] (149.7)	14.07
2-Fluoro-4-methylpyridine	165.51 [164.50] (184.9)	109.90 [111.12] (136.1)	147.53 [150.70] (146.3)	122.25 [122.80] (120.1)	153.00 [148.20] (151.5)	20.80
2-Fluoro-5-methylpyridine	163.51 [161.70] (182.1)	108.89 [110.40] (110.9)	141.56 [142.50] (138.1)	130.50 [131.00] (128.3)	147.12 [149.00] (152.3)	17.19
2-Fluoro-6-methylpyridine	164.39 [164.50] (184.9)	106.07 [107.60] (108.1)	141.00 [141.70] (137.3)	120.25 [122.80] (120.1)	157.50 [157.20] (160.5)	23.52

[ ] Values calculated from pyridine derivatives.

( ) Values calculated from benzene derivatives.

and nitrogen is possible i. e. C(2) of all investigated compounds 1–5, C(4) of the molecule 3 and C(5) of the molecule 4, because interactions of the type represented by 1–5 would tend to change the C–N  $\pi$  bond orders and the molecular electron distributions in a manner not reflected by substituent parameter additivity. The action of both nitrogen and fluorine on C(2) of all investigated compounds would then be expected to induce the largest deviation, as observed (Table 4). Presumably, withdrawing of electrons by the nitrogen is attenuated by competition from the electronegative fluorine.

Table 2

Correlation coefficient for all carbons of the series of studied 2-fluoropyridines

Correlation	<i>r</i>	S
$\delta_{\text{exp}} = 1.02 \delta_{\text{calc}}^* - 3.79$	0.996	1.701
$\delta_{\text{exp}} = 0.73 \delta_{\text{calc}}^{*2} + 33.73$	0.939	6.973

\* The effects of substituents were taken from pyridine derivatives.

\*2 The effects of substituents were taken from benzene derivatives, number of points — 25.

## GROUND STATE PROPERTIES

As one can see in Table 5 introduction of methyl group into 2-fluoropyridine brings about an increase in HOMO energies from -11,54 eV to -11,28 eV. The methyl group does not significantly influence the level of HOMO energy. The values of HOMO energies of studied fluoro compounds allow one to predict the order (*r*) of reactivity of nucleophilic substitution:

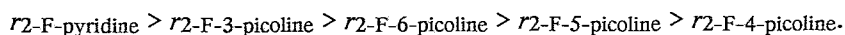


Table 3

Correlation coefficients (for chemical shifts of all carbon atoms) for every of the studied 2-fluoropyridine

Compound	Correlation	r	S
2-Fluoropyridine	$\delta_{\text{exp}} = 1.02 \delta_{\text{calc}}^* - 3.42$	1.000	0.463
	$\delta_{\text{exp}} = 0.73 \delta_{\text{calc}}^{*2} + 34.32$	0.975	5.663
2-Fluoro-3-methylpyridine	$\delta_{\text{exp}} = 0.96 \delta_{\text{calc}}^* + 5.45$	0.995	2.170
	$\delta_{\text{exp}} = 0.65 \delta_{\text{calc}}^{*2} + 46.14$	0.975	4.598
2-Fluoro-4-methylpyridine	$\delta_{\text{exp}} = 1.04 \delta_{\text{calc}}^* - 5.33$	0.992	3.305
	$\delta_{\text{exp}} = 0.80 \delta_{\text{calc}}^{*2} + 22.07$	0.883	14.644
2-Fluoro-5-methylpyridine	$\delta_{\text{exp}} = 1.04 \delta_{\text{calc}}^* - 6.67$	0.998	1.356
	$\delta_{\text{exp}} = 0.73 \delta_{\text{calc}}^{*2} + 34.14$	0.968	5.917
2-Fluoro-6-methylpyridine	$\delta_{\text{exp}} = 1.04 \delta_{\text{calc}}^* - 6.44$	1.000	0.748
	$\delta_{\text{exp}} = 0.77 \delta_{\text{calc}}^{*2} + 28.42$	0.969	7.068

\* The effects of substituents were taken from pyridine derivatives.

\*2 The effects of substituents were taken from benzene derivatives, number of points — 5.

Table 4

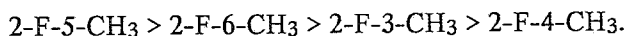
Correlation coefficient for every carbon of studied derivatives

Correlation	r	S
$\delta_{\text{exp}}C(2) = 0.25 \delta_{\text{calc}}^*C(2) + 123.97$	0.386	0.947
$\delta_{\text{exp}}C(2) = 0.25 \delta_{\text{calc}}^{*2}C(2) + 118.95$	0.386	0.947
$\delta_{\text{exp}}C(3) = 1.39 \delta_{\text{calc}}^*C(3) - 44.10$	0.997	0.551
$\delta_{\text{exp}}C(3) = 0.14 \delta_{\text{calc}}^{*2}C(3) + 94.57$	0.264	6.925
$\delta_{\text{exp}}C(4) = 0.74 \delta_{\text{calc}}^*C(4) + 36.68$	1.000	0.091
$\delta_{\text{exp}}C(4) = 0.74 \delta_{\text{calc}}^{*2}C(4) + 39.45$	1.000	0.089
$\delta_{\text{exp}}C(5) = 1.14 \delta_{\text{calc}}^*C(5) - 19.36$	0.979	1.071
$\delta_{\text{exp}}C(5) = 1.14 \delta_{\text{calc}}^{*2}C(5) - 16.27$	0.979	1.071
$\delta_{\text{exp}}C(6) = 1.02 \delta_{\text{calc}}^*C(6) - 2.62$	0.865	3.042
$\delta_{\text{exp}}C(6) = 1.05 \delta_{\text{calc}}^{*2}C(6) - 11.17$	0.849	3.202

\* The effects of substituents were taken from pyridine derivatives.

\*2 The effects of substituents were taken from benzene derivatives, number of points — 5.

Table 5 also summarizes the calculated excessive charge densities on the atoms of all the compounds studied. Comparison of the excessive charge densities on the nitrogen atom of 2-fluoropyridine and 2-fluoropicolines points out that the degree of intramolecular charge transfer in the ground state is the highest for 2-fluoro-6-methylpyridine. The charge distribution explains the mechanism and kinetics of ethanolsis of 2-fluoropicolines [16]. A positive charge at position 2 results in the possibility of replacement of the fluorine atom with sodium ethoxide. The calculated dipole moments of title compound in the ground state decrease in the following order:



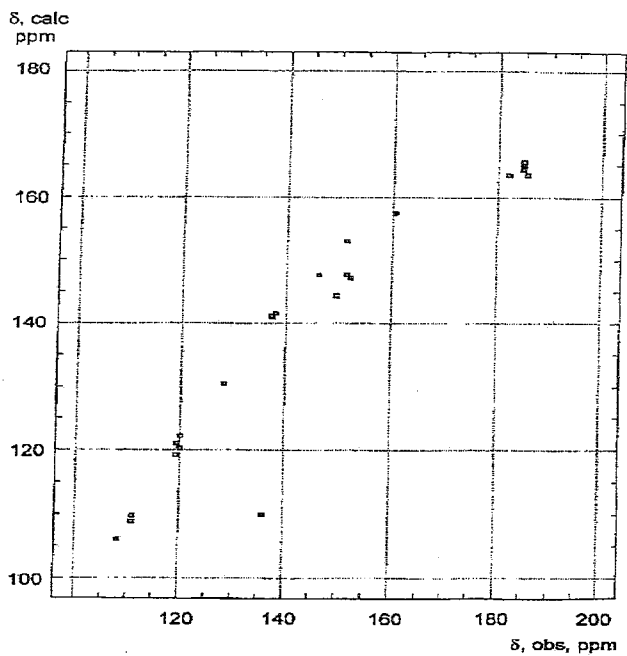


Fig. 1. Plot of experimental vs calculated  $^{13}\text{C}$  chemical shifts of 2-fluoropyridine and 2-fluoropicolines (substituent effect of fluorine was from fluorobenzene)

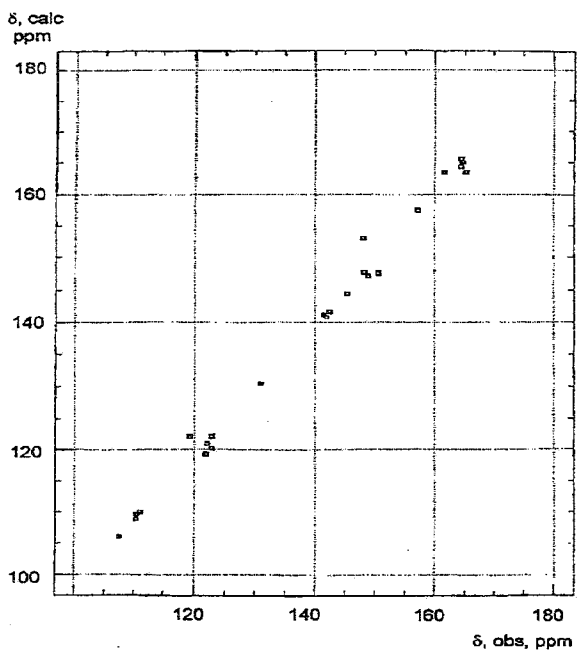


Fig. 2. Plot of experimental vs calculated  $^{13}\text{C}$  chemical shifts of 2-fluoropyridine and 2-fluoropicolines (substituent effect of fluorine was taken from 2-fluoropyridine)

The values of net electronic charges on the atoms and HOMO—LUMO energies of 2-fluoropyridine and its methyl derivatives in the ground state ( $S_0$ ) and the first excited state ( $S_1$ )

Atom	2-Fluoropyridine		2-Fluoro-3-methylpyridine		2-Fluoro-4-methylpyridine		2-Fluoro-5-methylpyridine		2-Fluoro-6-methylpyridine	
	$S_0$	$S_1$	$S_0$	$S_1$	$S_0$	$S_1$	$S_0$	$S_1$	$S_0$	$S_1$
N <sub>(1)</sub>	-0.353	0.047	-0.349	0.041	-0.260	0.153	-0.349	0.044	-0.393	0.008
C <sub>(2)</sub>	0.218	0.004	0.586	0.460	0.223	0.093	-0.180	-0.026	0.310	0.098
C <sub>(3)</sub>	-0.075	-0.044	-0.011	-0.000	-0.116	-0.110	0.032	0.067	-0.119	-0.070
C <sub>(4)</sub>	0.072	-0.117	0.031	-0.158	0.173	-0.179	0.032	-0.158	0.079	-0.111
C <sub>(5)</sub>	-0.124	0.117	-0.066	-0.038	-0.165	-0.247	-0.116	-0.113	-0.132	-0.131
C <sub>(6)</sub>	0.625	0.496	0.209	0.001	0.631	0.606	0.617	0.488	0.631	0.514
C <sub>(7)</sub>			-0.080	-0.068	-0.090	-0.083	-0.081	-0.075	-0.104	-0.075
F <sub>(8)</sub>	-0.349	-0.334	-0.346	-0.331	-0.350	-0.331	-0.348	-0.334	-0.351	-0.336
HOMO (eV)	-11.540		-11.310		-11.540		-11.280		-11.340	
LUMO (eV)	-2.260		-1.710		-2.210		-2.190		-2.230	

Table 6

Comparison of the computed and experimental electronic spectra  
of 2-fluoropyridine and 2-fluoropyridines

Compound	State	Symmetry	Calculated			Experimental	
			energy (eV)	oscillator strength	dipole moment (D)	energy (eV)	$\epsilon \times 10^{-3}$
1	2	3	4	5	6	7	8
2-Fluoro- pyridine	S <sub>0</sub>	—	0	—	3.59		
	S <sub>1</sub> ( $\pi, \pi^*$ )	A'	4.05	0.002	1.75		
	S <sub>2</sub> ( $\pi, \pi^*$ )	A'	4.89	0.000	3.38		
	S <sub>3</sub> (n, $\pi^*$ )	A''	5.04	0.099	3.37	4.18	0.24
	S <sub>4</sub> (n, $\pi^*$ )	A''	5.66	0.067	3.79	4.76	2.90
	S <sub>5</sub> ( $\pi, \pi^*$ )	A'	7.31	1.040	3.92	6.27	4.64
	S <sub>6</sub> ( $\pi, \pi^*$ )	A'	7.49	1.166	3.34		
	S <sub>7</sub> ( $\pi, \pi^*$ )	A'	7.91	0.005			
	S <sub>8</sub> (n, $\pi^*$ )	A''	8.06	0.034			
	S <sub>9</sub> ( $\pi, \pi^*$ )	A'	8.46	0.000			
S <sub>10</sub> ( $\pi, \pi^*$ )	A'	9.47	0.019				
2-Fluoro- 3-methyl- pyridine	S <sub>0</sub>	—	0	—	3.57		
	S <sub>1</sub> ( $\pi, \pi^*$ )	A'	4.00	0.002	0.33		
	S <sub>2</sub> ( $\pi, \pi^*$ )	A'	4.84	0.000	3.22		
	S <sub>3</sub> (n, $\pi^*$ )	A''	4.94	0.112	3.59	4.72	3.63
	S <sub>4</sub> (n, $\pi^*$ )	A'	5.51	0.083	3.97		
	S <sub>5</sub> (n, $\pi^*$ )	A''	7.16	1.079	3.98	6.03	5.56
	S <sub>6</sub> ( $\pi, \pi^*$ )	A'	7.35	1.136	3.74		
	S <sub>7</sub> ( $\pi, \pi^*$ )	A'	7.82	0.002			
	S <sub>8</sub> ( $\pi, \pi^*$ )	A'	7.88	0.011			
	S <sub>9</sub> (n, $\pi^*$ )	A''	8.19	0.006			
S <sub>10</sub> ( $\pi, \pi^*$ )	A'	9.56	0.022				
2-Fluoro- 4-methyl- pyridine	S <sub>0</sub>	—	0	—	3.27		
	S <sub>1</sub> ( $\pi, \pi^*$ )	A'	4.50	0.001	4.12		
	S <sub>2</sub> ( $\pi, \pi^*$ )	A'	4.89	0.000	3.07		
	S <sub>3</sub> (n, $\pi^*$ )	A''	5.02	0.085	3.81	4.39	2.63
	S <sub>4</sub> ( $\pi, \pi^*$ )	A'	5.61	0.021	4.40		
	S <sub>5</sub> (n, $\pi^*$ )	A''	7.12	0.999	5.10	6.03	5.27
	S <sub>6</sub> ( $\pi, \pi^*$ )	A'	7.25	1.303	4.41		
	S <sub>7</sub> (n, $\pi^*$ )	A''	8.04	0.023			
	S <sub>8</sub> ( $\pi, \pi^*$ )	A'	8.76	0.000			
	S <sub>9</sub> ( $\pi, \pi^*$ )	A'	9.07	0.008			
S <sub>10</sub> ( $\pi, \pi^*$ )	A'	9.85	0.016				
2-Fluoro- 5-methyl- pyridine	S <sub>0</sub>	—	0	—	3.75		
	S <sub>1</sub> ( $\pi, \pi^*$ )	A'	4.01	0.002	1.95		
	S <sub>2</sub> ( $\pi, \pi^*$ )	A'	4.86	0.000	3.37		
	S <sub>3</sub> ( $\pi, \pi^*$ )	A'	4.92	0.116	4.10	4.66	3.39
	S <sub>4</sub> (n, $\pi^*$ )	A''	5.51	0.119	4.34		
	S <sub>5</sub> (n, $\pi^*$ )	A''	7.23	1.047	4.04	6.12	4.91
	S <sub>6</sub> ( $\pi, \pi^*$ )	A'	7.40	1.147	3.97		
	S <sub>7</sub> ( $\pi, \pi^*$ )	A'	7.83	0.002			
	S <sub>8</sub> (n, $\pi^*$ )	A''	7.84	0.020			
	S <sub>9</sub> ( $\pi, \pi^*$ )	A'	8.19	0.007			
S <sub>10</sub> (n, $\pi^*$ )	A''	9.50	0.002				

Table 6 (continued)

1	2	3	4	5	6	7	8
2-Fluoro-6-methylpyridine	S <sub>0</sub>	—	0	—	3.67		
	S <sub>1</sub> ( $\pi, \pi^*$ )	A'	4.09	0.003	1.84		
	S <sub>2</sub> ( $\pi, \pi^*$ )	A'	4.88	0.000	3.50		
	S <sub>3</sub> ( $n, \pi^*$ )	A''	4.96	0.114	3.55	4.73	4.42
	S <sub>4</sub> ( $\pi, \pi^*$ )	A'	5.55	0.079	3.83		
	S <sub>5</sub> ( $n, \pi^*$ )	A''	7.19	1.070	3.81	6.02	5.51
	S <sub>6</sub> ( $\pi, \pi^*$ )	A'	7.40	1.093	2.93		
	S <sub>7</sub> ( $\pi, \pi^*$ )	A'	7.87	0.006			
	S <sub>8</sub> ( $\pi, \pi^*$ )	A'	7.92	0.054			
	S <sub>9</sub> ( $n, \pi^*$ )	A''	8.41	0.043			
S <sub>10</sub> ( $\pi, \pi^*$ )	A'	8.56	0.004				

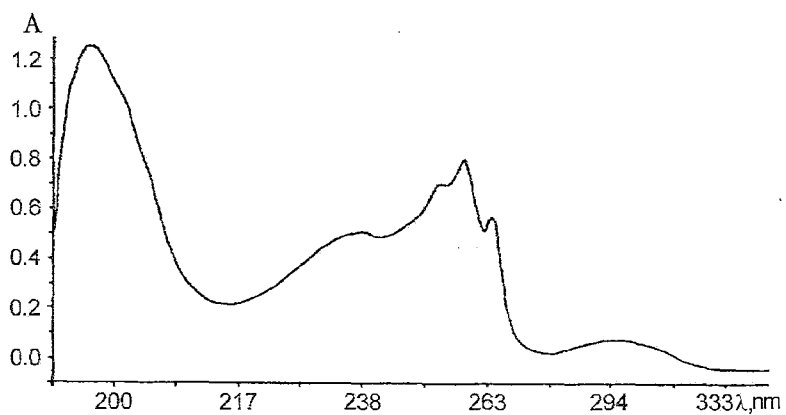


Fig. 3. Absorption spectrum of 2-fluoropyridine

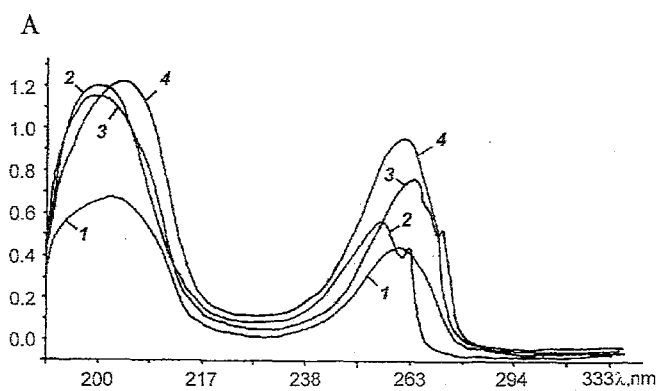


Fig. 4. Absorption spectra of 2-fluoropicolines: 1 — 2-fluoro-3-methylpyridine; 2 — 2-fluoro-4-methylpyridine; 3 — 2-fluoro-5-methylpyridine; 4 — 2-fluoro-6-methylpyridine



Table 7

IR spectra of 2-fluoropyridine and 2-fluoropicolines  
in the region of 2900÷400 cm<sup>-1</sup>

Compound	Wavelength, intensity	Assignment	Wavelength, intensity	Assignment
1	2	3	4	5
2-Fluoro- pyridine	420 m	$\nu_{26} \phi$ (CC)	1150 m	$\nu_{12} \beta$ (CH)
	525 m	$\nu_{26} \phi$ (CC)	1180 w	
	560 m	$\nu_{18} X_{sens}$	1250 s (sh)	$\alpha$ (CC)
			1300 m (sh)	
	625 m	$\nu_{17}$ (CCC)	1380 w (sh)	
	670 w		1440 d s	$\nu$ (CC, CN)
			1480 d s	
	740 w (sh)	$\nu_{24} \phi$ (CC)	1510 w	
	780 s	$\nu_{23} \gamma$ (CH)	1550 w	
	830 s	$\nu_{16} X_{sens}$	1580 d s	$\nu$ (CC)
	845 s		1600 d	
	880 w	$\nu_{22} \gamma$ (CH)	1620 m (sh)	
	940 w	$\nu_{21} \gamma$ (CH)	2920 w	$\nu_3$
	970 w	$\nu_{20} \gamma$ (CH)	2940 w	$\nu_4$
	1000 m	$\nu_{15}$ ring	3020 w	$\nu_2$
	1050 m	$\nu_{14} \beta$ (CH)	3080 w	$\nu_1 \gamma$ (CH)
	1100 w	$\nu_{13} \beta$ (CH)	3490 br	
2-Fluoro- 3-methyl- pyridine	495 w	$\nu_{19} X_{sens}$	1160 w	
	510 w	$\nu_{25} \phi$ (CC)	1185 m	
	530 w		1250 s	$\nu_{11} X_{sens}$
	540 m		1280 m	$\nu_{10} \alpha$ (CC)
	560 w	$\nu_{18} X_{sens}$	1310 w	$\nu_9 \beta$ (CH)
	570 w	$\nu_{17} \alpha$ (CCC)	1390 m	
	755 m	$\nu_{23} \gamma$ (CH)	1430 d s	$\nu_7$ (CC, CN)
			1460 d s	$\nu_8$ (CC, CN)
	800 s	$\nu_{16} X_{sens}$	1490 s	
	830 m (sh)		1590 d s	$\nu_5$ (CC)
			1620 d	$\nu_6$ (CC)
	870 m	$\nu_{22} \gamma$ (CH)	2340 w	
	930 w	$\nu_{21} \gamma$ (CH)	2880 w	
	940 w	$\nu_{20} \gamma$ (CH)	2940	
	1000 m	$\nu_{15}$ ring	2980	
	1045 w	$\nu_{14} \beta$ (CH)	2990	
	1070 w	$\nu_{13} \beta$ (CH)	3040	
1140 m	$\nu_{12} \beta$ (CH)	3090		
2-Fluoro- 4-methyl- pyridine	460 m	$\nu_{26} \phi$ (CC)	1120 w	$\nu_{14} \beta$ (CH)
	480 w	$\nu_{19} X_{sens}$	1150 s	$\nu_{13} \beta$ (CH)
				$\nu_{12} \beta$ (CH)
	500 w		1250 m	$\nu_{10} \beta$ (CH)
				$\nu_{11} X_{sens}$
	520 m	$\nu_{25} \phi$ (CC)	1290 m	$\nu_9 \alpha$ (CC)
	570 m	$\nu_{18} X_{sens}$	1330 w	
	590 m		1410 s	
	630 w	$\nu_{17} \alpha$ (CCC)	1440 m	$\nu_8$ (CC, CN)
	760 m	$\nu_{24} \phi$ (CC)	1480 d m	
			1490 d m	$\nu_7$
	790 m	$\nu_{23} \gamma$ (CH)	1510 w	
	830 m	$\nu_{16} X_{sens}$	1570 d s	$\nu_5, \nu$ (CC)
			1620 d s	$\nu_6, \nu$ (CC)
	870 w	$\nu_{22} \gamma$ (CH)	2940 w	$\nu_4, \nu$ (CH)
	945 s	$\nu_{21} \gamma$ (CH)	3040 w	$\nu_3, \nu$ (CH)
	1000 m	$\nu_{20} \gamma$ (CH)	3080 w	$\nu_2, \nu$ (CH)
1050 w	$\nu_{15}$ ring	3520 br	$\nu_1, \nu$ (CH)	

Table 7 (continued)

1	2	3	4	5
2-Fluoro-5-methylpyridine	430 w	$\nu_{19} X_{sens}$ , $\nu_{26} \phi(CC)$	1230 d sh, 1250 d sh	$\nu_9 \beta(CH)$ $\nu_{10} \alpha(CC)$
	445 w		1300 m	
	490 m		1380 s	
	520 m		1480d s 1490d w	$\nu_7 \gamma(CC,CN)$ $\nu_8$
	595 w	$\nu_{18} X_{sens}$	1610	$\nu_5 \gamma(CC)$
	620 w	$\nu_{17}, \alpha(CCC)$	1680	$\nu_6 \gamma(CC)$
	650 s		2880 w	
	660 w		2940 m	$\nu_4 \gamma(CH)$
	745 s	$\nu_{23} \gamma(CH)$ $\nu_{24} \phi(CC)$	2980 m	$\nu_3 \gamma(CH)$
	830 d s	$\nu_{16} X_{sens}$ , $\nu_{25} \phi(CC)$	3020 m	$\nu_2 \gamma(CH)$
	870 d s	$\nu_{15}$ ring		
	920 w	$\nu_{14} \beta(CH)$ , $\nu_{20} \gamma(CH)$ , $\nu_{21} \gamma(CH)$	3080	$\nu_1 \gamma(CH)$
	1030 s	$\nu_{12} \beta(CH)$ , $\nu_{15}$ ring	3210 w	
	1130 s	$\nu_{12} \beta(CH)$	3520 m br	
2-Fluoro-6-methylpyridine	475 m	$\nu_{19} X_{sens}$ , $\nu_{26} \phi(CC)$	1230 s	$\nu_{11} X_{sens}$
	500 w	$\nu_{25} \phi(CC)$	1270 m	$\nu_9 \beta(CH)$
	555 m	$\nu_{18} X_{sens}$	1290 s	$\nu_{10} \alpha(CC)$
	730 m	$\nu_{17} \alpha(CCC)$	1320 w	
	790 s	$\nu_{23} \gamma(CH)$	1380 m	
	850 m	$\nu_{16} X_{sens}$	1460 s	$\nu_8 \gamma(CC,CN)$
	890 w	$\nu_{22} \gamma(CH)$	1490 w	$\nu_7$
	940 m	$\nu_{21} \gamma(CH)$	1555m	
	990 m	$\nu_{15}$ ring	1580d s 1610d s	$\nu_5$ $\nu_6$
	1030 m	$\nu_{20} \gamma(CH)$	2920 w	$\nu_3 \gamma(CH)$
	1060 w	$\nu_{14} \beta(CH)$	2980 w	$\nu_2 \gamma(CH)$
	1085 m	$\nu_{13} \beta(CH)$	3000 w	$\nu_1 \gamma(CH)$
	1150 m		3400 w	
	1180 w	$\nu_{12} \beta(CH)$	3520 br	

## ELECTRONIC SPECTRA AND EXCITED STATE PROPERTIES

Figs. 3, 4 and Table 6 show the UV spectra of 2-fluoropyridine and 2-fluoropicolines. Spectra of all compounds exhibit their characteristic bands in the regions of 196...227 nm and 237...280 nm. These bands are due to the  $\pi \rightarrow \pi^*$  transition of the aromatic pyridine ring or the  $\pi_{ring} \rightarrow \pi_F$  transition and are common to  $\pi \rightarrow \pi^*$  bands of aromatic fluoropyridines and fluoropicolines where C—F and C=C groups form a conjugated system. An additional band appears in the case of 2-fluoropyridine in the region of 278...333 nm ( $\lambda_{max}$  295 nm); that is a very weak absorption band with very low intensity (about  $2.4 \times 10^2$ ), which can be assigned to  $n \rightarrow \pi^*$  transition. The spectra of 2-fluoropicolines are shifted to shorter wavelengths due to conjugation between the fluoro substituent and methyl group and the bonds  $n \rightarrow \pi^*$  are obscured by the strong  $\pi^* \rightarrow \pi$  bands. The spectra of 2-fluoropicolines are characterized by the regular two bands. Among 2-halopicolines, the intensity of 2-iodopicolines is the highest [17, 18]. This feature is related to a  $d$  orbital resonance of iodine [18].

Transition from ground state to an excited one is related to charge density changes in the molecule (Table 5). On passing from the ground state to the first excited state in 2-fluoropyridine and its methyl derivatives the value of the negative charge on the fluorine atom is lowered and that of the carbon in position 4 increased. The value of negative charge on nitrogen atom undergoes a significant decrease in all compounds investigated on transition from  $S_0$  to  $S_1$ .

Energies of transitions from the ground state to excited states, their symmetry orbital nature and dipole moments have been calculated, and these results are presented in Table 6. Satisfactory agreement between the calculated and experimental spectra of studied compounds has been obtained.

The calculated electric dipole moments of the ground and various excited singlet states provide the measure for the electron transfer. The change in dipole moment during electron excitation to the first excited singlet state is calculated as  $\approx 1.84 D$  for 2-fluoropicoline,  $3.24 D$  for 2-fluoro-3-methyl-,  $0.85 D$  for 2-fluoro-4-methyl-,  $1.80 D$  for 2-fluoro-5-methyl-, and  $1.83 D$  for 2-fluoro-6-methylpyridine.

The differences in values of the HOMO—LUMO energies range for examined compounds from  $-9.28 eV$  to  $-10.00 eV$  and are smaller than those for 2-iodopicolines ( $-10.13$  to  $-10.19 eV$ ). These facts should indicate the higher susceptibility of 2-fluoropicolines in photochemical reaction as compared to 2-iodopicolines.

The values of LUMO energies (E) on electrophilic substitution are as follows:  $E_{2-F-4-picoline} > E_{2-F-5-picoline} > E_{2-F-6-picoline} > E_{2-F-3-picoline} > E_{2-F-pyridine}$ .

The interpretation of IR spectra follows from preceding results and observed contours for some bands [3, 6] (Table 7). For 2-fluoropyridine the bands at  $(560, 830, 845, 1250) cm^{-1}$  are X-sensitive mode.

For 2-fluoropicolines these bands undergo a shift to longer wavelengths  $(560, 830, 1250) cm^{-1}$  for 2-fluoro-3-methylpyridine,  $(570, 830, 1250) cm^{-1}$  for 2-fluoro-4-methylpyridine,  $(595, 830, 1230) cm^{-1}$  for 2-fluoro-5-methylpyridine and  $(555, 850, 1230) cm^{-1}$  for 2-fluoro-6-methylpyridine.

In the spectra of all studied compounds the strong  $\alpha(C-C)$  band lies in the region of  $1280 \div 1300 cm^{-1}$  and  $\gamma(C-C)$  at  $1570 \div 1620 cm^{-1}$ .

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