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THE ^{13}C NMR, UV AND IR SPECTRA OF 2-FLUOROPYRIDINE METHYL DERIVATIVES

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^{13}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}H NMR spectra of methyl derivatives of 2-fluoropyridine were analyzed in [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 σ-electron system but leaves the π-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±0.03 Hz in 2-fluoro-5-methylpyridine compared to 1.15±0.02 Hz in *p*-fluorotoluene.

Lichter and Wasylishen [2] measured ^{13}C NMR and carbon-fluorine coupling constants of 2-, 3-, and 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 $^{1}J_{CF}$ in 2-fluoropyridine is algebraically more positive than $^{1}J_{CF}$ in 3- and 4-fluoropyridine, in agreement with the positive contribution associated with the presence of an 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_{CH} in pyridine and fluorobenzene as well as some other heterocycles, although only a 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 in [3]. 2-Substituted pyridines in the infrared spectra are characterized by two relatively intense bands near 600 and 400 cm^{-1}. The vapor-phase contours of the far infrared bands of 2-fluoro- and 2-chloropyridine indicate that the bands at 600 and 400 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 CCl_4 solution. In the liquid phase, not only the individual bands but also the center of gravity of the bands are shifted to longer wavelengths,

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while the intensities are generally larger than those measured in CCl_4 solution. The differences between the intensities in the liquid phase and 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 σ_I [5]. The interpretation of these facts leads to conclusions concerning the polarity of the C–H band moments of the investigated pyridine derivatives. The influence of the heteroatom N on the C–H bond moments are discussed in [5].

The IR and Raman spectra of 2-fluoropyridine were reported and interpreted in [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, and its unique electronic properties provide the biological properties of aromatic fluorides [7]. Thus, Ar–F bonds appear in a broad variety of molecules having 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 an understanding of the mechanism of their biological activity. Earlier published works [1-7] did not included ^{13}C NMR, IR, and electronic spectra of methyl derivatives of 2-fluoropyridine.

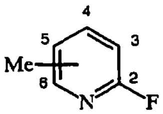
EXPERIMENTAL

The 2-fluoropicolines used in the study were synthesized by a method previously described [8, 9]. The ^{13}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° (13 μs), and repetition time 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 $CDCl_3$ as solvent, and the centers of the $CDCl_3$ 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 procedures. 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 comparing 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. Better agreement between calculated and experimental chemical shifts were obtained when the effect of fluorine was taken from ^{13}C NMR of 2-fluoropyridine [2]. For each compound satisfactory correlations were obtained (0.992 - 1, Fig. 1). The measured and calculated chemical shifts are compared in Fig. 2, where $r = 0.996$ (Tables 2 and 3). The correlation in Fig. 1 demonstrates that fluorine substituent effects are additive over a fairly large set of ring positions (only in the case where substituent effects were taken from ^{13}C NMR of 2-fluoropyridine [2]). The largest donations might be expected in those cases where extensive conjugative interaction between fluorine 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



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

TABLE 1. ^{13}C NMR Chemical Shifts of 2-Fluoropyridine and Its Methyl Derivatives

Compound	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	C–CH_3
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-methyl-pyridine	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-methyl-pyridine	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-melhyl-pyridine	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-methyl pyridine	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.

TABLE 2. Correlation Coefficient for All Carbon Atoms of the Series of Studied 2-Fluoropyridines

Correlation	r	S
$\delta_{exp} = 1.02\ \delta^{*}_{calc} - 3.79$	0.996	1.701
$\delta_{exp} = 0.73\ \delta^{*2}_{calc} + 33.73$	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.

molecule **4**, because interactions of the type represented by **1-5** would tend to change the C–N π 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 the 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.

GROUND STATE PROPERTIES

As one can see in Table 5, introduction of the 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 the studied fluoro compounds allow one to predict the order (r) of reactivity of nucleophilic substitution:

$$r^2\text{-F-pyridine} \gg r^2\text{-F-3-picoline} \gg r^2\text{-F-6-picoline} \gg r^2\text{-F-5-picoline} \gg r^2\text{-F-4-picoline}.$$

Table 5 also summarizes the calculated excess charge densities on the atoms of all the compounds studied. Comparison of the excess 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 ethanolysis of 2-fluoropicolines

TABLE 3. Correlation Coefficients (for Chemical Shifts of All Carbon Atoms) for Each of the Studied 2-Fluoropyridines

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

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

[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:

$$2\text{-F-5-CH}_3 \gg 2\text{-F-6-CH}_3 \gg 2\text{-F-3-CH}_3 \gg 2\text{-F-4-CH}_3.$$

ELECTRONIC SPECTRA AND EXCITED STATE PROPERTIES

Figures 3 and 4 and Table 6 show the UV spectra of 2-fluoropyridine and 2-fluoropicolines. The spectra of all the 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 (λ_{max} 295 nm), that is, a very

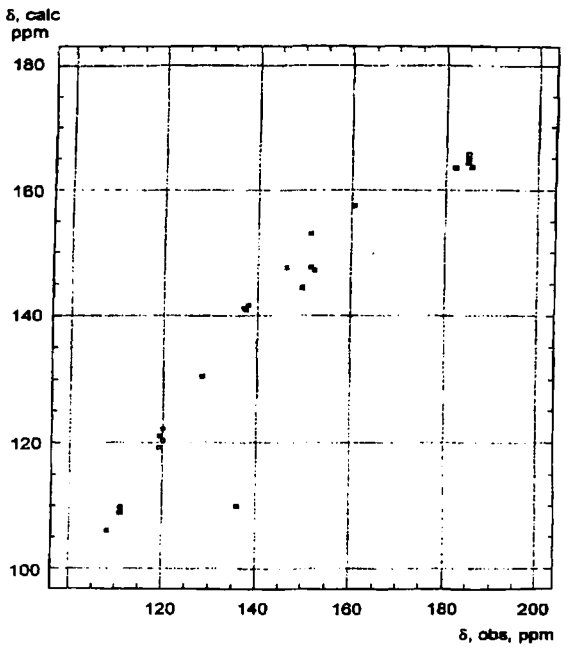


Fig. 1. Plot of experimental *vs* calculated ^{13}C chemical shifts of 2-fluoropyridine and 2-fluoropicolines (substitution effects of fluorine was from fluorobenzene).

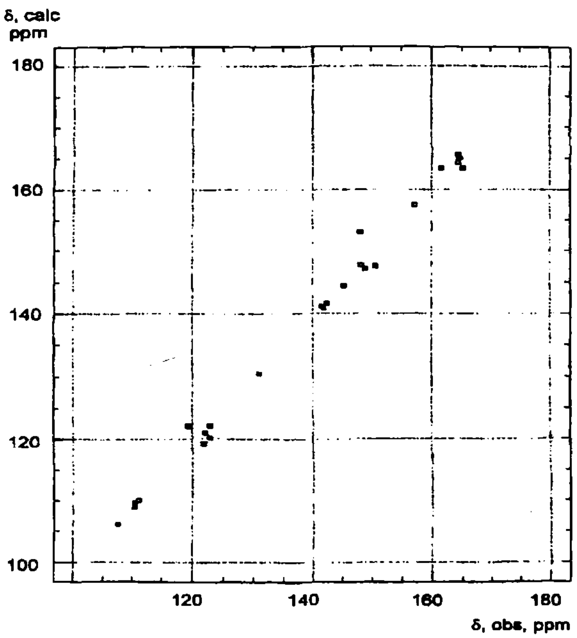


Fig. 2. Plot of experimental *vs* calculated ^{13}C chemical shifts of 2-fluoropyridine and 2-fluoropicolines (substitution effects of fluorine was from fluoropyridine).

weak absorption band with very low intensity (about 2.4×10^2), which can be assigned to the $n \rightarrow \pi^*$ transition. The spectra of 2-fluoropicolines are shifted to shorter wavelengths due to conjugation between the fluoro substituent and the 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 the *d*-orbital resonance of iodine [18].

TABLE 5. 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
$N_{(1)}$	-0.353	0.047	-0.349	0.041	-0.260	0.153	-0.349	0.044	-0.393	0.008
$C_{(2)}$	0.218	0.004	0.586	0.460	0.223	0.093	-0.180	-0.026	0.310	0.098
$C_{(3)}$	-0.075	-0.044	-0.011	-0.000	-0.116	-0.110	0.032	0.067	-0.119	-0.070
$C_{(4)}$	0.072	-0.117	0.031	-0.158	0.173	-0.179	0.032	-0.158	0.079	-0.111
$C_{(5)}$	-0.124	0.117	-0.066	-0.038	-0.165	-0.247	-0.116	-0.113	-0.132	-0.131
$C_{(6)}$	0.625	0.496	0.209	0.001	0.631	0.606	0.617	0.488	0.631	0.514
$C_{(7)}$			-0.080	-0.068	-0.090	-0.083	-0.081	-0.075	-0.104	-0.075
$F_{(8)}$	-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-Fluoropicolines

Compound	State	Symmetry	Calculated			Experimental	
			energy (eV)	oscillator strength	dipole moment (D)	energy (eV)	$\varepsilon \times 10^{-3}$
2-Fluoro-pyridine	S_0	—	0	—	3.59		
	S_1 (π,π*)	A'	4.05	0.002	1.75		
	S_2 (π,π*)	A'	4.89	0.000	3.38		
	S_3 (n,π*)	A"	5.04	0.099	3.37	4.18	0.24
						4.76	2.90
	S_4 (n,π*)	A'	5.66	0.067	3.79		
	S_5 (π,π*)	A'	7.31	1.040	3.92	6.27	4.64
	S_6 (π,π*)	A'	7.49	1.166	3.34		
	S_7 (π,π*)	A'	7.91	0.005			
	S_8 (n,π*)	A"	8.06	0.034			
	S_9 (π,π*)	A'	8.46	0.000			
	S_{10} (π,π*)	A'	9.47	0.019			
2-Fluoro-3-methyl-pyridine	S_0		0	—	3,57		
	S_1 (π,π*)	A'	4.00	0.002	0.33		
	S_2 (π,π*)	A'	4.84	0.000	3.22		
	S_3 (n,π*)	A"	4.94	0.112	3.59	4.72	3.63
	S_4 (n,π*)	A'	5.51	0.083	3.97		
	S_5 (n,π*)	A"	7.16	1.079	3.98	6.03	5.56
	S_6 (π,π*)	A'	7.35	1.136	3.74		
	S_7 (π,π*)	A'	7.82	0.002			
	S_8 (π,π*)	A'	7.88	0.011			
	S_9 (n,π*)	A"	8.19	0.006			
	S_{10} (π,π*)	A'	9.56	0.022			
2-Fluoro-4-methyl-pyridine	S_0	—	0	—	3.27		
	S_1 (π,π*)	A'	4.50	0.001	4.12		
	S_2 (π,π*)	A'	4.89	0.000	3.07		
	S_3 (n,π*)	A"	5.02	0.085	3.81	4.39	2.63
	S_4 (π,π*)	A'	5.61	0.021	4.40		
	S_5 (n,π*)	A"	7.12	0.999	5.10	6.03	5.27
	S_6 (π,π*)	A'	7.25	1.303	4.41		
	S_7 (n,π*)	A"	8.04	0.023			
	S_8 (π,π*)	A'	8.76	0.000			
	S_9 (π,π*)	A'	9.07	0.008			
	S_{10} (π,π*)	A'	9.85	0.016			
2-Fluoro-5-melhyl-pyridine	S_0	—	0	—	3.75		
	S_1 (π,π*)	A'	4.01	0.002	1.95		
	S_2 (π,π*)	A'	4.86	0.000	3.37		
	S_3 (π,π*)	A'	4.92	0.116	4.10	4.66	3.39
	S_4 (n,π*)	A"	5.51	0.119	4.34		
	S_5 (n,π*)	A"	7.23	1.047	4.04	6.12	4.91
	S_6 (π,π*)	A'	7.40	1.147	3.97		
	S_7 (π,π*)	A'	7.83	0.002			
	S_8 (n,π*)	A"	7.84	0.020			
	S_9 (π,π*)	A'	8.19	0.007			
	S_{10} (n,π*)	A"	9.50	0.002			
2-Fluoro-6-methyl pyridine	S_0	—	0	—	3.67		
	S_1 (π,π*)	A'	4.09	0.003	1.84		
	S_2 (π,π*)	A'	4.88	0.000	3.50		
	S_3 (n,π*)	A"	4.96	0.114	3.55	4.73	4.42
	S_4 (π,π*)	A'	5.55	0.079	3.83		
	S_5 (n,π*)	A"	7.19	1.070	3.81	6.02	5.51
	S_6 (π,π*)	A'	7.40	1.093	2.93		
	S_7 (π,π*)	A'	7.87	0.006			
	S_8 (π,π*)	A'	7.92	0.054			
	S_9 (n,π*)	A"	8.41	0.043			
	S_{10} (π,π*)	A'	8.56	0.004			

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

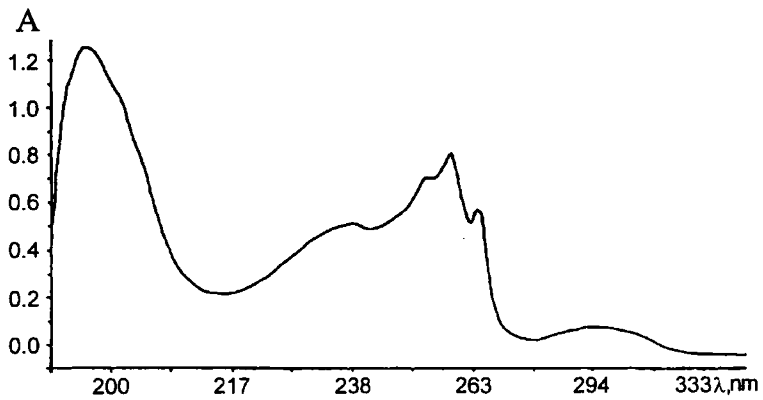


Fig. 3. Absorption spectrum of 2-fluoropyridine.

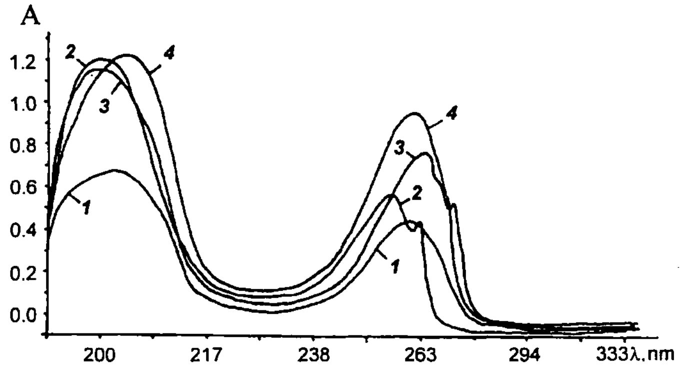


Fig. 4. Absorption spectrum of 2-fluoropicolines: *1* - 2-fluoro-3-methylpyridine; *2* - 2-fluoro-4-methylpyridine; *3* - 2-fluoro-5-methylpyridine; *4* - 2-fluoro-6-methylpyridine.

value of the negative charge on the nitrogen atom undergoes a significant decrease in all compounds investigated on transition from S_0 to S_1.

The energies of transitions from the ground state to the excited states, their symmetry orbital nature, and the dipole moments have been calculated, and these results are presented in Table 6. Satisfactory agreement between the calculated and experimental spectra of the 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 ≈ 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 for the examined compounds range 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 reactions as compared to 2-iodopicolines.

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

The interpretation of the IR spectra follows from the preceding results and the 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 the studied compounds the strong α(C–C) band lies in the region of 1280-1300 cm^{-1} and γ(C–C) at 1570-1620 cm^{-1}.

TABLE 7. IR Spectra of 2-Fluoropyridine and 2-Fluoropicolines in the Region of 2900-400 cm^{-1}

Compound	Wavelength, intensity	Assignment	Wavelength, intensity	Assignment
1	2	3	4	5
2-Fluoropyridine	420 m	ν_{26} φ(CC)	1150 m	ν_{12} β(CH)
	525 m	ν_{26} φ(CC)	1180 w	
	560 m	ν_{18} X_{sens}	1250 s (sh)	α(CC)
			1300 m (sh)	
	625 m	ν_{17} (CCC)	1380 w (sh)	
	670 w		1440 d s	ν(CC,CN)
			1480 d s	
	740 w (sh)	ν_{24} φ(CC)	1510 w	
	780 s	ν_{23} γ(CH)	1550 w	
	830 s	ν_{26} X_{sens}	1580 d s	ν(CC)
	845 s		1600 d	
	880 w	ν_{22} γ(CH)	1620 m (sh)	
	940 w	ν_{21} γ(CH)	2920 w	ν_3
	970 w	ν_{20} γ(CH)	2940 w	ν_4
	1000 m	ν_{15} ring	3020 w	ν_5
	1050 m	ν_{14} β(CH)	3080 w	ν_1 γ(CH)
	1100 w	ν_{13} β(CH)	3490 br	
2-Fluoro-3-methyl-pyridine	495 w	ν_{19} X_{sens}	1160 w	
	510 w	ν_{25} φ(CC)	1185 m	
	530 w		1250 s	ν_{11} X_{sens}
	540 m		1280 m	ν_{10} α(CC)
	560 w	ν_{18} X_{sens}	1310 w	ν_9 β(CH)
	570 w	ν_{17} α(CCC)	1390 m	
	755 m	ν_{23} γ(CH)	1430 d s	ν_7 (CC,CN)
			1460 d s	ν_8 (CC,CN)
	800 s	ν_{16} X_{sens}	1490 s	
	830 m (sh)		1590 d s	ν_5 (CC)
			1620 d	ν_6 (CC)
	870 m	ν_{22} γ(CH)	2340 w	
	930 w	ν_{21} γ(CH)	2880 w	
	940 w	ν_{20} γ(CH)	2940	
	1000 m	ν_{15} ring	2980	
	1045 w	ν_{14} β(CH)	2990	
	1070 w	ν_{13} β(CH)	3040	
	1140 m	ν_{12} β(CH)	3090	
2-Fluoro-4-methyl-pyridine	460 m	ν_{26} φ(CC)	1120 w	ν_{14} β(CH)
	480 w	ν_{19} X_{sens}	1150 s	ν_{14} β(CH)
				ν_{14} β(CH)
	500 w		1250 m	ν_{14} β(CH)
				ν_{11} X_{sens}
	520 m	ν_{25} φ(CC)	1290 m	ν_9 α(CC)
	570 m	ν_{18} X_{sens}	1330 w	
	590 m		1410 s	
	630 w	ν_{17} α(CCC)	1440 m	ν_8 (CC,CN)
	760 m	ν_{24} φ(CC)	1480 d m	
			1490 d m	ν_7
	790 m	ν_{23} γ(CH)	1510 w	
	830 m	ν_{16} X_{sens}	1570 d s	ν_5, ν(CC)
			1620 d s	ν_6, ν(CC)
	870 w	ν_{22} γ(CH)	2940 w	ν_4, ν(CH)
	945 s	ν_{21} γ(CH)	3040 w	ν_3, ν(CH)
	1000 m	ν_{20} γ(CH)	3080 w	ν_2, ν(CH)
	1050 w	ν_{15} ring	3520 br	ν_1, ν(CH)

TABLE 7 (continued)

1	2	3	4	5
2-Fluoro-5-melhyl-	430 w	ν_{19} X_{sens}	1230 d sh,	
pyridine		ν_{26} ϕ(CC)	1250 d sh	ν_9 β(CH)
	445 w		1300 m	ν_{10} α(CC)
	490 m		1380 s	
	520 m		1480 d s	ν_7 γ(CC,CN)
			1490 d w	ν_8
	595 w	ν_{18} X_{sens}	1610	ν_5 γ(CC)
	620 w	ν_{17} α(CCC)	1680	ν_6 γ(CC)
	650 s		2880 w	
	660 w		2940 m	ν_4 γ(CH)
	745 s	ν_{23} γ(CH)	2980 m	ν_3 γ(CH)
		ν_{24} ϕ(CC)		
	830 d s	ν_{16} X_{sens}	3020 m	ν_2 γ(CH)
		ν_{25} ϕ(CC)		
	870 d s	ν_{15} ring		
	920 w	ν_{14} β(CH),	3080	ν_1 γ(CH)
		ν_{20} γ(CH),		
		ν_{21} γ(CH)		
	1030 s	ν_{12} β(CH),	3210 w	
		ν_{15} ring		
	1130 s	ν_{12} β(CH)	3520 m br	
2-Fluoro-6-methyl	475 m	ν_{19} X_{sens}	1230 s	ν_{11} X_{sens}
pyridine		ν_{26} ϕ(CC)		
	500 w	ν_{25} ϕ(CC)	1270 m	ν_9 β(CH)
	555 m	ν_{18} X_{sens}	1290 s	ν_{10} α(CC)
	730 m	ν_{17} α(CCC)	1320 w	
	790 s	ν_{23} γ(CH)	1380 m	
	850 m	ν_{16} X_{sens}	1460 s	ν_8 γ(CC,CN)
	890 w	ν_{22} γ(CH)	1490 w	ν_7
	940 m	ν_{21} γ(CH)	1555 m	
	990 m	ν_{15} ring	1580 d s	ν_5
			1610 d s	ν_6
	1030 m	ν_{20} γ(CH)	2920 w	ν_3 γ(CH)
	1060 w	ν_{14} β(CH)	2980 w	ν_2 γ(CH)
	1085 m	ν_{13} β(CH)	3000 w	ν_1 γ(CH)
	1150 m		3400 w	
	1180 w	ν_{12} β(CH)	3520 br	

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