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THE ^{13}C NMR, UV AND IR ABSORPTION SPECTRA OF PYRIDINEDICARBOXYLIC ACIDS

The ^{13}C NMR, UV and IR absorption spectra of 2,3- 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridinedicarboxylic acids were recorded and their spectral parameters were assigned. The influence of electronic properties of the substituents on the direction of the chemical shifts is discussed. The ultraviolet absorption spectra of the title compounds were recorded. The influence of substituents in molecule on λ_{max} and ϵ_{max} of spectral band are discussed. On the base of ^{13}C NMR, UV and IR absorption spectra it was found that there is a disturbance of mutual electronic interaction of substituents by a steric *ortho* effect. This effect is reflected in paramagnetism of the carboxyl group, value of correlation coefficient, deformation C—O stretching bands and decrease of intensity of CT band.

INTRODUCTION

In recent years, the ultraviolet absorption spectra of pyridine derivatives were investigated by various workers [1—5]. However the complex spectroscopic properties of carboxyl derivatives of pyridine were not studied in detail although these compounds are important in the fields of organic and biological chemistry [6]. Methyl pyridinecarboxylic esters and their derivatives are frequently used in indole alkaloid synthesis [7]. In addition, it has been reported [8] that pyridinecarboxylic acids accelerate the oxidation-reduction reaction between alcohols and chromic acid by factors up to 10^4 and form complexes with transition metals [9, 10].

In the literature there are data about effect of dipicolinic acid on the ultraviolet radiation resistance of *Bacillus cereus* Spores [11] and effect of oxygen on photo-metoxylation of dimethyl 2,4- and 3,4-pyridinedicarboxylate [12, 13].

Besides, the compounds studied are of interest for the study of interaction of carboxyl group with nitrogen atom of pyridine ring and the competition of both carboxyl substituents in withdrawing electrons from pyridine ring.

1. EXPERIMENTAL

The title compounds were synthesized by previously described methods [12].

The ^{13}C NMR were recorded with a Tesla BS 589 A Spectrometer at 25.142 MHz. Typical conditions were: spectral width 7600 Hz, 8 K data points, pulse angle 90° (13 s) and repetition time 2 s. These conditions resulted in digital resolution of 21.22 Hz (i. e., 0.005 ppm). All spectra were proton decoupled, samples were ca 10% in DMSO or CDCl_3 . The assignments were carried out on the bases of previous literature values [14, 15], additivity rules, model studies, and single resonance spectra. The ^{13}C NMR chemical shifts were calculated on the bases of additivity rules and the effects of substituent for pyridinedicarboxylic acids (the chemical shifts for the ring carbons of pyridine [14] and the effect of carboxyl group [15] were taken from literature). The calculated shifts are compared with the experimental data in Table 2. The IR spectra were recorded on Specord IR 80 in KBr. The UV spectra of 0.1 n solutions in ethanol were recorded by means of a specord UV-vis spectrophotometer equipped with a thermostated cell compartment, keeping temperature at 25°C and a quartz cell of 0.097 cm thickness.

Table 1

Ultraviolet absorption spectra of pyridinedicarboxylic acids

Compound	Wavelength [nm]			Molar extinction coefficient		
2,3-Pyridinedicarboxylic acid	197	217	265	22192	18991	2713
2,4-Pyridinedicarboxylic acid	197	217	270	31340	13278	11546
2,5-Pyridinedicarboxylic acid	196	222	278	34893	5948	3767
2,6-Pyridinedicarboxylic acid	199	222	270	36315	9737	3553
3,4-Pyridinedicarboxylic acid	198	223	270	18125	5312	2187
3,5-Pyridinedicarboxylic acid	199	217	269	32805	5065	1854

2. RESULTS AND DISCUSSION

In order to obtain the knowledge on the effect on electron withdrawing substituents, the mutual interaction between two carboxyl groups situated at various positions in pyridine ring, the ultraviolet spectra of isomeric disubstituted pyridinedicarboxylic derivatives in ethanol were measured.

The absorption at about 257 nm of pyridine in methanol shifts to longer wavelength by the introduction of two carboxyl groups to pyridine nucleus [6]. This effect is regarded as mainly due to the electron migration effect from the pyridine ring to the carboxyl group. Pyridinemonocarboxylic acids absorb at the

Table 2

¹³C NMR chemical shifts δ experimental and [(calculated)*]^{#2} of pyridinedicarboxylic acids and some esters in DMSO

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C ^{COOH} or C ^{COOCH3}	OCH ₃
2,3-Pyridine-dicarboxylic acid	151.52 (153.80) [149.20]	124.82 (127.50) [124.00]	137.81 (137.50) [138.30]	125.67 (129.00) [127.20]	152.38 (155.30) [153.60]	167.82 166.44	
2,4-Pyridine-dicarboxylic acid	148.11 (152.30) [148.90]	125.52 (126.90) [120.80]	139.20 (138.10) [138.60]	128.79 (130.50) [126.70]	148.11 (150.20) [148.80]	158.05 158.05	
2,5-Pyridine-dicarboxylic acid	150.70 (157.40) [151.70]	123.46 (125.40) [121.30]	125.92 (137.50) [138.30]	139.55 (143.60) [129.90]	149.60 (151.70) [151.10]	165.63 165.53	
2,6-Pyridine-dicarboxylic acid	148.17 (152.30) [148.10]	127.54 (130.90) [124.90]	139.29 (136.06) [138.30]	127.54 (130.50) [124.90]	148.17 (152.30) [148.10]	165.51	
3,4-Pyridine-dicarboxylic acid	149.76 (156.80) [151.90]	121.71 (126.00) [125.80]	141.48 (139.00) [138.60]	125.72 (127.00) [123.10]	152.46 (156.80) [153.40]	167.65 166.54	
3,5-Pyridine-dicarboxylic acid	153.24 (156.80) [154.70]	126.72 (126.00) [126.30]	137.09 (139.00) [138.30]	126.72 (126.00) [126.30]	153.24 (156.80) [154.70]	165.56	
Dimethyl 2,5-pyridine-dicarboxylate	150.86 (156.30)	124.70 (124.70)	138.34 (136.80)	128.64 (130.00)	150.76 (151.00)	164.92 164.5	53.21 52.77
Dimethyl 2,6-pyridine-dicarboxylate	148.26 (151.80)	128.06 (129.20)	138.42 (135.60)	128.06 (129.20)	148.26 (151.8)	165.07	53.20

* The effects of substituents calculated from benzene derivatives [15].

#2 The effects of substituents calculated from pyridine derivatives [14].

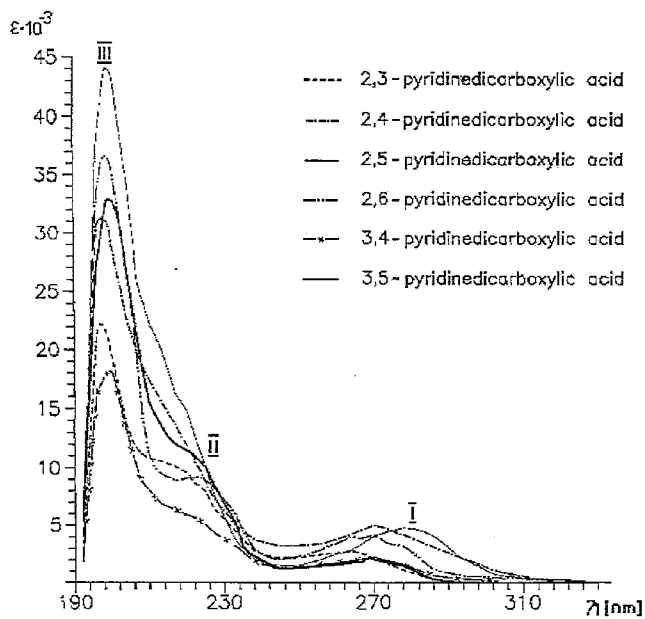


Fig. 1. Absorption spectra of pyridinedicarboxylic acids

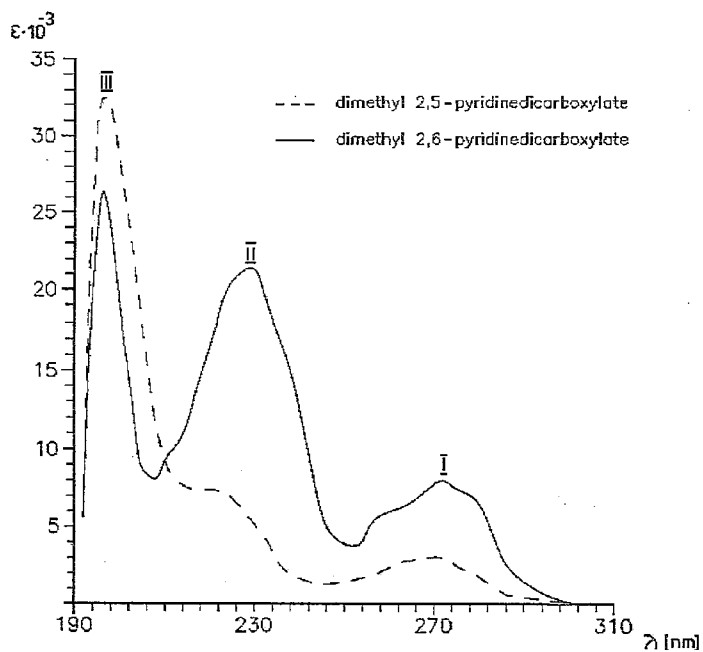
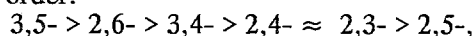


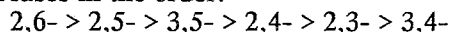
Fig. 2. Absorption spectra of dimethyl pyridinedicarboxylates

shorter wavelength than benzoic acid does, because the electron attracting power of nitrogen atom of pyridine nucleus competes with those of carboxyl groups. The pyridinedicarboxylic acids absorb at longer wavelength (196...198 nm, 217...224 nm, 265...278 nm) than monocarboxylic acids [6] (262...271 nm) (Table 1, Fig.1). The competitive resonance interaction between the nitrogen atom and the carboxyl group is the greatest in 2,5-pyridinedicarboxylic acid. In this molecule resonance occurs not only between nitrogen atom and carboxyl groups but between both carboxyl groups, which are situated in *para* position one to another in pyridine ring. This fact can be explained by complementary effect of substituents and the enlargement of conjugated system.

Among studied compounds 2,3- and 3,4-pyridinedicarboxylic acid shows the smallest intensity, which can be explained by the steric interaction between both vicinal carboxyl groups. As seen from the Table 1 the maximum wavelength of band III lies in the order:

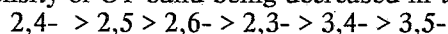


but the intensity decreases in the order:



Spectra of all compounds exhibit their characteristic bands in the region 196...278 nm.

The band I in the longest wavelength contributes a large share of an electron transition from the highest occupied MO and brings about a large charge transfer from carboxyl group situated in various position of pyridine ring in studied compounds to 2-carboxyl group via the pyridine nucleus, i. e., charge transfer (CT) band. The intensity of CT band being decreased in the following order:



As is mentioned previously, a partial disorder of the conjugation effect of the carboxyl group is a result of the mutual electrostatic as well as steric interaction between the *ortho* carboxyl groups.

The spectra in the region 190...240 nm are characterized by two bands; band III occurs in the region (190...220 nm) and is characterized by much better resolved structure than band II (220...240 nm). These bands are due to $\pi^* \leftarrow \pi$ transition of the aromatic pyridine ring or $\pi_{CO} \leftarrow \pi_{ring}$ transition and are common to $\pi^* \leftarrow \pi$ band of aromatic compounds in which C=O and C=C groups form a conjugated system.

The spectra of dimethyl 2,6- and 2,5-pyridinedicarboxylate are characterized by regular three band structure and are shifted (in respect to their carboxylic derivatives) to longer wavelength due to +M mesomeric effect of methyl group (Fig. 2).

The transition from pyridine to pyridinedicarboxylic acids is reflected in the largest charge in the *ipso* carbon resonance frequency according to a substantial paramagnetic effect, specific to carboxyl group. The *ipso* deshielding effect of the carboxyl group in studied compounds varies between $\delta = 158.05$ ppm and $\delta = 167.65$ ppm (Table 2). The smallest paramagnetic effect on the carboxyl group occurs in the spectra of 2,4-pyridinedicarboxylic acid but the highest one appears in 3,4-pyridinedicarboxylic acid.

The quantity value of paramagnetic effect of the carboxyl group in title compounds testifies the withdrawing effect of electrons from the 2-carboxyl and 6-carboxyl group by the nitrogen of pyridine ring.

The comparison of calculated chemical shifts with experimental ones of studied compounds shows a remarkable agreement.

Greater differences were found for atoms C₍₂₎ and C₍₄₎ in 3,5-, 2,5- and C₍₃₎ and C₍₅₎ in 2,3- and 3,4-pyridinedicarboxylic acids. The correlation of experimental shifts and the calculated ones obtained by addition of the benzene substituent increments [15] shows a large steric effect for C₍₃₎ in the molecule of 2,3- and 3,4-pyridinedicarboxylic acids ($r = 0.652$ for carbons in position 2, Table 3, Fig. 3).

Table 3

Correlation coefficient for *ipso* carbon atom (C₍₂₎)
(number of points — 6)

Correlation	<i>r</i>	<i>S</i>
$\delta_{\text{exp}C(2)} = 0.55 \delta_{\text{calc}C(2)}^* + 65.38$	0.652	1.691
$\delta_{\text{exp}C(2)} = 0.63 \delta_{\text{calc}C(2)}^{*2} + 56.01$	0.776	1.406

* The effects of substituents calculated from benzene derivatives [15].

*2 The effects of substituents calculated from pyridine derivatives [14].

Table 4

Correlation coefficient for all carbons of studied pyridinedicarboxylic acids
(number of points — 30)

Correlation	<i>r</i>	<i>S</i>
$\delta_{\text{exp}} = 0.91 \delta_{\text{calc}}^* + 10.66$	0.970	2.785
$\delta_{\text{exp}} = 0.90 \delta_{\text{calc}}^{*2} + 14.35$	0.957	3.325

* The effects of substituents calculated from benzene derivatives [15].

*2 The effects of substituents calculated from pyridine derivatives [14].

Better concordance is obtained by addition of the pyridine substituent increments [14] ($r = 0.776$ for carbon in position 2, Table 3, Fig. 4). This poor correlation can be explained by adjacent position of 2-carboxyl group to nitrogen of pyridine ring and mutual interaction with second carboxyl groups. If one takes into consideration all carbons of all studied compounds ($n = 30$, Table 4), then the correlation coefficient increases to 0.957...0.970. The best correlation is obtained for 3,5- and 2,6-pyridinedicarboxylic acid ($r = 0.999$ and $r = 1.000$, respectively, Table 5).

Table 5

Correlation coefficient for carbons in different position
for studied compounds (number of points — 5)

Compound	Correlation	<i>r</i>	<i>S</i>
2,3-Pyridinedicarboxylic acid	$\delta_{\text{exp}} = 1.00 \delta_{\text{calc}}^* - 2.17$	0.994	1.666
	$\delta_{\text{exp}} = 1.02 \delta_{\text{calc}}^{*2} - 2.44$	0.993	1.818
2,4-Pyridinedicarboxylic acid	$\delta_{\text{exp}} = 0.92 \delta_{\text{calc}}^* + 10.14$	0.988	1.877
	$\delta_{\text{exp}} = 0.83 \delta_{\text{calc}}^{*2} + 24.93$	0.988	0.690
2,5-Pyridinedicarboxylic acid	$\delta_{\text{exp}} = 0.97 \delta_{\text{calc}}^* - 1.56$	0.950	4.621
	$\delta_{\text{exp}} = 0.79 \delta_{\text{calc}}^{*2} + 28.91$	0.815	8.572
2,6-Pyridinedicarboxylic acid	$\delta_{\text{exp}} = 0.90 \delta_{\text{calc}}^* + 12.32$	0.960	3.344
	$\delta_{\text{exp}} = 0.89 \delta_{\text{calc}}^{*2} + 16.50$	1.000	0.853
3,4-Pyridinedicarboxylic acid	$\delta_{\text{exp}} = 0.89 \delta_{\text{calc}}^* + 12.49$	0.973	3.730
	$\delta_{\text{exp}} = 0.96 \delta_{\text{calc}}^{*2} + 4.98$	0.977	3.446
3,5-Pyridinedicarboxylic acid	$\delta_{\text{exp}} = 0.86 \delta_{\text{calc}}^* + 17.83$	1.000	0.424
	$\delta_{\text{exp}} = 0.92 \delta_{\text{calc}}^{*2} + 10.69$	0.999	0.520
Dimethyl 2,5-pyridinedicarboxylate	$\delta_{\text{exp}} = 0.89 \delta_{\text{calc}}^* + 14.96$	0.984	2.461
Dimethyl 2,6-pyridinedicarboxylate	$\delta_{\text{exp}} = 0.86 \delta_{\text{calc}}^* + 18.30$	0.979	2.352

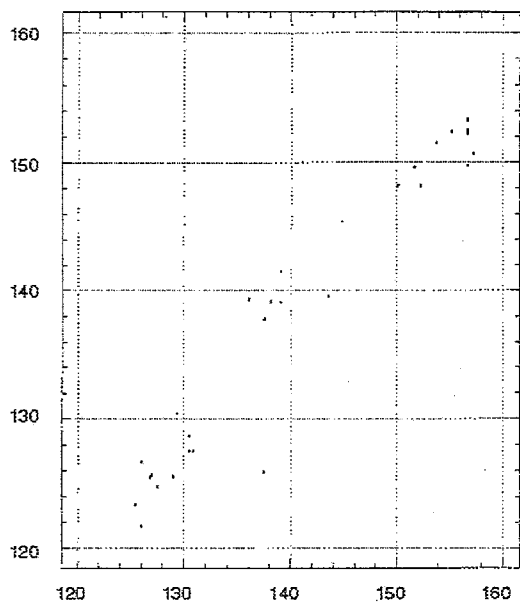


Fig. 3. Plot of experimental chemical shift data vs calculated chemical shift.
The effects of substituents were taken from benzene derivatives [15]

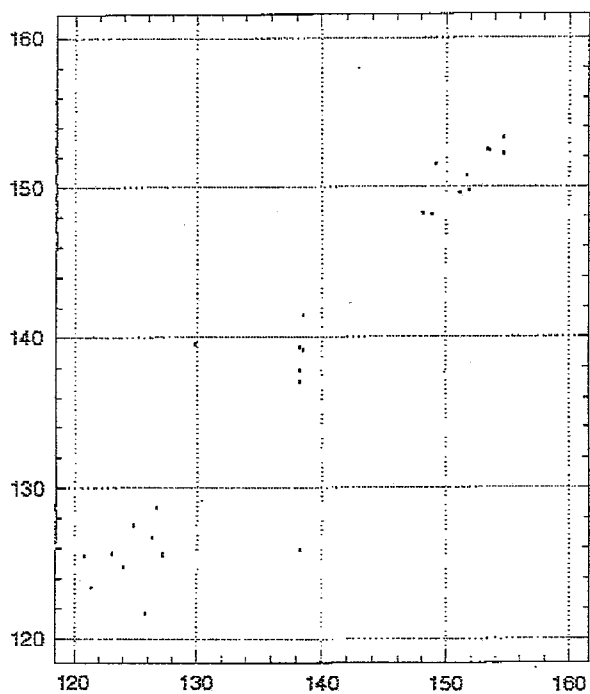


Fig. 4. Plot of experimental chemical shift data vs calculated chemical shift.
The effects of substituents were taken from pyridine derivatives [14]

Table 6

IR spectra of pyridinedicarboxylic acids in KBr

Compound	IR*, cm ⁻¹ (KBr)	Assignment	IR*, cm ⁻¹ (KBr)	Assignment	
1	2	3	4	5	
2,3-Pyridine-dicarboxylic acid	3450 br	ν NH	1060...1000 br	γ OH	
	3110	γ OH	850		
	1610 s	ν CO	790 d	ν ring	
	1580 s	ν OH ν ring	770		
	1480 s		680m		
	1430 s		660 m		
	1420 s	δ OH	620 m		
	1310 s		600 s		
	1280 m	ν CO	570 m		
	1240 m		460 m		
	1170 s		440 w		
	1140 s		420 w		
	2,4-Pyridine-dicarboxylic acid	3490	ν NH	1080 m	
		2920 br	γ OH	1000 m	
2420...2520 br		γ OH	890 w		
2100...1900 br			850 w		
1730 s		ν CO	760 s		
1590 m		ν ring	700 s	ν ring	
1550 w			650 m		
1500 m			570 w		
1390 m			530 w		
1310 s			500 m		
1270 s		ν CO	420 w		
1180 m			440 w		
2,5-Pyridine-dicarboxylic acid		3580		1400	
		3510 br		1260...1130 br	ν CO γ OH
	3080 d m		980 m		
	3105		890 d		
	2620 br		870		
	2170 m		810 m	ν ring	
	2080 w		770 s		
	1730		700 d s		
	1770 br s	ν CO	680		
	1790		570 m		
	1610 s	γ OH ν ring	520 s		
	1420 m		500		
	1470 m		420 s		
	2,6-Pyridine-dicarboxylic acid	3450 br	ν NH	1270 s	ν CO
3080		γ OH	1180	γ OH	
2820...3080 br		γ OH	1170 d w		
2550			1080 w		
2640			1000		
1690			950...920 br	γ OH	
1710 d s		ν CO	860 w		
1580		γ OH ν ring	760 m	ν ring	
1460			705 m		
1470 d m		δ OH	650 m		
1420 m			520 w		
1340 m			580 w		
1300 m					

Table 6 (ending)

1	2	3	4	5	
3,4-Pyridine-dicarboxylic acid	3450 br	ν NH	1250 s	ν CO	
	3080 d m	γ OH	1040 m		
	3090		990 m	ν ring	
	2900 m	γ OH	940 s		
	1720 s	ν CO	880 m	ν ring	
	1640 s		760 m		
	1600 s	ν ring	725 m		
	1520 w		660 m		
	1480 w		575 m		
	1370...1340 br		440 m		
	3,5-Pyridine-dicarboxylic acid	3450 br	ν NH	1270 m	
		3100 m	γ OH	1220 s	ν CO
		2600...2300 br		1160 s	
1730 s		ν CO	1150 m		
1630 m		ν ring	1060 m		
1690 m		ν ring	950 m		
1590 m			760 s	ν ring	
1470 w			690 s		
1430 w			550 m		
1390 w			480 m		
Dimethyl 2,5-pyridine-dicarboxylate		3420 br	γ NH	1200 m	ν CH
		3110 w	γ OH	1140 s	ν CH
		3210 w		1025 s	γ OH
	2970 m		960 s		
	2860 w		880 m	ν ring	
	1720 s	ν CO	825 m		
	1600 m	ν ring	750 s		
	1480 m		700 m		
	1440 s	δ OH	640 m		
	1390 s		500 m		
	1290		460 w		
	1250 d s	ν CO	430 m		
	Dimethyl 2,6-pyridine-dicarboxylate	3460 br	γ NH	1080 s	δ OH
3070 m		γ OH	1000 s		
2980 m			960 m		
1750 s		ν CO	855 m		
1575 s			815		
1455			760 s		
1440 d s		ν ring δ OH	730 s	ν ring	
1300 s			700 s		
1250 s		ν CO	650 m		
1200 m			570 w		
1170 s			465 m		
1150 s			440 m		

* s — strong, br — broad, w — weak.

The disagreement between the calculated and experimental chemical shifts seems to reflect the strong electronegativity of carboxyl group or the particular configuration of the substituent. The difference between the experimental chemical shifts and the calculated ones is a measure of interaction of substituents because these calculations do not take into consideration mutual interaction of carboxyl group with each others and pyridine ring.

The magnitude of steric effect was evaluated on the basis of ν CO in IR Spectra of pyridinedicarboxylic acids. Characteristic bands IR Spectra are collected in Table 6.

The frequency vibration ν NH in *para* substituted pyridinedicarboxylic acids (3580 cm^{-1} for 2,5-pyridinedicarboxylic acid and 3420 cm^{-1} for its dimethyl ester) is in accordance with stronger electron acceptoring property of 2-carboxyl group in relation to 5-carboxyl group. This fact can be qualitatively explained by assumption that the carboxyl group changes the basicity of the adjacent nitrogen heteroatom. These interaction is reflected in ν CO band; in this band one can distinguish three signals (at 1790, 1770 cm^{-1} and 1730 cm^{-1}). The IR spectra of pyridinedicarboxylic acids about symmetrical structure e. g., 2,6- and 3,5-pyridinedicarboxylic acids are characterized by sharp single signals about great intensity.

The influence of nitrogen heteroatom on frequency stretching vibration ν CO is the highest in 2,6- and the smallest in 3,5-pyridinedicarboxylic acids, what is accordance with expectations.

The IR spectra of *ortho* disubstituted carboxylic acids of pyridine are characterized by broad bands ν C=O, which are shifted to lower frequency in comparison to others studied compounds. This fact can be explained by closed position of electronic pairs and competition in withdrawing electrons from pyridine ring by both carboxyl groups. In this case the major role is played by the steric effects.

It is known, that two electron-withdrawing substituents located in *para* position of aromatic ring cause reversal interaction with the ring e. g., inhibites its impoverishing in electrons.

The spectra of 2,3- and 3,4-pyridinedicarboxylic acid contains broad band for ν CO (at 1610, 1280 cm^{-1} and 1720, 1250 cm^{-1} , respectively), which is attributed to the mutual interaction between both carboxyl group and their interaction with nitrogen atom of pyridine ring.

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