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

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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 influence of substituents in the molecule on λ_{max} and ε_{max} of the UV-spectral band is disscused. Analizing ^{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, the value of the correlation coefficient, deformation C—O stretching bands, and the decrease in the intensity of the CT band.

INTRODUCTION

In recent years, the ultraviolet absorption spectra of pyridine derivatives were investigated by various scientists [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 [61]. Methyl pyridinecarboxylic acid 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 transitions metals [9, 10].

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

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

EXPERIMENTAL

The title compounds were synthesized by previously described methods [12]. The ^{13}C NMR spectra were recorded on 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 based on previous literature values [14, 15], additivity rules, model studies, and single resonance spectra. The chemical shifts in ^{13}C NMR spectra were calculated based on additivity rules and the effects of substituent for pyridinedicarboxylic acids (the chemical shifts for the ring carbon atoms of pyridine [14]

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and the effect of carboxyl group [15] were taken from the 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 the temperature at 25°C and using a quartz cell of 0.097 cm thickness.

RESULTS AND DISCUSSION

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

TABLE 1. Ultraviolet Absorption Spectral Characteristics 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

TABLE 2. ^{13}C 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_{COOCH_3}	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-dicarboxyiic 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-dicarboxyiic 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].

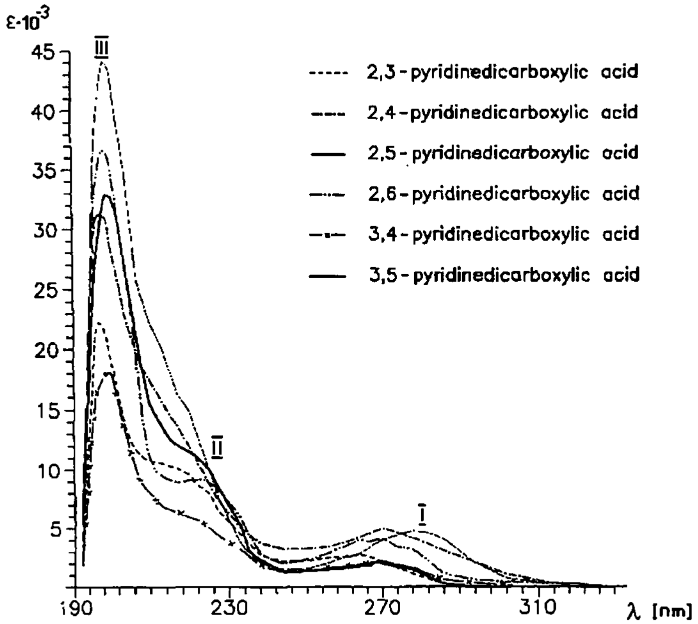

Fig. 1. Absorption spectra of pyridinedicarboxylic asids.

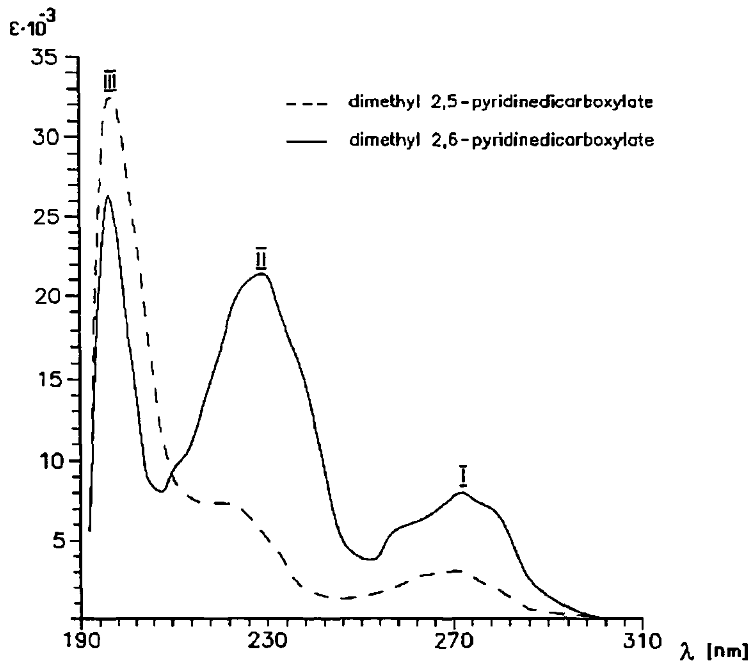

Fig. 2. Absorption spectra of dimethyl pyridinedicarboxylates.

Absorption band of pyridine in methanol at about 257 nm shifts to longer wavelengths at introduction of two carboxyl groups to the 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 a shorter wavelength than benzoic acid, because the electron attracting power of the nitrogen atom of the pyridine nucleus competes with that of carboxyl groups. 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 the pyridine ring. This fact can be explained by the complementary effect of substituents and the enlargement of conjugated system.

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

$$3,5- > 2,6- > 3,4- > 2,4- \approx 2,3- > 2,5-,$$

but the intensity decreases in the order:

$$2,6- > 2,5- > 3,5- > 2,4- > 2,3- > 3,4-$$

The spectra of all compounds exhibit characteristic bands in the region of 196-278 nm.

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

$$2,4- > 2,5 > 2,6- > 2,3- > 3,4- > 3,5-$$

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

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

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 of carboxyl group. The *ipso* deshielding effect of the carboxyl group in the 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 spectrum of 2,4-pyridinedicarboxylic acid, but the highest one appears in spetrum of 3,4-pyridinedicarboxylic acid.

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

Comparison of the calculated chemical shifts with the experimental ones of the 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. A 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 carbon atoms in position 2, Table 3, Fig. 3).

Better concordance is obtained by addition of the pyridine substituent increments [14] ($r = 0.776$ for carbon atom in position 2, Table 3, Fig. 4). This poor correlation can be explained by the adjacent position of the 2-carboxyl group to the nitrogen atom of the pyridine ring and the mutual interaction with the second carboxyl groups. If one takes into consideration all the carbon atoms of all the 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 3. Correlation Coefficient for *ipso* Carbon Atom ($C_{(2)}$) (Number of Points — 6).

Correlation	*r*	s
$\delta_{expC(2)} = 0{,}55\ \delta^{*}_{calcC(2)} + 65{,}38$	0,652	1,691
$\delta_{expC(2)} = 0{,}63\ \delta^{*2}_{calcC(2)} + 56{,}01$	0,776	1,406

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* 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 Carbon Atoms of Studied Pyridinedicarhoxylic Acids (Number of Points — 30).

Correlation	*r*	s
$\delta_{exp} = 0{,}91\ \delta^{*}_{calc} + 10{,}66$	0,970	2,785
$\delta_{exp} = 0{,}90\ \delta^{*2}_{calc} + 14{,}35$	0,957	3,325

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

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

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

The magnitude of the steric effect was evaluated on the basis of ν_{CO} in IR spectra of pyridinedicarboxylic acids. The characteristic bands of the IR spectra are shown in Table 6.

TABLE 5. Correlation Coefficient for Carbon Atoms in Different Positions for the Studied Compounds (Number of Points — 5).

Compound	Correlation	*r*	s
2,3-Pyridinedicarboxylic acid	$\delta_{exp} = 1{,}00\ \delta^{*}_{calc} + 2{,}17$	0,994	1,666
	$\delta_{exp} = 1{,}02\ \delta^{*2}_{calc} + 2{,}44$	0,993	1,818
2,4-Pyridinedicarboxylic acid	$\delta_{exp} = 0{,}92\ \delta^{*}_{calc} + 10{,}14$	0,988	1,877
	$\delta_{exp} = 0{,}83\ \delta^{*2}_{calc} + 24{,}93$	0,988	0,690
2,5-Pyridinedicarboxyiic acid	$\delta_{exp} = 0{,}97\ \delta^{*}_{calc} + 1{,}56$	0,950	4,621
	$\delta_{exp} = 0{,}79\ \delta^{*2}_{calc} + 28{,}91$	0,815	8,572
2,6-Pyridinedicarboxylic acid	$\delta_{exp} = 0{,}90\ \delta^{*}_{calc} + 12{,}32$	0,960	3,344
	$\delta_{exp} = 0{,}89\ \delta^{*2}_{calc} + 16{,}50$	1,000	0,853
3,4-Pyridinedicarboxylic acid	$\delta_{exp} = 0{,}89\ \delta^{*}_{calc} + 12{,}49$	0,973	3,730
	$\delta_{exp} = 0{,}96\ \delta^{*2}_{calc} + 4{,}98$	0,977	3,446
3,5-Pyridinedicarboxyiic acid	$\delta_{exp} = 0{,}86\ \delta^{*}_{calc} + 17{,}83$	1,000	0,424
	$\delta_{exp} = 0{,}92\ \delta^{*2}_{calc} + 10{,}69$	0,999	0,520
Dimethyl 2,5-pyridinedicarboxylate	$\delta_{exp} = 0{,}89\ \delta^{*}_{calc} + 14{,}96$	0,984	2,461
Dimethyl 2,6-pyridinedicarboxylate	$\delta_{exp} = 0{,}86\ \delta^{*}_{calc} + 18{,}30$	0,979	2,352

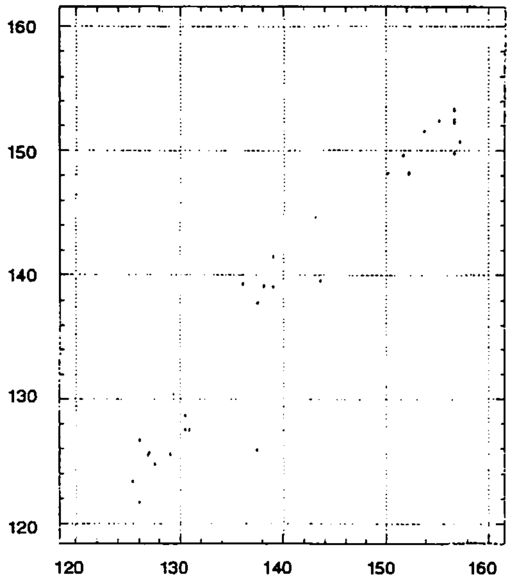

Fig. 3. Plot of experimental chemical shift data *vs* calculated chemical shift. The effects of substituents were taken from benzene derivatives [15].

The frequency of 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 the stronger electron acceptor activity of the 2-carboxyl group in relation to the 5-carboxyl group. This fact can be qualitatively explained by the assumption that the carboxyl group changes the basicity of the adjacent nitrogen heteroatom. This interaction is reflected in the 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 with symmetrical structure e.g., 2,6- and 3,5-pyridinedicarboxylic acids, are characterized by sharp single signals with great intensity.

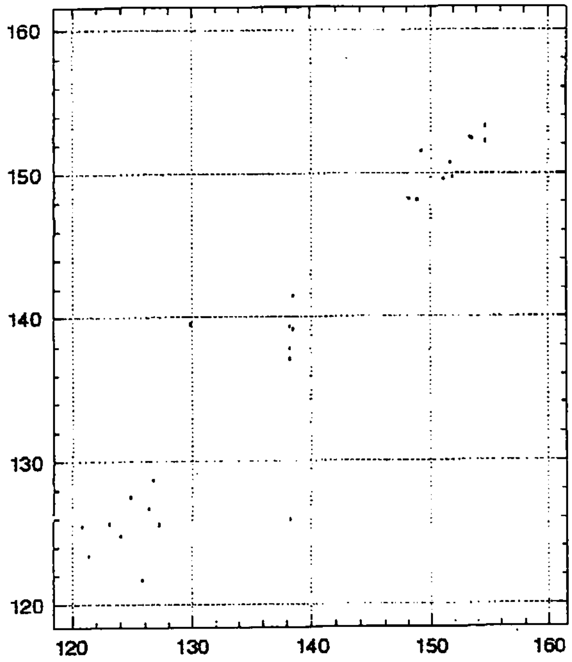

Fig. 4. Plot of experimental chemical shift data *vs* calculated chemical shift. The effects of substituents were taken from pyridine derivatives [14].

TABLE 6. IR Spectral Characteristics of Pyridinedicarboxylic Acids in KBr.

Compound	IR*, cm^{-1} (KBr)	Assignment	IR*, cm^{-1} (KBr)	Assignment
1	2	3	4	5
2,3-Pyridinedicarboxylic 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		680 m	
	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-Pyridinedicarboxylic 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-Pyridinedicarboxylic 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 br. s	ν_{CO}	700 ds	
	1770 br. s	ν_{CO}	680	
	1790 br. s	ν_{CO}	570 m	
	1610 s	γ_{OH} ν_{ring}	520 s	
	1420 m		500	
	1470 m		420 s	
2,6-Pyridinedicarboxylic acid	3450 br	ν_{NH}	1270 s	ν_{CO}
	3080	γ_{OH}	1180 d w	γ_{OH}
	2820...3080 br	γ_{OH}	1170 d w	γ_{OH}
	2550		1080 w	
	2640		1000	
	1690 d s	ν_{CO}	950... 920 br	γ_{OH}
	1710 d s	ν_{CO}	860 w	
	1580	γ_{OH} ν_{ring}	760 m	ν_{ring}
	1460 d m	δ_{OH}	705 m	
	1470 d m	δ_{OH}	650 m	
	1420 m		520 w	
	1340 m		580 w	
	1300 m			
3,4-Pyridinedicarboxylic 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	

TABLE 6 (continued)

1	2	3	4	5
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}
	2970m		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 d s	ν_{CO}	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 d s	ν_{ring} δ_{OH}	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	

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* s — strong, br — broad, w — weak.

The influence of the nitrogen heteroatom on the frequency of stretching vibration ν_{CO} is the highest in 2,6- and the smallest in 3,5-pyridincdicarboxylic acids, which is in accordance with expectations.

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

It is known that the two electron-withdrawing substituents located in the *para* position of the aromatic ring cause a reverse interaction with the ring e.g., inhibits its impoverishment in electrons.

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

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