

THE INFLUENCE OF STERIC EFFECT OF ^{13}C NMR OF METHYLATED
DERIVATIVES OF 4-NITROPYRIDINE N-OXIDE

ANIELA PUSZKO, LUCYNA WASYLINA

Department of Organic Chemistry
Academy of Economics, PL - 53-342 Wrocław

^{13}C NMR spectra of 2-methyl-, 3-methyl-, 2,3-dimethyl-, 2,5-dimethyl-, 2,6-dimethyl-, 3,5-dimethyl-, and 2,3,6-trimethyl-4-nitropyridine N-oxide were recorded. The influence of electron properties of substituents in changes of chemical shifts was analyzed. It was found that "ortho-effect" of methyl group inhibits paramagnetism of nitro group. The ratio between a given substituted heterocyclic compound and its parent and the identically substituted benzene derivatives has been determined.

Substituent effect on reactivities and physical properties of substituted pyridine N-oxides or the related compounds have investigated by means of N-O stretching frequencies ^{13}C NMR, ^{17}O NMR [1-2].

In the physico-chemical research scheme, carried on in our Department on the reactivity of interesting class of compounds i.e. 2-halopicoline N-oxides their 4-halo- and 4-nitro derivatives, 2-halopyridinecarboxylic acid N-oxides, picoline-2-thiol N-oxides and picoline-2,4-dithiol N-oxides [3,4], 3-halo-2,6-dimethyl- and 3-halo-2,6-dimethyl-4-nitropyridine N-oxides it was purposefull to measure the spectra ^{13}C NMR. Spectra of methylated derivatives of 4-nitropyridine N-oxides, the more so as they can provide many interesting data about the structure these molecules and the influence of methyl group with the pyridine ring.

The present paper the effect of the substituents and their interaction on the changes of the back donation as well as chemical shifts in the compounds studied were investigated.



Experimental

The ^{13}C NMR were recorded on Tesla BS 589 A spectrometer at 25.142 MHz. Typical conditions were spectral width 7600 Hz, 8K data points, pulse angle 90 (13 s) and repetition time 2s. These conditions resulted digital.

All spectra were ca 10 % CDCl_3 as solvent and the centres of the CDCl_3 peaks (77.21 ppm) were used as an internal reference. The methyl derivatives of 4-nitropyridine N-oxide used in the study were synthesized by previously described methods.

The assignments were carried out on the basis of previous literature values [1-4], additivity rules, model studies, single resonance spectra and ^1H NMR. The ^{13}C NMR chemical shifts were calculated on the basis additivity rules, and the effects of substituents for studied compound (the chemical shifts for pyridine ring carbons were taken from literature [1] as were the substituents effects i.e. CH_3 [1,2] and NO_2 [1,2]). The assignments for the studied compounds were carried out on coupling constant of protons of these compounds. The calculated chemical shifts are compared with experimental data in Table 1.

Results and discussion

The transition from pyridine N-oxide to 4-nitropyridine N-oxide the largest change in the *ipso* carbon resonance frequency according to a substantial paramagnetic effect, specific to the nitro group. The *ipso* deshielding effect of nitro group in methylated derivatives of 4-nitropyridine N-oxide varies between 15.56 + 21.40 ppm (Table 1). The smallest paramagnetic effect of nitro group occurs in spectra of 2,6-di-methyl-4-nitropyridine N-oxide but the highest one appears in 3,5-dimethyl-4-nitropyridine N-oxide. The value of paramagnetic effect of nitro group in title compounds testifies the competitive withdrawing effect of electrons from 2-methyl and 6-methyl group by N-oxide group and from 3-methyl and 5-methyl by nitro group. The comparison of calculated chemical shifts with the experimental ^{13}C NMR spectral parameters of studied compounds shows a remarkable agreement. Bigger differences were found for the C-3 in 2,3-dimethyl-4-nitropyridine N-oxide, 3,5-

dimethyl-4-nitropyridine N-oxide and 2,3,6-trimethyl-4-nitropyridine N-oxide. The disagreement between the calculated and experimental shifts seems to reflect the strong electronegativity of the 4-nitro group, the substituent steric effect or the particular configurations of the substituents. The difference between the experimental chemical shifts and those calculated is the measure of inner interaction substituents with each other as well as their interaction.

These calculations do not take into consideration mutual interaction of a nitro group in position 4 with the methyl groups in various positions and N-oxide group. The presence of four substituents (three methyl groups and one nitro group) in molecule causes worse conformability of experimental chemical shifts with calculated ones in comparison to monosubstituted pyridine N-oxides. The π -excessive and π -deficient heterocyclic compounds can be described in terms .

$$\rho^{13} = \frac{\delta^{(\text{ppm})}_{\text{substituted pyridine N-oxide}} - \delta^{(\text{ppm})}_{\text{pyridine N-oxide}}}{\delta^{(\text{ppm})}_{\text{substituted benzene}} - \delta^{(\text{ppm})}_{\text{benzene}}}$$

The effect of substituents benzene derivatives were taken from literature. Based on the description, ρ^{13} should be less than 1 and π -deficient system and greater than 1 in π -excessive one. These results should be help to predict the susceptibility on nucleophilic substitution of studied compounds. The deficient system favours nucleophilic substitution. The methyls group inhibit this substitution due to steric and inductive effect. The steric hindrance occurring in 2,3-dimethyl-4-nitro- and 2,6-dimethyl-4-nitropyridine N-oxide disturb conjugations as nitro and N-oxide group with the ring as well.

References

1. Katrytzky A.R., Lagowski J.M., *Chemistry of Heterocyclic N-oxides*, Academic press, London 1971
2. Rusała D., Gawinecki R., *Bull.Soc.Chim.*, 128,201 (1991)
3. Puszko A., *Mag.Res.Chem.*, 30,271 (1992)
4. Puszko A., *Pol.J.Chem.*, 66,1979 (1992)

TABLE 1 ^{13}C NMR chemical shifts experimental and (calculated) of methyl derivatives of 4-nitropyridine N-oxide in CDCl_3

No	Compound	Chemical shifts (δ ppm)						
		C-2	C-3	C-4	C-5	C-6		
1	2-methyl-4-nitropyridine N-oxide	151.12 (151.03)	121.17 (123.38)	142.24 (142.1)	118.83 (120.27)	140.59 (141.42)	2-CH ₃	18.45
2	3-methyl-4-nitropyridine N-oxide	142.18 (141.13)	133.42 (133.69)	143.58 (144.02)	122.52 (122.35)	138.43 (138.47)	3-CH ₃	18.62
3	2,3-dimethyl-4-nitropyridine N-oxide	151.2 (150.86)	130.14 (134.47)	144.7 (143.22)	118.56 (120.19)	137.76 (138.59)	2-CH ₃ 3-CH ₃	14.66 16.22
4	2,5-dimethyl-4-nitropyridine N-oxide	148.58 (148.21)	122.29 (123.1)	143.13 (143.22)	130.36 (131.56)	142.08 (141.25)	2-CH ₃ 5-CH ₃	17.79 18.16
5	2,6-dimethyl-4-nitropyridine N-oxide	150.97 (151.16)	118.48 (121.25)	141.26 (141.3)	118.48 (121.25)	150.97 (151.16)	2-CH ₃ 6-CH ₃	18.98 18.98
6	3,5-dimethyl-4-nitropyridine N-oxide	139.32 (138.3)	129.92 (133.41)	147.1 (145.14)	129.92 (133.41)	139.32 (138.30)	3-CH ₃ 5-CH ₃	15.93 15.93
7	2,3,6-trimethyl-4-nitropyridine N-oxide	151.49 (150.98)	127.22 (132.34)	144.82 (142.42)	118.7 (120.97)	148.06 (148.32)	2-CH ₃ 3-CH ₃ 6-CH ₃	15.55 16.37 18.76