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THE IR SPECTRA OF 2-ALKYLAMINO- AND ALKYLNITRAMINO-3- OR 5-NITRO-4-METHYLPYRIDINE DERIVATIVES

IR spectra of some N-substituted 2-amino-3-nitro- and 2-amino-4-methyl-5-nitropyridines were measured and interpreted. Assignments and the influence of substituents on vibration of pyridine ring were established.

Keywords: N-substituted 2-amino-3-nitropyridines, N-substituted 2-amino-4-methyl-5-nitropyridines, IR spectra.

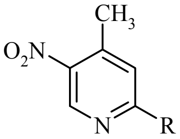
This paper is a part of our systematic spectroscopic investigations on alkylamino- and alkylnitramino-3- or 5-nitropicolines [1–4]. It is interesting how the presence of three substituents of different electronic properties influence spectra of studied compounds.

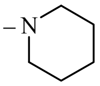
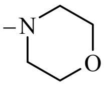
EXPERIMENTAL

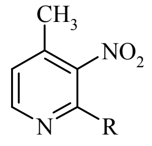
Syntheses of the investigated compounds have been described in previous publication [5]. The IR spectra were recorded on a Specord IR-80 (Zeiss, Jena) spectrophotometer as nujol mulls.

RESULTS AND DISCUSSION

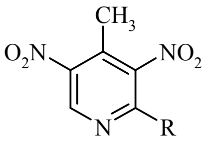
Infrared spectra of new synthesized pyridine derivatives **1–15** were obtained:



1–8 R= $-NHCH_3$, $-NHC_2H_5$, $-NHC_3H_7$, $-N(CH_3)_2$, , , $-NHPh$, $-NCH_3NO_2$



9–13 R = $-NHCH_3$, $-NHC_2H_5$, $-NHPh$, $-NCH_3NO_2$, $-NC_2H_5NO_2$



14, 15 R = $-NHCH_3$, $-NHC_2H_5$

From the spectra of 2-N-substituted derivatives of 2-amino-4-methyl-3(or 5)-nitropyridine there were separated bands corresponding to vibrations of pyridine ring, *i.e.* stretching vibrations of C–H, C–C, C–N, bending vibrations of C–H in plane (β-CH) and bending vibrations of C–H beyond the plane (γ-CH) and of substituents stretching (ν) and deformation (δ) vibrations of CH_3 group, stretching (ν) asymmetric and symmetric vibrations of NO_2 group, as well as stretching (ν) and deformation (δ) vibrations of NH group.

The data concerning studies of the IR spectra of pyridine [6], substituted pyridine derivatives [7–11] as well as trisubstituted benzene derivatives [12, 13] were used for the interpretation of the results (Tables 1–6).

In the spectral region of 3090–3010 cm^{-1} there was distinguished one weak band (with exception of compound **7**, Table 1) related to stretching vibrations of CH group in pyridine ring. On transition from compound **1** to **8** the position of this band shifted by about 20 cm^{-1} (Table 1).

Table 1

Frequencies of the stretching vibrations CH, CC, CN in pyridine ring for 2-substituted derivatives of 4-methyl-5-nitropyridine

No	Substituent (in position 2)	νCH cm^{-1}	νCC νCN cm^{-1}	νCC νCN cm^{-1}	νCC νCN cm^{-1}	νCC νCN cm^{-1}
1	NHMe	3090w	1610s	1560s	1450m	1437s
2	NHEt	3087w	1610s	1580s	1450s	1427m
3	NHPr	3090w	1610vs	1590vs	1450s	1425m
4	$N(Me)_2$	3060w	1610vs	1550s	1435m	1410m
5	NC_5H_{10}		1590vs	1510m	1475m	1440m
6	NC_4H_8O		1600vs		1490s	1440s
7	NHPh	3060w 3027w 3010w	1607s	1590s	1490s	1450s
8	$NMeNO_2$	3113m	1610s	1517m	1473m	1423w

Table 2

Frequencies of the stretching vibrations CH, CC, CN in pyridine ring for 2-substituted derivatives of 4-methyl-3-nitropyridine

No	Substituent	νCH cm^{-1}	νCC νCN cm^{-1}	νCC νCN cm^{-1}	νCC νCN cm^{-1}	νCC νCN cm^{-1}
9	NHMe	3040w	1590s	1563sh	1443s	1377sh
10	NHEt		1590vs	1563m	1447s	1380m
11	NHPh	3050w	1606s	1567s	1450m	1383m
12	$NMeNO_2$		1600s	1560sh	1430w	1400w
13	$NEtNO_2$	3077w	1600s	1543sh	1450m	1387sw
14	NHMe-5-NO_2		1610s	1550s	1460m	1387sh
15	NHEt-5-NO_2		1610s	1540s	1450sh	1380sh

In the region of 1610–1370 cm^{-1} (Table 1 and 2) there were distinguished four bands of different intensities (within the ranges 1610–1590, 1590–1510, 1490–1435 and 1450–1377 cm^{-1}), which correspond to stretching vibrations of C–C and C–N in pyridine ring. The first band is the strongest, its position shifting only slightly with change of the substituent. The second band is characterized by variable intensity, from high for compounds **1–4**, **7**, **11**, **14** and **15** to low for the other compounds examined. The position of the band shifts on transition of compound **1** (through **2**) to compound **3** (*i.e.* at growing length of alkyl chain). The position of the band under discussion also shifted (even markedly) at transition from alkylamine to alkylnitramine derivative (of compounds **1** and **8**). The third band of high or medium intensity is positioned similarly for most of the compounds examined; however, even here it gets shifted when passing from alkylamine to corresponding alkylnitramine derivatives of pyridine (compare *e.g.* compounds **9** and **12**). The intensity, and at the same time the frequency of this band is highest for compounds with piperidino, morpholino and phenylamino substituents (compounds **5**, **6** and **7**, respectively, Table 1).

The fourth of the bands under discussion is characterized by high intensity only for compounds **1**, **6** and **7** (Table 1), while for other ones this band has medium or weak intensity. The position of the band shifts with the length of chain or number of alkyl substituents (of compounds from **1** to **4**, Table 1), as well as (like in the former cases) on transition from alkylamine to corresponding alkylnitramine derivatives of appropriate nitropicoline.

In the spectral region of 1285–937 cm^{-1} there were distinguished bands corresponding to deformation vibrations of CH groups in and beyond the plane of pyridine ring (Table 3 and 4). Separated were four bands related to bending vibrations of CH groups in the plane, situated in the regions of 1297–1250, 1220–1210, 1160–1100 and 1040–1020 cm^{-1}. The most intensive band lies in the region of 1297–1250 and the weakest one in that of 1160–1100 cm^{-1}. Three bands situated in the region of 990–810 cm^{-1} are related to non-planar bending vibrations of CH groups of the ring (Table 3 and 4).

Table 3

Frequencies of the bending vibrations of CH in (β) and beyond the plane (γ) in pyridine ring for 2-substituted derivatives of 4-methyl-5-nitropyridine

No	Substituent	β-CH cm^{-1}	β-CH cm^{-1}	β-CH cm^{-1}	β-CH cm^{-1}	γ-CH cm^{-1}	γ-CH cm^{-1}	γ-CH cm^{-1}
1	NHMe	1260s	1200w	1160w	1020w	960w	940m	850m
2	NHEt	1250s	1200w	1150w	1030w	950w	930w	820w
3	NHPr	1250m	1200w	1140w	1020w	950m	910w	
4	$N(Me)_2$	1285s	1210sh	1130w	1020w	980w	880w	840m
5	NC_5H_{10}	1290s	1210sh	1100s	1025m	950w	840m	
6	NC_4H_8O	1290s	1210sh	1110s	1040m	960m	850m	825m
7	NHPh	1273m	1220sh	1110m	1030w	960m	843m	
8	$NMeNO_2$	1297s		1143w	1047m 1023m	980m 937m	840m	

Table 4

Frequencies of the bending vibrations of CH in (β) and beyond the plane (γ) in pyridine ring for 2-substituted derivatives of 4-methyl-3-nitropyridine

No	Substituent	β-CH cm^{-1}	β-CH cm^{-1}	β-CH cm^{-1}	β-CH cm^{-1}	γ-CH cm^{-1}	γ-CH cm^{-1}	β-CH cm^{-1}
9	NHMe	1257s	1150w	1100m	1063m	999w	870m	833m
10	NHEt	1247vs	1163w	1087w	1063w	990w	870m	860m
11	NHPh	1237m	1177m	1140sh	1063m	987w	867m	813m
12	NMeNO$_2$	1267s	1150w	1090w	1040w	990m	857m	850m
13	NEtNO$_2$	1263s	1160w	1087w	1040m	990w	875w	860m
14	NHMe-5-NO$_2$	1225w	1140w	1100w	1025w	970w	870w	830w
15	NHEt-5-NO$_2$	1225w	1130m	1070w	1025w 1040w	970w	870w	830w

The position of the bands shifts differently with change of substituent in the pyridine ring. The greatest shifts in position are observed on transition from compound **1** to compound **8** (Table 3).

Tables 5 and 6 present the frequencies of vibrations of substituents, *i.e.* groups CH$_3$, NO$_2$ and NH in the compounds examined. The band corresponding to stretching vibration of CH$_3$ group lies in the region of 2987–2927 cm^{-1} and is characterized by medium or weak intensity. Now, the deformation vibrations of that group, with frequency within the interval 1450–1370 cm^{-1}, are strong ones. The bands related to oscillations of nitro group at the ring lie in following regions: 1560–1540 and 1360–1325 cm^{-1} (Table 5) for compounds substituted in position 5 or 1560–1530 and 1360–1310 cm^{-1} (Table 6) for compounds substituted in position 3 with nitro group, as well as for 3,5-dinitroderivatives. The bands of NO$_2$ groups (ν_{as} and ν_s) for the first group of compounds (compounds **1**–**12**, Table 5 and 6) are the strongest ones in the spectrum; for other compounds they are of medium intensity.

In the regions of 3240–3217 and 3407–3300 cm^{-1} there lie singlet bands related to stretching vibrations of NH group of appropriate 2-substituted alkyl or phenylamine derivative of and 4-methyl-5(and 3)-nitropyridine (Table 5 and 6). The deformation vibrations are strong ones, their frequency lying within the interval 1610–1590 cm^{-1} (Table 5 and 6).

Table 5

Vibration frequencies of CH$_3$, NO$_2$ and NH groups for 2-substituted derivatives of 4-methyl-5-nitropyridine

No	Substituent	νCH$_3$ cm^{-1}	δCH$_3$ cm^{-1}	ν_{as} NO$_2$ cm^{-1}	ν_S NO$_2$ cm^{-1}	νNH cm^{-1}	δNH cm^{-1}
1	2	3	4	5	6	7	8
1	NHMe	2990m	1450m 1437m 1375m	1540s	1340s	3233s	1610s
2	NHEt	2977m 2863m	1450s 1427m 1380m 1373m	1540s	1343s	3217s	1610s
3	NHPr	2970m 2940m 2970w	1450s 1425m 1387sh 1377s	1530vs	1340vs	3240s	1610s

Table 5 (continued)

1	2	3	4	5	6	7	8
4	$N(Me)_2$	2940m 2990w	1435m 1410m 1370sh 1360sh	1550s	1330s		
5	NC_5H_{10}	2940m	1440m	1540s	1325s		
6	NC_4H_8O	2960w	1440m 1425sh 1375m 1365m	1540s	1340s		
7	NHPh	2979w	1450m 1393w	1560s	1337s	3237w	1607s
8	$NMeNO_2$	2930w	1423m 1390w	1550s	1360s		

Table 6

Vibration frequencies of CH_3, NO_2 and NH groups for 2-substituted derivatives of 4-methyl-3-nitropyridine

No	Substituent	νCH_3 cm^{-1}	δCH_3 cm^{-1}	$\nu_{as} NO_2$ cm^{-1}	$\nu_S NO_2$ cm^{-1}	νNH cm^{-1}	δNH cm^{-1}
9	NHMe	2987w 2927m	1443s 1413m 1317m	1563m	1363s	3400s	1590s
10	NHEt	2973m 2930m	1450s 1427m 1380m 1373m	1567m	1353s	3407s	1590s
11	NHPh	2970m 2940m 29870w	1450sh 1435sh 1387m 1377sh	1560s	1340s	3300w	1606s
12	$NMeNO_2$	2927w	1435m 1410m 1370sh 1360sh	1530s	1357s		
13	$NEtNO_2$	2980w 2940w	1450m 1387w	1527s	1363s		
14	$NHMe\text{-}5\text{-}NO_2$	2950w	1460m 1425m 1380m	1525s	1310s	3407s	1610s
15	$NHEt\text{-}5\text{-}NO_2$		100m 1450sh 1370sh	1525s	1310s	3390s	1610s

Gloss: s - strong, sh - shoulder, m - medium, w - weak, vs - very strong

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