

CORRELATION OF SOME INFRARED SPECTRA REGIONS WITH THE STRUCTURE OF A SUBSTITUTED PYRIDINE RING SYSTEM

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The infrared spectra of a numerous series of pyridine homologues indicate that two regions are suitable for the correlation of the spectrum with the structure of the substituted ring: the band positions in the $900-700\text{ cm}^{-1}$ region can be employed with a high probability for the localization of the number and positions of the adjacent and isolated ring hydrogen atoms, the region $1650-1400\text{ cm}^{-1}$ can be utilized for the determination of the alkyl substituent positions based on the resemblance of the spectrum to that of the corresponding pyridine methyl homologue. The high number of the pyridine alkyl homologues examined made it possible to refine the wavenumber ranges characterizing the pyridine substitution pattern.

In the recent years, several papers have been published describing and analyzing in detail vibrational spectra of monomethylpyridines¹, dimethylpyridines², and trimethylpyridines³. The results obtained have been compared with the vibrational spectra of the corresponding isoelectronic benzene homologues — dimethylbenzenes⁴⁻⁶ and trimethylbenzene^{7,8}—published by the same authors. Among the first to be concerned with the correlation of the infrared spectra of some substituted pyridines with their molecular structure were Cook and Church⁹ and Shindo and Ikekawa¹⁰. From the spectra of methylpyridines¹¹ and some other pyridine homologues it was deduced — similarly as for benzene derivatives — that the principal factor governing the positions of the bands due to the C—H out-of-plane vibrations in the $900-700\text{ cm}^{-1}$ range is the number of the adjacent hydrogen atoms on the ring^{10,12}. All the alkylpyridines containing isolated hydrogen atoms on the pyridine ring display in this range a single band of the out-of-plane bending vibration, which shifts to lower wavenumbers as their number increases. For compounds containing a single ring proton, the frequency of the out-of-plane vibration decreases according to the position of the hydrogen atom with respect to the heterocycle nitrogen atom in the order $H^2 > H^4 \gg H^3$. The considerably lower frequency for compounds with the hydrogen atom in the position 2 has been related¹⁰ to the higher π -electron density at the C³ atom. The effect of each of the positions contributes additively to the band frequency¹⁰. The pyridine ring vibrations in the $1100-900\text{ cm}^{-1}$ range are for 2- and 4-substituted derivatives and for di- (except 2,5-) and trisubstituted pyridine derivatives localized in the region of $1000-985\text{ cm}^{-1}$, 3-substituted and 2,5-disubstituted derivatives display those vibrations at $1035-1000\text{ cm}^{-1}$ (ref.¹²). In the $1650-1400\text{ cm}^{-1}$ region, the total of four bands of the pyridine ring stretching vibrations have been observed, *viz.* in the ranges of $1615-1560$, $1590-1540$, $1520-1440$, and 1445 to 1400 cm^{-1} . The wavenumber difference of the two bands near 1600 cm^{-1} amounts to approximately 40 cm^{-1} for pyridine 4-alkyl homologues and approximately 20 cm^{-1} for 2- and 3-substituted homologues⁹. The intensities of the bands belonging to these stretching vibrations depend upon the substitution pattern¹⁰ and substituent nature¹³.

The overtone and combination bands in the region $2000-1650\text{ cm}^{-1}$ are characteristic of the pyridine alkyl homologues, too^{9,12}, a practical utilization of this finding is, however, rather limited¹³. The C—H stretching vibrations are localized near 3000 cm^{-1} . Substituted pyridines exhibit usually two bands in this region,¹⁴ at $3095-3060$ and $3055-3010\text{ cm}^{-1}$.

A methyl group on the ring is characterized¹² by a narrow band at $1370-1300\text{ cm}^{-1}$, an isopropyl group by a doublet in the region $1390-1370\text{ cm}^{-1}$, and a tert-butyl group by a band in the range $1380-1360\text{ cm}^{-1}$ and bands at $1250-1200\text{ cm}^{-1}$.

We made use of the results of all the papers cited for a partial identification of pyridine homologues isolated from coal tar fractions. During that work, more than fifty pyridine homologues were obtained — almost complete homologous and isomeric series and, in addition, some other polysubstituted homologues, including isomeric pairs. Having measured the infrared spectra we were able to test some published correlations between the band positions and the molecular structure and to refine them, since we employed a considerably larger collection of substances.

EXPERIMENTAL

The pyridine homologues were obtained mostly from coal tar fractions¹⁵⁻¹⁹; synthetic or commercial chemicals were used only exceptionally. An overall survey of the impurities present in the samples was gained from gas chromatographic measurements (1.5% Carbowax 1500 and 1400 in the ratio 2 : 1 on Chromaton N, 80°C); their contents did not exceed 2% wt. The infrared spectra were scanned on a double-beam instrument Unicam SP 200 G in 0.03 mm cells and on an apparatus Unicam 200 using a capillary layer of the substance between sodium chloride windows.

RESULTS AND DISCUSSION

Two regions, namely $900-700\text{ cm}^{-1}$ and $1650-1400\text{ cm}^{-1}$, proved to be the most convenient for the correlation of the infrared spectrum with the pyridine ring substitution, in accordance with the published findings.

Region 900—700 cm⁻¹. It has been shown^{1,10} that in simpler cases the out-of-plane vibrations of the pyridine ring C—H bonds can be employed for an assessment of the substitution on the ring. We could confirm that this region really is suitable for the localization of the pyridine ring substituents based on the number and positions of isolated and adjacent ring hydrogen atoms. The pyridine homologues and derivatives can be conveniently grouped according to this criterion if the isolated hydrogen atom in the position 2 or 6 is considered separately from the other isolated ring hydrogens. The various combinations in the pyridine ring substitution can be then divided into six groups characterized in Table I. The values for the group H were taken from the paper¹⁰, because these substances were not available to us.

Table II lists the characteristic very strong to medium absorption bands of the various pyridine homologues in the two regions under study, along with the groups to which the compounds examined belong according to Table I.

Plotting the positions of the strong and medium bands in the region in question in dependence on the increasing number of adjacent ring hydrogen atoms and on the positions of the isolated ring hydrogen atoms, we find a shift of these bands towards higher wavenumbers (Fig. 1). From the plot it also follows that the principal absorptions of the 2 H 1 H group are, in fact, sums of those of the groups 2 H and 1 H. The dependence shown in Fig. 1 applies not only to pyridine homologues, but also to its derivatives including benzo derivatives (quinoline, isoquinoline). It also holds

TABLE I

Classification of Pyridine Derivatives According to the Number and Positions of the Pyridine Ring Hydrogen Atoms

Group	Number of ring hydrogen atoms			Combinations of the substituted ring positions
	adjacent	isolated in the position(s)		
		3, 4, 5	2, 6	
4 H	4	—	—	2-
3 H	3	—	1	3-, 2,3-, 2,6-
2 H	2	—	1	4-, 2,5-, 3,4-, 2,3,4-, 2,3,6-
1 H	—	2	2	3,5-, 2,3,5-, 2,4,5-, 2,4,6-, 2,3,4,6-, 2,3,5,6-
H	—	—	2	3,4,5-, 2,3,4,5-
2 H 1 H	2	1	—	2,4-

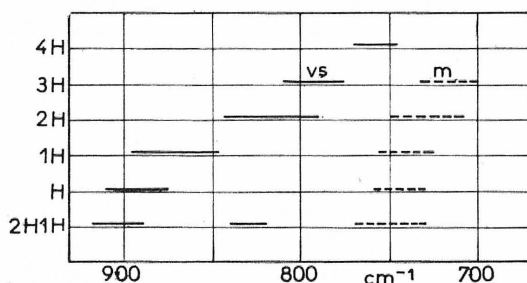


FIG. 1

Dependence of the Positions of Marked Absorption Bands in the Region 900—700 cm^{-1} on the Number of Adjacent Ring Hydrogen Atoms (4 H to 2 H) and on the Number and Position of the Isolated Ring Hydrogen Atoms

TABLE II

Band Positions of Pyridine Homologues in the Infrared Spectral Regions of 900–700 and 1 650–1 400 cm^{-1}

Pyridine ring substitution	Group	Spectral region, cm^{-1}	
		900–700	1 650–1 400
2-Methyl-	4 H	'760, 752, 734	1 590, 1 575, 1 485, 1 460–1 440
3-Methyl-	3 H	790, 713	1 602, 1 585, 1 486, 1 460, 1 420
4-Methyl-	2 H	800, 730	1 610, 1 570, 1 503, 1 450, 1 420
2-Ethyl-	4 H	800, 750	1 585, 1 575, 1 484, 1 460, 1 440
3-Ethyl-	3 H	812, 717	1 590, 1 578, 1 480, 1 462, 1 455, 1 422
4-Ethyl-	2 H	822, 777	1 600, 1 580, 1 500, 1 463, 1 412
2-Propyl-	4 H	765, 750	1 590, 1 570, 1 480–1 470, 1 457, 1 436
4-Propyl-	2 H	840, 790, 745	1 600, 1 555, 1 495, 1 463, 1 415
3-Isopropyl-	3 H	810, 715	1 590, 1 580, 1 485, 1 470, 1 460, 1 425
4-Isopropyl-	2 H	810, 750	1 600, 1 560, 1 497, 1 465, 1 415
3(1-Propenyl)-	3 H	825, 772	1 585, 1 570, 1 450, 1 422, 1 415
2,3-Dimethyl-	3 H	790, 730	1 585, 1 471, 1 455, 1 440
2,4-Dimethyl-	2 H 1 H	917, 820	1 612, 1 570, 1 560, 1 484, 1 460, 1 405
2,5-Dimethyl-	2 H	820, 730	1 610, 1 579, 1 500, 1 490, 1 455
2,6-Dimethyl-	3 H	778	1 600, 1 585, 1 475, 1 1460
3,4-Dimethyl-	2 H	840, 823, 725	1 600, 1 568, 1 495, 1 450, 1 410
3,5-Dimethyl-	1 H	862, 715, 710	1 608, 1 588, 1 470, 1 460, 1 430
4-Ethyl-2-methyl-	2 H 1 H	898, 838	1 610, 1 578, 1 560, 1 482, 1 465–1 450, 1 415
2-Ethyl-4-methyl-	2 H 1 H	890, 825	1 605, 1 565, 1 480, 1 463, 1 455, 1 402
5-Ethyl-2-methyl-	2 H	835, 740	1 610, 1 575, 1 500, 1 470, 1 460, 1 400
2-Ethyl-5-methyl-	2 H	830	1 605, 1 570, 1 490, 1 463, 1 455
2-Ethyl-6-methyl-	3 H	801, '750	1 590, 1 580, 1 564, 1 455
4-Ethyl-3-methyl-	2 H	835	1 600, 1 568, 1 500, 1 465, 1 460, 1 430, 1 410
3-Ethyl-4-methyl-	2 H	835	1 600, 1 565, 1 500, 1 465, 1 460, 1 415
3-Ethyl-5-methyl-	1 H	872, 720, 710	1 600, 1 580, 1 462, 1 455, 1 435
2-Methyl-4-propyl-	2 H 1 H	825	1 675, 1 562, 1 462–1 445, 1410
4-Methyl-2-propyl-	2 H 1 H	820	1 608, 1 565, 1 470–1 455, 1 410
5-Methyl-2-propyl-	2 H	840, 820	1 603, 1 570, 1 490, 1 465, 1 455
2-Methyl-6-propyl-	3 H	790, 770	1 595, 1 580, 1 460, 1 455
2-Ethyl-6-propyl-	3 H	810, 750	1 600–1 580, 1 468, 1 455
2-Methyl-5-propyl-	2 H	823	1 604, 1 570, 1 496, 1 489, 1 462, 1 458
2-Butyl-6-methyl-	3 H	775, 748	1 590, 1 580, 1 498, 1 470, 1 455
2,3,4-Trimethyl-	2 H	838, 825	1 595, 1 569, 1 462, 1 445, 1 408
2,3,5-Trimethyl-	1 H	880, 728, 718	1 608, 1 570, 1 482, 1 465, 1 460–1 435, 1 405
2,3,6-Trimethyl-	2 H	820	1 602, 1 589, 1475, 1 470, 1 460
2,4,5-Trimethyl-	1 H	925, 865	1 610, 1 568, 1 500, 1 455
2,4,6-Trimethyl-	1 H	925, 842	1 615, 1 580, 1 540, 1 520, 1 470, 1 460, 1 448, 1 413

TABLE II
(Continued)

Pyridine ring substitution	Group	Spectral region, cm^{-1}	
		900—700	1 650—1 400
2-Ethyl-4,6-dimethyl-	1 H	942, 845	1 610, 1 580—1 560, 1 540, 1 530, 1 515, 1 465, 1 455, 1 445, 1 415
2-Ethyl-3,6-dimethyl-	2 H	830	1 600, 1 582, 1 578, 1 483, 1 475, 1 465, 1 455
3-Ethyl-2,6-dimethyl-	2 H	830	1 599, 1 582, 1 578, 1 470, 1 465, 1 455
4-Ethyl-2,6-dimethyl-	1 H	890, 855	1 610, 1 575—1 565, 1 538, 465, 1 455, 1 440, 1 422
2,6-Diethyl-3-methyl-	2 H	830	1 595, 1 575, 1 481, 1 472, 1 460
2,6-Diethyl-4-methyl-	1 H	852, 830	1 610, 1 570, 1 510, 1 470, 1 462, 1 452
2,3-Dimethyl-6-propyl-	2 H	780, 752	1 593, 1 580, 1 578, 1 470, 1 462, 1 455
2-Isopropyl-3,6- or -5,6-dimethyl-	2 H	828	1 598, 1 581, 1 578, 1 479, 1 470, 1 465, 1 455
2-Ethyl-3,5-dimethyl-	1 H	888, 711	1 602, 1 568, 1 478, 1 470, 1 455, 1 427
2,3- or 2,5-Diethyl- -6-methyl-	2 H	820, 793	1 592, 1 575, 1 570, 1 465, 1 450
2-Butyl-3,6- or -5,6-dimethyl-	2 H	830	1 590, 1 570, 1 477, 1 465, 1 450
2-Ethyl-6-isopropyl-3- or 5-methyl-	2 H	825	1 590, 1 570, 1 470, 1 460, 1 450
2,4-Diethyl-6-methyl-	1 H	880, 860, 747	1 605, 1 570, 1 500, 1 462, 1 440
2,3,4,6-Tetramethyl-	1 H	865	1 600, 1 565, 1 555, 1 470, 1 460, 1 450, 1 445
2,3,5,6-Tetramethyl-	1 H	895	1 605, 1 570, 1462, 1 455, 1 435

for the substances studied by Katritzky and coworkers — these authors have published the vibrational spectra of 48 4-substituted, 35 2-substituted, and 27 2-substituted pyridine derivatives (refs²⁰⁻²², respectively). The very strong characteristic infrared bands of all these derivatives in the 900—700 cm^{-1} range, grouped according to the classification of Table I, are in accordance with the results presented in Fig. 1. Based on the wavenumbers of the very strong and strong to medium absorption bands in the region 900—700 cm^{-1} it is thus possible to localize the positions of the pyridine ring hydrogen atoms or substituents, irrespective of the chain length or branching or of the kind of the characteristic group or pyridine benzo derivative.

Region 1650—1400 cm^{-1} Another spectral region suitable for the identification of the substituted positions of the pyridine ring is the 1650—1440 cm^{-1} range. So far it has been supposed that the absorption bands in this range do not depend so markedly upon the substituent number and positions, although they are identical or at least comparable with those of the corresponding benzene derivatives²².

TABLE III
Wavenumber Ranges Characteristic of the Various Alkylpyridines, cm^{-1}

Substituted ring position(s)	Pyridine ring vibrations		C—H bond vibrations			n^a	
	stretching	“breathing”	stretching	in-plane bending	out-of-plane bending		
2-	1 595—1 590	1 000— 975	3 080—3 060	1 310—1 290	770—750	3	
	1 575—1 565		3 025—3 020	1 245—1 200			
	1 485—1 470			1 160—1 145			
	1 460—1 440			1 110—1 090			
3-	1 720—1 659	1 050—1 028	3 100—3 075	1 340—1 318	815—790	4	
	1 602—1 590		3 040—3 010	1 250—1 220			720—710
	1 587—1 578						
	1 480—1 455						
4-	1 670—1 660	1 000— 972	3 085—3 060	1 311—1 290	838—795	4	
	1 610—1 600		3 035—3 020	1 230—1 215			780—730
	1 580—1 555			1 090—1 070			
	1 503—1 490						
2,3-	1 592	999	3 070	1 280	790	1	
	1 580		3 010	1 243			
	1 455			1 185			
				1 130			
2,4-	1 610—1 603	1 000— 992	3 050—3 020	1 300—1 290	918—892	4	
	1 578—1 550		3 010—3 000	1 179—1 160			838—820
	1 468—1 460						763—732
	1 420—1 402						
2,5-	1 610—1 605	1 035—1 030	3 110—3 090	1 305—1 300	835—790	5	
	1 580—1 570		3 020—3 000	1 251—1 232			745—710
	1 500—1 485			1 145—1 134			
2,6-	1 610—1 500	1 000— 970	3 080—3 055	1 282—1 270	810—780	5	
	1 588—1 575		3 025—3 010	1 245—1 220			750—710
	1 470—1 465			1 160			
	1 420—1 405			1 110—1 090			
3,4-	1 600	1 000— 970	3 090—3 065	1 312—1 310	840—820	3	
	1 567—1 560		3 040—3 020	1 236—1 222			750—715
	1 500—1 492			1 200—1 195			
	1 412—1 410			1 150—1 081			
3,5-	1 610—1 600	1 040—1 030	3 090—3 065	1 330—1 320	872—862	2	
	1 590—1 580		3 040—3 020	1 280—1 265			728—710
	1 472—1 460			1 240—1 225			
	1 430			1 175—1 148			

TABLE III
 (Continued)

Substituted ring position(s)	Pyridine ring vibrations		C—H bond vibrations			<i>n</i> ^a
	stretching	“breathing”	stretching	in-plane bending	out-of-plane bending	
2,3,4-	1 593 1 569 1 470—1 462 1 410—1 405	980	3 050	1 265—1 255 1 194 1 110 1 070	882 838—825 734	1
2,3,5-	1 608—1 602 1 570—1 565 1 476—1 465	944	3 080—3 060	1 246—1 236 1 225—1 210 1 213—1 205	880 770—745 718—712	2
2,3,6-	1 603—1 593 1 588—1 575 1 482—1 455 1 460—1 440	921	3 070—3 030 3 025—3 010	1 270—1 250 1 180—1 155 1 135—1 122	830—820 750—735	9
2,4,5-	1 610 1 564—1 558 1 502—1 495	1 002	3 095 3 000	1 300 1 255—1 235 1 210	925 865 735—725	1
2,4,6-	1 620—1 605 1 580—1 560 1 540—1 510 1 470—1 420	1 000— 980	3 050—3 030	1 320—1 305 1 222—1 202 1 160—1 130	942—890 865—842 765—725	5
3,4,5-	1 602 1 570 1 491 1 429				876 722	1
2,3,4,6-	1 610 1 570—1 555 1 470—1 460 1 450—1 435	1 010— 984	3 070	1 220 1 152	952 855 738	1
2,3,5,6-	1 605 1 570 1 465—1 455 1 435	1 000	3 030 3 000	1 248 1 212	897 725	1
2,3,4,5-	1 600 1 572 1 480 1 450				905 854 734	1 ¹⁰

^a Number of the substances processed.

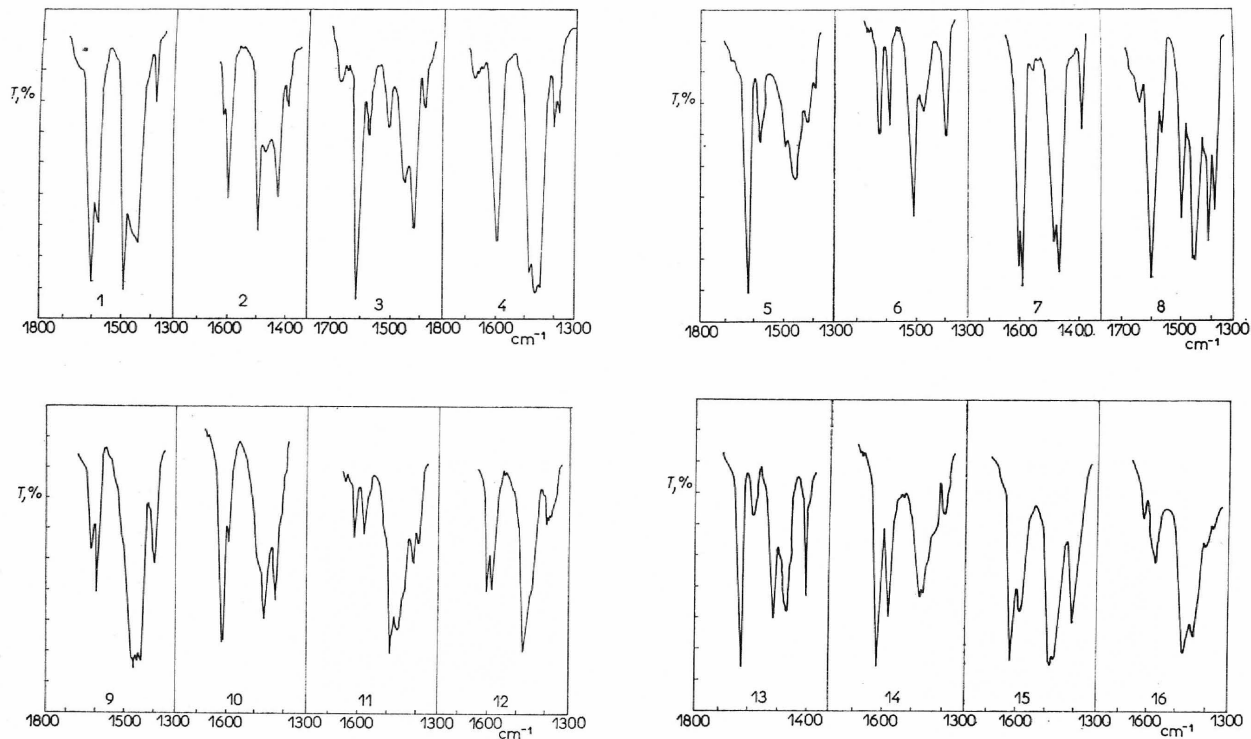


FIG. 2

Infrared Spectra of Pyridine Methyl Homologues in the Region $1650\text{--}1400\text{ cm}^{-1}$

1 2-Methylpyridine, 2 3-methylpyridine, 3 4-methylpyridine, 4 2,3-dimethylpyridine, 5 2,4-dimethylpyridine, 6 2,5-dimethylpyridine, 7 2,6-dimethylpyridine, 8 3,4-dimethylpyridine, 9 3,5-dimethylpyridine, 10 2,3,4-trimethylpyridine, 11 2,3,5-trimethylpyridine, 12 2,3,6-trimethylpyridine, 13 2,4,5-trimethylpyridine, 14 2,4,6-trimethylpyridine, 15 2,3,4,6-tetramethylpyridine, 16 2,3,5,6-tetramethylpyridine.

We measured the almost complete series of pyridine methyl homologues (except for 3,4,5-tri-, 2,3,4,5-tetra-, and pentamethylpyridine) and found that the positions and intensities of the absorption bands in the region in question are different for all the sixteen pyridine homologues; on the other hand, the band positions and to an extent also intensities of pyridine alkyl homologues remain the same as for the respective methyl homologues, regardless of the complexity of the alkyl substituent. It is thus sufficient for the identification of the substituted position(s) to confront the absorptions in the region $1650-1400\text{ cm}^{-1}$ with those shown in Fig. 2 and generalized in Table III. Since the differences in the numerical expression of the band positions are not very descriptive, the spectral patterns in the range in question are shown in Fig. 2 for all the pyridine methyl homologues. In conjunction with the C—H out-of-plane bending vibrations, the region of the pyridine ring stretching vibrations allows a unique determination of the positions of the alkyl substituents on the pyridine ring. A somewhat more complicated situation occurs if the substitution pattern is to be determined in the case of other pyridine derivatives, be it benzo derivatives or substances containing characteristic groups as the substituents; in this case the information obtained from the region of the pyridine ring stretching vibrations cannot be regarded unambiguous.

Spectral regions characterizing the pyridine substitution patterns. The spectra obtained from more than fifty pyridine homologues allowed us to refine some generalized conclusions concerning the infrared spectral ranges characterizing the various substitution patterns. Since the spectra of 3,4,5-tri- and 2,3,4,5-tetrasubstituted pyridines lacked for the set of the theoretically possible substitution combinations to be complete, the spectra obtained by Shindo and Ikekawa¹⁰ were taken into the treatment. The results obtained are summarized in Table III. The number of the pyridine alkyl homologues evaluated was limited to those present in coal tar. As the basis for the band assignment served the works by Green¹⁻³ and Mehdi^{23,24}. The span of the individual ranges is given by the highest and lowest values within each of the groups treated.

In the region of the C—H stretching vibrations, two groups of absorption bands usually appear, *viz.* at $3100-3060$ and $3040-3000\text{ cm}^{-1}$, except for 2,3,4-, 2,3,5- and 2,4,6-trialkylpyridines and 2,3,4,6-tetramethylpyridine, for which a single absorption was observed at $3080-3030\text{ cm}^{-1}$.

The pyridine ring (C—C and C—N bonds) stretchings appear in the region 1620 to 1400 cm^{-1} . Four absorption ranges are usually found in this interval for most pyridine alkyl homologues save 3- and 4-monoalkylpyridines, for which this span extends up to 1700 cm^{-1} and where five absorption ranges can be identified; in the case of 2,3- and 2,5-dialkyl- and 2,4,5-trialkylpyridines, on the other hand, only three absorption ranges can be found in the $1620-1400\text{ cm}^{-1}$ range.

The in-plane bending vibrations of the C—H bonds are concentrated in the region

1340–1055 cm^{-1} ; in this region are observed three or four absorption bands, exceptionally two only (2,4-dialkyl- and tetramethylpyridine) or five (2-alkylpyridines)

The "breathing" vibrations of the pyridine ring are localized in a narrow range of 1000 to 970 cm^{-1} . 3-Alkyl- and 2,5- and 3,5-dialkylpyridines are exceptions, where these vibrations are shifted to 1050–1030 cm^{-1} , 2,3,5- and 2,3,6-trialkylpyridines display these vibrations shifted to as low wavenumbers as 945–920 cm^{-1} .

The out-of-plane bending vibrations of the C—C bonds are observed at 900 to 700 cm^{-1} and divide usually up to two or three narrower regions.

In the region of combination frequencies, a marked absorption was found at 1940 cm^{-1} for all the 4-alkylsubstituted pyridine homologues and derivatives¹. An analogous absorption was observed in the 1935–1920 cm^{-1} range for all the 2,4-dialkylpyridines. 2,3,5-Trialkylpyridines exhibit a medium intensity absorption at 1795 cm^{-1} , 2,3,4-trimethylpyridine at 1900 cm^{-1} . The other pyridine homologues show only weak or very weak absorptions in the whole region 2600–1700 cm^{-1} , which are not characteristic of the pyridine ring substitution patterns.

Region of vibrations characterizing the alkyl groups. The alkyl groups are commonly identified by employing the symmetric bending vibration of the methyl group in the range 1400–1350 cm^{-1} . The measurements with the homologues listed in Table II showed that one or two bands are characteristic of a methyl group, whereas an isopropyl group is characterized by two absorptions at 1390 and 1370 cm^{-1} , in accordance with the published data¹². For most of the pyridine alkyl homologues, the presence of a methyl group is characterized by a single band in the narrower wavenumber range 1390–1375 cm^{-1} , only in the case of 2,3-, 2,3,5-, 2,3,6-, and 2,3,5,6-substituted homologues two absorptions were found, *viz.* at 1390–1380 and 1380–1370 cm^{-1} . Two absorptions in these narrow ranges were also observed in some instances of 2,5- and 2,4,6-alkylsubstituted pyridines.

For monomethylpyridines, the coefficient of the characteristic absorption of the methyl group decreases in the order of the substituted positions $3 < 4 < 2$; these differences drop as the alkyl chain length grows.

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