MASS SPECTRA OF ARYLALKYLPYRIDINES*

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The basic principles of the mass-spectral fragmentation of arylalkylpyridines that contain substituents in various positions were established. The principle ions that can be used in chromatographic mass-fragmentographic analysis in the study of liquid-crystal compositions were determined for each specific case.

Liquid crystals have found extensive application in technology and in the national economy, and, although thousands of liquid-crystal substances are known, the search for new, practically useful mesogens, particularly those that contain a heteroaromatic ring as a structural element, continues. When a heteroring is introduced, the unshared pair of electrons of the heteroatom (or heteroatoms), as a result of intra- and intermolecular interactions with the p and π electrons of the other structural fragments of the molecule, may affect the polarity and polarizability of the molecule and the angles of rotation between the individual fragments, thereby changing the temperatures of the phase transitions, as well as the type of mesophase and the sign and magnitude of dielectric anisotropy – in other words, it may determine the principal physicochemical parameters of the liquid crystal [1].

The IR, UV, and NMR spectra of liquid crystals have been investigated extensively; however, mass-spectral data are virtually absent (there are only individual communications [2]), evidently as a consequence of the specific characteristics of mass-spectral experiments, in which the properties of the individual molecule rather than of their ensemble are studied. Nevertheless, mass-spectral information regarding liquid crystals can be extremely useful not only for the identification of individual substances but also in the chromatographic mass-spectrometric analysis of their mixtures without prior separation. The latter factor is the most important, since different compositions and multicomponent mixtures of mesogens are almost always employed when a liquid crystal is used; when a liquid crystal is put into use any of the components in the mixture may undergo destruction, thereby suffering a change in its original composition. These changes can be monitored by chromatographic mass-spectrometric and mass-fragmentographic methods of analysis, for the development of which one must first make a preliminary study of the mass spectra of the individual mesogens and also investigate the general principles of the fragmentation of liquid-crystal compounds of various classes under the conditions of the mass-spectral experiments. In the present research we investigated the PMR spectra and electron-impact mass spectra of 12 alkylaryl derivatives of phenylpyridines, which are liquid-crystal mesogens (Table 1).

The most characteristic signals in the PMR spectra are the signals of the protons of the pyridine ring. The signal of the α-H proton in α'-substituted pyridines stands out in an isolated fashion at weak field (8.35-8.88 ppm) in the form of a doublet (J = 2.0 Hz) [3-5], whereas in the case of β-arylpyridine I, in addition to the doublet of the α proton, one observes a doublet of doublets of an α' proton at 8.51 ppm (J = 5.0 and 2.0 Hz).

The intensities of the peaks of the molecular (M^+) and principal fragment ions in the mass spectra of I-XII in percent of the total ion current are presented in Table 2. One of the principal pathways of the fragmentation of the M^+ ions of the investigated compounds is the characteristic (for alkyl aromatic compounds [6]) cleavage of the β-C–C bond with the elimination of an alkyl radical and the formation of a charged fragment with the azatropylium structure (the F_1 ion). This fragmentation may be accompanied by migration of a hydrogen atom from the γ-carbon atom of the alkyl substituent to the β position of the aromatic ring

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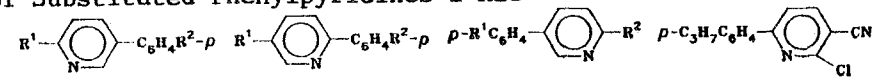
TABLE 1. PMR and Mass Spectra of Substituted Phenylpyridines I-XII



I, II III–V, X, XI VI–IX XII

Compound	R^1	R^2	δ, ppm (in CCl_4) α-H ($^4J_{\alpha\gamma}$ = 2,0 Hz)	β-H ($^3J_{\beta\gamma}$ = 8,0 Hz)	γ-H	C_6H_4 ($^3J_{AB}$ = 8,5 Hz)	CH_3, t ($^3J_{HH}$ = 6,5 Hz)	$(CH_2)_n$	CH_2Ph, t ($^3J_{HH}$ = 6,5 Hz)	m/z (relative intensities of the ion peaks in percent of the maximum peak)*
I	H	I	8,68 d 8,51 dd	7,18 dd	7,78 dd	7,22, 7,71	—	—	—	282 (13), 281 (100), 154 (25), 153 (6), 128 (6), 127 (26), 126 (9), 101 (4), 77 (4), 75 (4)
II	C_6H_{13}	I	8,58 d	6,98 d	7,62 dd	7,18, 7,78	0,88	1,38 br.s (8H)	2,58	356 (6), 322 (8), 309 (5), 308 (15), 296 (14), 295 (100), 181 (6), 168 (16), 167 (11), 166 (6)
III	C_5H_{11}	Br	8,35 d	7,27—7,46 m (4H)		7,75	0,88	1,28 br.s (6H)	2,58	305 (66), 303 (66), 249 (15), 248 (95), 247 (16), 246 (100), 167 (18), 141 (30), 140 (30), 139 (20)
IV	C_5H_{11}	CN	8,43 d	7,41—7,62 m (4H)		7,98	0,88	1,35 br.s (6H)	2,58	251 (10), 250 (53), 207 (4), 194 (25), 193 (100), 192 (9), 167 (3), 166 (14), 140 (14), 139 (5)
V	C_5H_{11}	C_6H_4CN-*p*	8,45 d	7,46 d	7,52 dd	7,68 (4H), 8,08 d (4H)	0,95	1,45 br.s (6H)	2,70	328 (3), 327 (23), 326 (82), 270 (23), 269 (100), 268 (3), 242 (12), 240 (9), 227 (10), 216 (7)
VI	C_6H_{13}	CN	8,83 d	7,78 d	7,98 d	7,25, 7,78	0,93	1,40 br.s (8H)	2,68	265 (10), 264 (49), 208 (4), 207 (13), 195 (6), 194 (4), 193 (100), 192 (26), 191 (4), 166 (5)
VII	C_8H_{17}	CN	8,88 d	7,77 d	7,98 dd	7,30, 7,50	0,88	1,28 br.s (12H)	2,58	293 (12), 292 (57), 227 (8), 195 (6), 194 (46), 193 (100), 192 (16), 166 (6), 57 (12), 55 (7)
VIII	C_5H_{11}	C_6H_4CN-*p*	8,88 d	7,82 d	7,92 dd	7,25 and 7,48, 7,72 and 8,15	0,96	1,42 br.s (6H)	2,65	327 (17), 326 (59), 270 (25), 269 (100), 268 (8), 267 (4), 219 (4), 166 (4), 140 (4), 115 (5)
IX	C_5H_{11}	C_6H_4Br-*p*	8,85 d	7,61 d	7,71 dd	7,18, 7,38, 7,51, 7,85	0,88	1,35 br.s (6H)	2,58	382 (19), 381 (81), 380 (20), 379 (78), 325 (20), 324 (100), 325 (25), 322 (96), 244 (15), 243 (14)
X	C_8H_{17}	C_2H_5	8,38 d	7,15 d	7,38 dd	7,15, 7,88	0,88	1,28 br.s (11H)	2,58	296 (19), 295 (75), 294 (12), 280 (11), 259 (9), 211 (16), 210 (45), 197 (54), 196 (100), 181 (21)
XI	C_6H_{13}	$C_6H_4C_8H_{17}$-*p*	8,58 d	7,32—7,50 m (4H)		7,13, 7,53 and 7,97	0,92	1,38 br.s (20H)	2,62	429 (7), 428 (38), 427 (100), 356 (20), 329 (21), 328 (73), 270 (10), 258 (13), 257 (49), 57 (11)
XII	—	—	—	7,78 d	7,85 d	7,18, 7,55	0,95	1,65 m (2H)	2,52	258 (11), 257 (6), 256 (32), 241 (6), 229 (30), 228 (17), 227 (100), 226 (7), 192 (8), 191 (8)

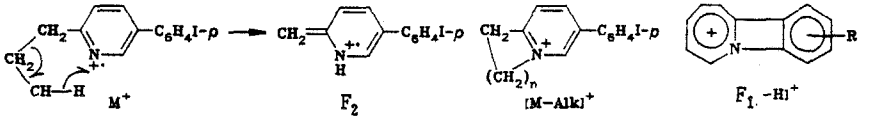
*The 10 most intense peaks are presented.

TABLE 2. Intensities of the Peaks of the Molecular and Principal Fragment Ions in the Mass Spectra of I-XII (Σ_{41})

Compound	M^+ (W_M)	F_1	F_1^*	F_2	$[F_1-H]^+$	F_3	$[M-Alk]^+$	$[F_1-HCN]^+$
I	50,9	—	—	—	—	—	—	13,8
II	2,7	1,5	—	49,7	—	—	12,8	6,2
III	26,5	37,2	—	1,0	—	—	0,8	0,4
IV	24,3	42,5	—	4,4	3,6	—	1,9	1,5
V	34,4	38,5	—	0,7	2,2	—	0,5	3,8
VI	20,7	37,7	—	10,8	10,0	—	4,8	2,6
VII	19,2	29,8	—	9,5	4,8	—	0,8	2,2
VIII	27,4	41,8	—	1,9	3,1	—	0,5	0,3
IX	35,4	40,9	—	0,7	0,4	—	0,4	1,5
X	17,3	20,6	1,9	6,9	1,3	5,2	16,0	1,5
XI	29,7	5,1	18,7	0,2	—	13,2	4,1	—
XII	18,0	52,2	—	0,4	2,9	—	3,1	5,0

(with respect to the alkyl group [7]), as a result of which an olefin molecule is split out in the form of a neutral fragment, and the charge is retained in the aromatic system (the McLafferty rearrangement; the F_2 ion). The indicated processes depend markedly on the position and length of the alkyl substituent, which not only determine the dissociative ionization processes but also affect the stability of the molecule in general and the thermal stability in particular.

Compound I, which does not have an alkyl substituent, differs from all of the alkylarylpyridines with respect to its high stability to electron impact; 51% of the total ion current is due to the M^+ ion. The $[M - I]^+$, $[M - HI]^+$, and $[M - I, - HCN]^+$ ions make a substantial contribution (30%) to the total ion current for this compound. The introduction of an alkyl substituent into the α position of the pyridine ring (II) sharply decreases the W_M value, and the dominating process becomes fragmentation via the mechanism of the McLafferty rearrangement, which is determined by primary localization of the cation-radical center in M^+ on the nitrogen atom:



Adjacency of the alkyl substituent to the pyridine nitrogen atom is also manifested in the simultaneous splitting out from M^+ of alkyl radicals with different lengths and stabilization of the resulting radical centers through cyclization at the nitrogen atom [8]; the substituent as a whole may be eliminated from M^+. The sum of the currents of the indicated $[M - Alk]^+$ ions without allowance for tropylium fragment F_1 is 13%; this is not observed in the mass spectra of the other compounds.

When the alkyl substituent is located in the γ position of the pyridine ring (III-V), the stability of M^+ increases substantially, the rearrangement process is suppressed, and β-cleavage of the substituent with the formation of phenylazatropylium cation F_1 becomes dominant.

It should be noted that the stability of M^+ depends not only on the position and length of the aliphatic chain but also on the electronic properties of the other substituents. Thus replacement of the Br atom by a stronger acceptor nitrile group (IV) decreases W_M; the fraction of the current of the F_2 ions increases in this case. A strong acceptor substituent in the para position of the phenyl ring, by drawing away the electrons from the pyridine ring, evidently concentrated the residual electron density in its α and γ positions and thereby facilitates the rearrangement process. This effect of an acceptor is weakened in the fragmentation of V.

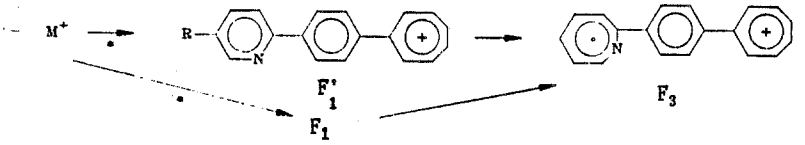
One's attention is directed to the absence in the mass spectrum of III of a tricyclic $[F_1 - H]^+$ ion, which is characteristic for β-phenylpyridines [6]. This fact is possibly explained by the specific behavior of the Br atom, splitting out of which by F_1 ions proves to be a more favorable fragmentation process, and a similar tricyclic fragment, which, however, does not contain a substituent, is formed as a result of a sigmatropic shift. Peaks

of $[F_1 - H]^+$ ions are observed in the mass spectra of most of the other investigated compounds; the genetic relationship between the F_1 and $[F_1 - H]^+$ ions is confirmed by corresponding metastable transformations.

The addition of yet another aromatic ring markedly increases the W_M value, and this principle is observed in all cases (V, VIII, IX, XI).

Compounds VI-IX contain alkylbenzene fragments. It is known [7] that with an increase in the length of the alkyl chain from $C_{(1)}$ to $C_{(20)}$ the fraction of the tropylium cations in the total ion current changes from 39% to 19%, passing through a maximum of 51% for $C_{(3)}$, whereas the fraction of the ion formed as a result of the McLafferty rearrangement is approximately the same for $C_{(4)}$–$C_{(20)}$ alkylbenzenes and amounts to ~16-18%.* It is apparent from Table 2 that the change in the current of the F_1 ions as a function of the length of the normal alkyl chain obeys the above-indicated principle; however, the contribution of the F_2 rearrangement ions to the total current is significantly lower and in only two cases (VI and VII) gives a value of the same order of magnitude. Particular attention should be directed to the very intense signal of the $[F_1 - H]^+$ ion in the case of VI, in which the alkylphenyl substituent, in contrast to the other compounds, is located in the β position; this facilitates the formation of the tricyclic ion discussed above. This feature can be used in the mass-spectrometric determination of the position of the aryl substituent in such arylpyridines.

The presence of two alkyl substituents in both the benzene and pyridine rings of XI and XII leads to the development of an additional fragmentation pathway with β cleavage of both substituents in a different sequence with the formation of, in addition to F_1 fragments, F'_1 and F_3 ions. The first acts in the fragmentation are confirmed by the peaks of the corresponding metastable ions.



It should also be noted that in the mass spectrum of X one observes an intense (11.6% in the total current) peak of $[M - C_6H_{13}]^+$ ions, the formation of which does not fit into the general scheme of the fragmentation and is due to cleavage of the γ-C–C bond in M^+.

Thus, on the basis of this analysis of the PMR and mass spectra of arylalkylpyridines it may be concluded that these methods make it possible to reliably identify the position of the alkyl and aryl substituents in the pyridine ring. The fragmentation of arylalkylpyridines is described by a single general scheme and is characterized by high selectivity (the M^+ ion and the three principal fragment ions constitute more than 50% of the total ion current). These results can be used in the chromatographic mass-spectrometric identification of compounds of this class, and the signals of the $F_1 - F_3$ fragment ions, together with the M^+ signal, can serve as a standard for mass-fragmentographic analysis.

EXPERIMENTAL

Compounds I-XII were synthesized by the methods in [9-12]. The PMR spectra were obtained with a Tesla BS-467 spectrometer (60 MHz). The mass spectra were obtained with an MKh-1320 mass spectrometer at 20°C; the ionizing energy was 50 eV, and the cathode emission current was 0.6 mA.

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*It is 1.5% for propylbenzene.

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STEREOCHEMISTRY OF NITROGEN HETEROCYCLES. 62.* CONFORMATIONAL ANALYSIS OF ISOMERS OF 2-METHYL-cis-DECAHYDRO-5-QUINOLINOL

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Isomers of 2-methyl- and 1,2-dimethyl-cis-decahydro-5-quinolinol with a syn orientation of the hydroxy and amino groups and different orientations of the methyl group relative to the methylene group at $C_{(8)}H_2$ were subjected to conformational analysis. In the case of a cis orientation of the methyl and methylene groups the equilibrium is shifted completely to favor the conformation with an intramolecular hydrogen bond, whereas in the case of their trans orientation the mole fraction of this conformation amounts to 21-24% for the secondary amino alcohol and 18-21% for the tertiary amino alcohol. The energies of the hydrogen bonds were determined from the intensities of the absorption bands of the free and associated hydroxy groups in the IR spectra: for the secondary hydroxy amine, according to the band of the free hydroxy group, $\Delta G^{\circ}_{OH/N}$ is −0.8 kcal/mole, whereas, according to the band of the associated hydroxy group, it is −0.9 kcal/mole; the values for the tertiary hydroxy amine are, respectively, −0.7 and −0.8 kcal/mole.

In previous studies we have described the synthesis and structures of isomers of 2-methyl- and 1,2-dimethyldecahydro-5-quinolinol [2-4]; it was shown that the isomers of 2α-methyl- and 1,2α-dimethyl-cis-decahydro-5α-quinolinol† (I and II) with a syn orientation of the hydroxy and amino groups and a cis orientation of 2-CH_3 relative to $C_{(8)}H_2$ exist in a conformation with an intramolecular hydrogen bond both in the crystalline state and in solution. This bond is retained both for the base and for the hydrochloride – only its character changes: OH···N for the base, and N^+H···O for the hydrochloride.

For the other isomer – with cis fusion of the rings and a syn orientation of the hydroxy and amino groups but with a trans orientation of the methyl group relative to $C_{(8)}$ [2β-methyl-cis-decahydro-5α-quinolinol (III)], which, according to x-ray diffraction analysis [5], exists in the crystalline state in a steroid conformation with equatorial hydroxy and methyl groups – a band of the stretching vibration of an associated hydroxy group at 3390 cm^{-1} of

*See [1] for Communication 61.

†The symbol α denotes a trans orientation of the substituent with respect to 9-H, while β denotes a cis orientation.

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