CORRELATIONS OF INFRARED AND MASS SPECTRA WITH THE STRUCTURE OF ALKYLPYRIDINES

Zdeněk HEJDA[a] and Jan VYMĚTAL[b]

[a] *Moravian Chemical Works, 709 03 Ostrava and*
[b] *Research Institute of Coal Tar Chemistry, Urx Works, 757 27 Valašské Meziříčí*

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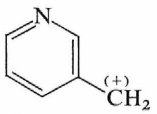
The mass and infrared spectra of a series of alkylpyridines are shown to complement each other conveniently.The infrared spectra yield information on the mutual positions of the alkyl substituents and the hydrogen atoms at the pyridine ring, while the mass spectral patterns are governed both by the alkyl nature and by its position with respect to the hetero atom. Mutual correlations of the two types spectra indicate that the structure of any alkylpyridine can be determined based on simple criteria.

The hitherto achieved results of structure determination of alkylpyridines from their mass spectra[1] can be briefly summarized as follows. Typical of pyridine methyl homologues is the high stability of the heterocyclic system; the most intense line belongs to the molecular ion, and thus the position of the methyl group cannot be inferred from the mass spectrum[2]. Information on the mutual position of the alkyl group and the hetero atom can be obtained from the mass spectra only if the alkylpyridines contain at least two carbon atoms in the side chain[3]. In pyridine homologues with an alkyl group in the position 3 the simple β-cleavage is, owing to the higher electron density[4], markedly favoured, which leads to the formation of the stable ion *I*. A 2-substituted alkylpyridine is characterized by the γ-cleavage[5], with the assumed formation of the ion *II*. If the conditions required for the McLafferty rearrangement are satisfied in the 2-alkylsubstituted pyridine, the ion *III* is stabilized, as a result of β-cleavage associated with the migration of the hydrogen atom to the hetero atom[6]. Pyridine homologues alkyl-substituted in the position 4 stand approximately between the two previous types; both cleavage products are always found in the spectrum, with a marked intensity of the fragments.



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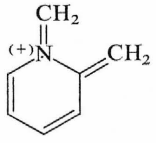

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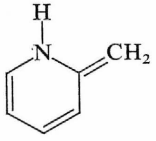


III

These principal findings concerning the behaviour of alkylpyridines during the ionization by electrons together with the results of the study of the light absorption of pyridines in the infrared spectral region[7] have been applied to the identification of the pyridine homologues isolated

from basic fractions of coal tar[8-12]. These works revealed that by a suitable correlation of the infrared and mass spectra, pyridine homologues can be identified uniquely, even in cases where the NMR spectra yield ambiguous results[13].

EXPERIMENTAL

The total impurity contents in the pyridine homologue samples were monitored by means of gas chromatography on an instrument Hewlett–Packard 5711A on a column SCOT packed with the phase PEG 20 M, column length 15 m, i.d. 0·5 mm, at the temperature of 150°C. The records were evaluated quantitatively on an integrator HP 3380 A by the "Area %" technique. The pyridine homologues isolated were pure to at least 98%. The infrared spectra were measured on a spectrometer Unicam SP 200 as a film between sodium chloride windows. The mass spectra were run on a mass spectrometer Jeol JMS 02 A, ionization energy 70 eV and resolution $R_{10} = 1000$.

RESULTS AND DISCUSSION

For the correlation of the infrared and mass spectra with the structure of the alkylpyridines, four fundamental characteristics were chosen: the spectral patterns in two infrared spectral ranges, the molecular weight, and the relative intensities of four fragments in the mass spectrum. These are fully sufficient for a reliable identification of any alkylpyridine.

Infrared Spectra

Spectral range of $900-700\ cm^{-1}$. From the spectral patterns in this range the number and positions of the isolated and adjacent ring hydrogen atoms can be inferred. For a characterization of the pyridine homologue according to this feature it appeared convenient to regard the ring hydrogen atoms in the positions 2 or 6 separately from the isolated hydrogen atoms in the positions 3, 4, or 5. The various combinations of the pyridine ring substitutions can be then divided into six groups, as characterized in detail in our previous paper[7].

Spectral range of $1650-1400\ cm^{-1}$. The measurements of almost complete homologous series of pyridine mono- to tetramethyl homologues (except for 3,4,5-tri- and 2,3,4,5-tetramethylpyridine) showed that none of the indicated sixteen pyridine methyl homologues display the same positions and intensities of the absorption bands. Moreover, the band positions and to an extent also the intensities were found to be the same irrespective of the nature of the alkyl substituents. For an identification of the substitution positions of the pyridine alkyl homologue it is thus sufficient to compare the wavenumber range of $1650-1400\ cm^{-1}$ with that for the basic series of the methyl homologues[1].

Mass Spectra

The mass spectra of 46 alkylpyridines showed that the molecular ion (M^+) can be always reliably identified in the spectra and thus the molecular weight can be determined. The relative intensity of the molecular ion depends upon the alkyl chain length and its position at the pyridine ring; it decreases with the increasing chain length, a decreasing trend is observed in the order of substitution positions 4, 3, 2. In the alkylpyridine series measured (Table I) the least intense molecular ion was found in the case of 2-butyl-6-methylpyridine, hence the homologue possessing the longest alkyl substituent in the position 2. Although the relative intensity amounted to 1% only, it enabled an unambiguous determination of the molecular weight of the substance. The number of the carbon atoms contained in the alkyl chains of the alkylpyridine molecule (n) can be readily determined using the simple relation $n = (M-79)/14$.

In addition to the molecular weight and the molecular ion intensity, the relative intensities of the fragments $(M-1)^+$, $(M-15)^+$, $(M-28)^+$ or $(M-42)^+$, and $(M-29)^+$ or $(M-43)^+$ are relevant to the elucidation of the mass spectra. The elucidation and consideration what alkyl groups are attached to the pyridine ring and in which positions, are facilitated by the fact that the substitution position affects the three fundamental cleavage types as follows:

Simple β-cleavage	3- > 4- ⩾ 2-
γ-cleavage	2- > 4- ⩾ 3-
β-cleavage with hydrogen migration	2- > 4- ⩾ 3-

The last type – β-cleavage with hydrogen migration (β^H) – can, naturally, occur only with alkyl groups containing at least three carbon atoms in the straight chain. If the pyridine ring is more than one alkyl group substituted, the positions 2 and 6, and 3 and 5 are, of course, to be considered equivalent, with regard to the symmetry of the molecule.

Structure Determination of a Pyridine Homologue by Elucidation of its Infrared and Mass Spectra

Table I lists the results of evaluation of the mass spectra of all the alkylpyridines studied. These results were fully confirmed by NMR spectroscopic data[8–13] and also by comparing with the tabulated data on mass[1] and infrared[14] spectra. During the interpretation of the information obtained from the spectra it is advisable to proceed as follows: *a*) From the infrared spectra, the number of the isolated or adjacent hydrogen atoms on the ring are determined from the wavenumbers of the maxima of the intensive absorption bands in the region of 900–700 cm^{-1}. By comparing the spectral patterns in the region of 1650–1400 cm^{-1} with those of the pyridine

TABLE I

Evaluation of the Mass Spectra of Pyridine Alkyl Homologues

Pyridine substitution	Relative intensity, %					Cleavage type	Structure confirmation	
	M^+	$(M-1)^+$	$(M-15)^+$	$(M-28)^+$ $(M-42)^+$	$(M-29)^+$ $(M-43)^+$		MS^2	IR^{14}
2-Methyl-	100	21	20	19	5	M, β	+	+
3-Methyl-	100	31	5	28	5	M, β	+	+
4-Methyl-	100	24	5	24	5	M, β	+	+
2,3-Dimethyl-	100	58	20	20	4	M, β	+	+
2,4-Dimethyl-	100	32	18	24	4	M, β	+	+
2,5-Dimethyl-	100	63	15	31	6	M. β	+	+
2,6-Dimethyl-	100	30	18	11	3	M, β	+	+
3,4-Dimethyl-	100	54	24	11	7	M, β	+	+
3,5-Dimethyl-	100	52	23	38	10	M, β	+	+
2-Ethyl-	53	100	3	38	20	γ, M	+	+
3-Ethyl-	83	49	100	17	9	β, M, γ	+	
4-Ethyl-	100	81	53	28	10	M, γ		
2,3,4-Trimethyl-	100	55	24	6	2	M, β		
2,3,5-Trimethyl-	100	44	29	7	2	M, β	+	
2,3,6-Trimethyl-	100	63	19	5	1	M, β	+	+
2,4,5-Trimethyl-	100	46	27	9	5	M, β		
2,4,6-Trimethyl-	100	23	16	2	1	M, β	+	+
4-Ethyl-2-methyl-	100	26	49	8	4	M, β		
5-Ethyl-2-methyl-	64	20	100	6	2	β, M, γ	+	+
2-Ethyl-6-methyl-	56	100	3	26	9	γ, M	+	
4-Ethyl-3-methyl-	100	60	64	19	19	M, β, γ		
3-Ethyl-5-methyl-	90	56	100	11	7	β, M, γ		
2-Ethyl-4-methyl-	58	100	2	28	10	γ, M		
3-Ethyl-4-methyl-	69	28	100	9	5	β, M, γ		
2-Ethyl-5-methyl-	54	100	4	24	8	γ, M		
2-n-Propyl-	2	10	29	100	8	β^H, γ	+	+
4-n-Propyl-	98	14	48	100	50	β^H, M, γ		
4-Isopropyl-	56	14	100	3	3	β, M, γ	+	
2,3,4,6-Tetramethyl-	100	47	22	4	1	M, β		
2,3,5,6-Tetramethyl-	100	50	24	2	1	M, β		
2-Ethyl-4,6-dimethyl-	56	100	7	28	13	γ, M	+	
3-Ethyl-2,6-dimethyl-	52	14	100	5	4	β, M	+	
4-Ethyl-2,6-dimethyl-	100	17	39	5	4	M, β		
2-Ethyl-3,6-dimethyl-	52	100	5	21	10	γ, M		
4-Methyl-2-propyl-	17	38	25	100	10	β^H, β, M		
5-Methyl-2-propyl-	29	57	36	100	17	β^H, β, M		
2,4-Diethyl-	47	100	18	29	18	γ, M		
2,6-Diethyl-4-methyl-	50	100	11	21	6	γ, M		
2,3-Dimethyl-6-propyl-	55	100	55	83	16	γ, M		

TABLE I
(*Continued*)

Pyridine substitution	Relative intensity, %					Cleavage type	Structure confirmation	
	M^+	$(M-1)^+$	$(M-15)^+$	$(M-28)^+$ $(M-42)^+$	$(M-29)^+$ $(M-43)^+$		MS^2	IR^{14}
2,5-Dimethyl-6-propyl-	50	100	48	80	20	γ, M		
2,4-Diethyl-6-methyl-	49	100	12	43	10	γ, M		
2-Isopropyl-3,6-dimethyl-	23	32	100	30	3	β, γ		
2-Isopropyl-5,6-dimethyl-								
2-Butyl-6-methyl-	1	2	14	5/100	25/7	β^H, γ		
2,6-Diethyl-4-methyl-	53	100	3	21	3	γ, M		
2,4,6-Triethyl-	49	100	3	21/2	3/8	γ, M		
2-Ethyl-6-isopropyl-3-methyl-	35	45	100	32	4	β, γ, M		
2-Ethyl-6-isopropyl-5-methyl-								

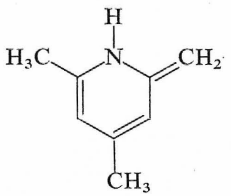
methyl homologue series, the positions substituted are found. The two informations must be in mutual accordance. *b*) From the mass spectrum, molecular weight and the number of carbon atoms involved in the chains are determined. *c*) All the theoretical combination possibilities of substitution by various alkyl groups are considered taking into account the above results. *d*) From the intensities of the mass spectral lines (M^+), $(M-1)^+$, $(M-28)^+$ or $(M-42)^+$, and $(M-29)^+$ or $(M-43)^+$, all the possibilities as obtained sub *c*) are regarded based on the preferred cleavage types, and the structure of the pyridine homologue to be identified is determined.

The interpretation leads in most cases to unambiguous conclusions. Only in the case of substitution in the positions 2,3,6- (or 2,5,6-), two alternative structures must be admitted for certain substituent combinations (Table I).

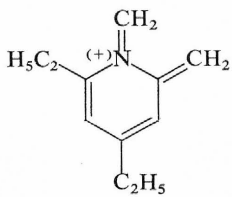
As an example of application of the procedure suggested can serve the determination of the structure of a pyridine homologue exhibiting intense absorption peaks at 890 and 880 cm^{-1} in the infrared spectrum. This indicates that only isolated ring protons are present (1 H or H type – see[7]). One of the combinations 3,5-, 2,3,5-, 2,4,5-, 2,4,6- 3,4,5-, 2,3,4,5-, 2,3,4,6-, or 2,3,5,6- should thus be realized. The agreement of the absorption bands in the 1650–1400 cm^{-1} region with those of 2,4,6-trimethylpyridine proves unequivocally the substitution in the positions 2,4,6 of the pyridine ring.

The molecular weight $M = 163$ was determined from the mass spectrum, six carbon atoms constitute thus the alkyl chains. For a 2,4,6-trialkylpyridine, fifteen combinations are theoretically conceivable as follows: eight butyl-dimethylpyridines

(pairs of n-butyl-dimethyl-, isobutyldimethyl-, sec-butyl-dimethyl-, and tert-butyl-dimethyl-); six ethyl-methyl-propylpyridines (three ethyl-methyl-n-propyl homologues and three ethyl-isopropyl-methyl homologues); one triethylpyridine.



IV



V

The possibility of the presence of the n-butyl and isobutyl groups is eliminated regarding the very low intensity of the $(M-42)^+$ ion (Table I). The positions 2,6 or 4 would require the formation of an intense ion at M/*e* 121, *i.e.* the stabilization of the ion *IV* and expulsion of propylene (McLafferty rearrangement – β^H cleavage). The low intensity of the ion $(M-28)^+$ rules out the presence of the n-propyl and sec-butyl groups in the molecule, for the same reason (expulsion of propylene). The absence of the tert-butyl group or the isopropyl group is indicated by the very low intensity of the $(M-15)^+$ ion. From the theoretically feasible combinations, the presence or absence of 2,4,6-triethylpyridine has to be confirmed. The fundamental $(M-1)^+$ ion characterizing the cleavage with the expulsion of hydrogen from the ethyl group and stabilization of the ion *V*, confirms this structure unambiguously. This fragmentation type (γ, M – see Table I) is characteristic of the presence of an ethyl group in the position 2 or 6. The substance under investigation is thus 2,4,6-triethylpyridine.

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