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^1H NMR spectra of 2-halo-4-nitropicolines were registered. The spectral parameters: i.e. chemical shifts as well as coupling constants were estimated. Influence of properties of substituents of chemical shifts and coupling constants have been discussed.

In the literature are not many dates dealing with coupling constants of disubstituted pyridines. The 2-halo-4-nitropicolines are particularly interesting, as in their molecules there are some substituents, which are situated in resonance positions in relation to each other and to pyridine nitrogen.

Experimental.

Synthesis of 2-halo-4-nitropicolines have been described in previous publications [1,2].

The ^1H NMR spectra of 2-halo-4-nitropicolines were obtained with Tesla BS 598 A 100 MHz at the temperature 30°C . CDCl_3 have been used as a solvent and TMS as an internal standard. The chemical shifts values by means of spectra analysis for protons of title compounds as well as coupling constants are contained in Table 1.

Results and discussion.

Conversion from pyridine 2-halo-4-nitropicolines causes the greatest change of the shielding of the proton adjacent to nitro group and varies for H-3 ($0,22 + 1,42$ ppm) and for H-5 - $0,03 + 0,58$ ppm. The observed deshielding effect of H-3 and



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H-5 in 2-halo-4-nitropicolines is consistent with the known nucleophilic reactivity of 4-nitropyridines (3). The spectra of 2-halo-3-methyl-4-nitropyridines, 2-halo-5-methyl-4-nitropyridines and 2-halo-6-methyl-4-nitropyridines were studied as being an AX type. The introducing of three substituents to pyridine (halogen in position 2, methyl group into position 3 and nitro group into position 4) causes the change of coupling constants $J_{5,6}$ from 5.5 Hz (3) to 3 Hz bromo derivatives and 7.5 Hz in the case of chloro and iodo derivatives. Only singlets were obtained in the spectra of 2-halo-5-methyl-4-nitropyridines. This fact testifies to the lack of coupling protons 3 and 6 in the compounds mentioned above or the magnitude of splitting in this case comparable with a natural width of the line.

The Π -excessive and Π -deficient compounds can be described in terms of ρ^{13} (4).

$$\rho^{13} = \frac{\delta \text{ (ppm)}_{2\text{-halo-4-nitropicolines}} - \delta \text{ (ppm)}_{\text{pyridine}}}{\delta \text{ (ppm)}_{2\text{-halo-4-nitrotoluenes}} - \delta \text{ (ppm)}_{\text{benzene}}}$$

The dependence of ρ^{13} against γ_{NO_2} (2) of 2-halo-4-nitropicolines is linear.

References

1. Puszko A., Talik Z., Prace Naukowe A.E. Wrocław, 167/189, 178 (1980)
2. Puszko A., Prace Naukowe A.E. Wrocław, 278, 169 (1989)
3. Katritzky A.R., Lagowski J.M., Chemistry of Heterocyclic N-Oxides, Academic Press, London 1971
4. Poudler W.W., Janovic M.V., Org. Magn. Res. 19/4, 192/1982

TABLE 1 . Chemical shifts coupling constants and ρ^{19} of 2-halo-4-nitropicolines of protons.

No	Compound	Chemical shifts (δ ppm)				Coupling constants		ρ^{19}
		H-3	H-5	H-6	H-CH ₃	J _{3,5}	J _{5,6}	
1.	2-chloro-3-methyl-4-nitro-pyridine	-	7.70	8.60	2.69	-	7.5	0.34
2.	2-chloro-5-methyl-4-nitro-pyridine	7.60	-	8.10	2.55	-	-	0.23
3.	2-chloro-6-methyl-4-nitro-pyridine	8.60	7.35	-	2.60	3.5	-	1.29
4.	2-bromo-3-methyl-4-nitro-pyridine	-	7.75	8.95	2.63	-	5.5	0.33
5.	2-bromo-5-methyl-4-nitro-pyridine	8.55	-	8.65	2.58	-	-	1.13
6.	2-bromo-6-methyl-4-nitro-pyridine	8.65	7.95	-	2.63	2.0	-	1.14
7.	2-iodo-3-methyl-4-nitro-pyridine	-	7.75	8.65	2.68	-	7.5	0.42
8.	2-iodo-5-methyl-4-nitro-pyridine	8.65	-	9.00	2.57	-	-	1.05
9.	2-iodo-6-methyl-4-nitro-pyridine	8.80	7.65	-	2.6	3.5	-	1.89