

¹³C NMR OF TAUTOMERIC SYSTEM OF PICOLINE-2-THIOL-
AND PICOLINE-2,4-DITHIOL N-OXIDES

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The ¹³C NMR of pyridine N-oxides have been investigated by several scientists [1-6] who concentrated on monosubstituted derivatives of pyridine N-oxides. The examinations of ¹³C NMR of the subject compounds provided valuable information on their structure. Within extensive investigations on the reactivity of pyridine N-oxide derivatives performed in this laboratory [5-11], 2-thiol derivatives represent a considerable contribution.

Experimental

The ¹³C NMR spectra were recorded on Tesla BS 580 spectrometer at 25.142 MHz. Typical conditions were spectral width 7800 Hz, 8 K data points, pulse angle 90° (13 s) and repetition time 2 s. These conditions resulted in digital resolution of 1.22 Hz (i.e. 0.05 ppm). All spectra were proton decoupled. Samples were ca 10 % in CDCl₃, and the centres of the CDCl₃ peaks (77.11 ppm) were used as an internal reference. The assignments were carried out on the basis of previous literature [1-6], model studies, additivity rules, single resonance spectra and on the basis of comparison chemical shifts and coupling constant of protons of picoline N-oxides, 2-halo-4-nitropicoline N-oxides [11] and picoline-2,4-dithiol N-oxides (H5 - 8.95 ppm, H6 - 7.90 ppm, CH₃ - 2.65 ppm, OH - 13.1 ppm, J_{5,6} - 10 Hz- for 3-methylpyridine-2,4-dithiol N-oxide, H3 - 7.85 ppm, H6 - 8.20 ppm, CH₃ - 2.30 ppm, OH - 12.15 ppm - for

5-methylpyridine-2,4-dithiol N-oxide, H3 - 8.80 ppm, H5 - 7.80 ppm, CH₃ - 2.25 ppm, OH - 11.30 ppm, J_{3,5} - 5 Hz - for 5-methylpyridine-2,4-dithiol N-oxide).

The ¹³C NMR chemical shifts were calculated on the basis of additivity rules and the effects of substituents for picoline-2-thiol N-oxides (the chemical shifts for the picoline N-oxides carbons were taken from the literature [1], the substituent effect of 2-SH group was taken from the literature as the difference $\delta_{\text{Pyr-2-thion NOH}} - \delta_{\text{Pyr NO}}$ [25,26] and for picoline-2,4-dithiol N-oxides (the substituent effect of 2-SH group was used in the same way as for picoline 2-thiol N-oxide, but the effect of 4-SH group was estimated as: $\delta_{\text{Pyr-2-SH}} - \delta_{\text{Pyr}}$ [27,28]). (In the literature there is no ¹³C NMR data of pyridine-3-thiol N-oxide).

The picoline-2-thiol N-oxides and picoline-2,4-dithiol N-oxides used in the study were synthesized by the previously described methods [9,10].

The IR spectra recorded on a Specord IR 79 (Zeiss, Jena) spectrophotometer as nujol mulls.

The absorption of the titled compounds were recorded on a UV-VIS spectrometer, using a quartz cell of 0.097 cm thickness. Samples were approximately 10⁻⁴ mole/dm³ in ethanol.

Results and discussion

¹H NMR spectra of picoline-2,4-dithiol N-oxides were recorded in order to facilitate the assignments of the chemical shift of carbons of examined compounds. The spectra 3-picoline-2,4-dithiol N-oxide and 5-picoline-2,4-dithiol N-oxide were studied as being on AB and AX type respectively. Similarly to ¹H NMR of 2-halo-5-methyl-4-nitropicoline N-oxides [11] only singles were obtained in the spectra of 5-picoline-2,4-dithiol N-oxide. This fact testifies to the lack of splitting in this case comparable with a natural width of the line. The introducing of three substituents to pyridine N-oxide (the thiol group in position 2 and 4 and methyl group into position 3) causes the change of coupling constant J_{5,6} from 6.8 Hz [26] to 10 Hz according to the influence of electronegativity of

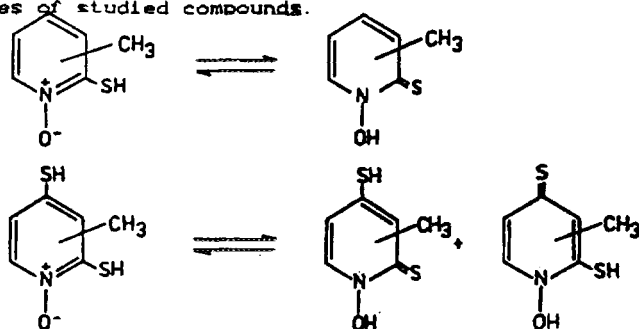
substituent on vicinal coupling constant. Conversion from picoline N-oxides [28] to picoline-2,4-dithiol N-oxides causes the greatest change of deshielding of the proton adjacent to the thiol group. The observed deshielding effect of two thiol groups oscillate from 0.8 to 1.6 ppm. The occurrence of the frequency signals at 11.3+13.1 ppm (OH) proves that picoline-2,4-dithiol N-oxides existance in the thione form. On comparison the carbon signals of the methyl groups in 3-picoline N-oxide [28] and 3-picoline-2,4-dithiol N-oxide it is clear that β -effect of two thiol groups has shifted this signal by about 0.4 ppm.

The transition from pyridine N-oxide to picoline N-oxide [1] provides the largest change in the "ipso" carbon resonance frequency according to the substantial paramagnetic effect specific to the methyl group. The "ipso" carbon deshielding in picoline N-oxides varies between 9.74 and 11.09 ppm. The chemical shifts of other carbons do not vary or undergo only very slight changes if they are in a close neighbourhood of a methyl group.

The great paramagnetic α effect the thiol group on carbon in position 2 (30.3 ppm) and in position 4 (50.4 ppm) in pyridine ring [27] undergoes the significant decrease on N-oxidation [25] (28.0 ppm and 14 ppm respectively). The introduction of the thiol group into position 2 of picoline N-oxide gives a deshielding effect at C-2 (27.21+28.87 ppm) according to a paramagnetic action of a thiol substituent on the "ipso" carbon.

At the transition from picoline N-oxides to picoline-2-thiol N-oxides, the chemical shifts of the methyl group carbons undergo slight changes (17.75+20.20 ppm \rightarrow 17.84+20.09 ppm). But the thiol group situated in ortho position to the methyl group in 3-methyl derivatives has the greatest influence. The introduction of the thiol group into position 4 to picoline-2-thiol N-oxides causes the largest change in the chemical shift of the "ipso" carbon, according to the paramagnetic effect characteristic for the thiol group (α effect). The value of the deshielding effect of the thiol group at C-4 in picoline-2,4-

dithiol N-oxides ranges from 21.01 + 28.70 ppm. The complete disagreement between the experimental and calculated chemical shift of carbons (if the effect of SH group was taken from benzene derivative [20]) points out on special interaction in molecules of studied compounds.



The good agreement between experimental and calculated chemical shift of C-2 and C-4 if the effect of 2- and 4-SH groups are calculated from the equations:

$$SCS_{2-SH} = (\delta_{\text{Pyr-2-thion NOH}} - \delta_{\text{Pyr NO}}) \quad [25,26]$$

$$SCS_{4-SH} = (\delta_{\text{Pyr-4-SH NO}} - \delta_{\text{Pyr NO}}) \quad [27,28]$$

prove the conclusion that 2-thiol group is responsible for creating the thione form not only in picoline-2-thiol N-oxides but also in picoline-2,4-dithiol N-oxides. Calculation of these effects by using an average value of substituent effect both 2- and 4-SH group from equation

$$SCS = 1/2 (\delta_{\text{Pyr-2-thion NOH}} - \delta_{\text{Pyr NO}} + \delta_{\text{Pyr-4-SH-NO}} - \delta_{\text{Pyr NO}}) + 1/2 (\delta_{\text{Pyr-2-SH NO}} - \delta_{\text{Pyr NO}} + \delta_{\text{Pyr-4-thion NOH}} - \delta_{\text{Pyr NO}})$$

[25,26,27] gives no agreement. The difference between the experimental chemical shifts and those calculated is a measure of inner interaction substituents with each other as well as their interaction with the ring. Bigger differences may also result from no taking into consideration of 4-thiol effect on all carbons except "ipso" carbon. These calculations do not take into consideration mutual interaction of the thiol group in position 2 with the thiol group in position 4 and the methyl group and N-oxide group.

The results of ^{13}C NMR spectra provide correct qualitative

predictions concerning the equilibrium compositions, but they cannot afford any quantitative information since the differences in the shifts of the corresponding carbon atoms in the model compounds are small.

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TABLE 1

¹³C NMR chemical shifts experimental and calculated /ppm/ /in parentheses/ and SCS of thiol group for picoline-2-thiol N-oxides and picoline-2,4-dithiol N-oxides

Compounds	C-2	C-3	C-4	C-5	C-6	C-CH ₃	Lit
3-methylpyridine N-oxide	139.23	137.59	126.82	126.92	136.57		/1/
3-methylpyridine- 2-thiol N-oxide	26.14	12.19	5.08	-12.50	-8.90	22.03	
	/28.20/	/4.8/	/7.20/	/-12.10/	/-5.40/		
4-methylpyridine N-oxide	139.40	128.00	136.79	128.40	139.10		/1/
4-methylpyridine- 2-thiol N-oxide	27.19	2.80	8.36	-11.86	-6.90	21.16	
5-methylpyridine N-oxide	138.23	127.48	126.82	138.29	139.23		/1/
5-methylpyridine- 2-thiol N-oxide	25.60	4.20	3.67	-14.18	-4.18	17.94	
6-methylpyridine N-oxide	139.52	125.07	124.30	127.98	149.14		/1/
6-methylpyridine- 2-thiol N-oxide	27.74	4.55	5.30	-13.58	16.59		

3-methylpyridine-	168.10	138.80	150.80	119.00	121.00	15.80
2,4-dithiol	27.74		23.98			
N-oxide	/28.2/		/22.2/			
5-methylpyridine-	165.54	131.58	147.83	124.31	124.30	17.34
2,4-dithiol	28.87		21.01			
N-oxide						
6-methylpyridine-	167.90	144.03	151.00	117.81	128.00	17.46
2,4-dithiol	27.21	18.99	26.70			
N-oxide						

The example of calculation of chemical shift for carbons for
3-methylpyridine-2,4-dithiol N-oxide

3-methylpyridine N-oxide	C-2	C-3	C-4	C-5	C-6
	139.23	137.59	126.82	126.02	136.57
SCS _{2-SH} /25/	28.20	4.80	7.20	-12.10	-5.40
SCS _{4-SH} /26/			15.00		

3-methylpyridine-2,4-di- thiol N-oxide	167.43	142.39	149.02	114.82	131.17