EFFECT OF THE POSITION AND NUMBER OF METHYL GROUPS ON THE ACOUSTIC PARAMETERS OF MONO- AND DIMETHYLPYRIDINES AND INTERRELATIONSHIP BETWEEN THE REACTIVITIES AND NONLINEAR PROPERTIES

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The effect of the position and number of methyl groups in a series of mono- and dimethylpyridines on the low-frequency spectrum of an acoustic wave passing through the liquid was studied. Evaluation of the correlation of the changes in the "nonlinearity parameter" with the ionization constants (pK_a) demonstrated that the nonlinear properties of mono- and dimethylpyridines, like the ionization constants, correlate with their structures and correspond to the known dependences on the inductive and mesomeric effects of substituents, which determine their reactivities.

The currently adopted structural formula of the pyridine ring satisfactorily explains the characteristic properties of pyridine derivatives, which are sometimes united [1] under the general concept of "aromaticity" of the 3 position in the pyridine ring and the "anomalous" behavior of the 2 and 4 (α and γ) positions. For methylpyridines, this is expressed in the activity of the hydrogens of the methyl groups of α- and γ-picolines and the relative inertness of β-picoline. The enumerated properties are in agreement with the modern theory of organic chemistry if it is taken into account that the heteroatom in pyridine has an activating effect on nucleophilic substitution in the 2 and 4 positions. This effect is also retained in methylpyridines due to the fact that the dipole moment caused by the electron pair of the nitrogen atom induces dipole moments (although considerably smaller) in the adjacent bonds. These induction (+I) and mesomeric (+M) effects affect the reactivity of the methylpyridine molecule [2]; this is especially graphically displayed on comparison of the ionization constants (pK_a) of methylpyridines [3]. It is known [3, 4] that the nitrogen atom in a heterocyclic ring changes its basicity as a function of the position and number of methyl substituents. This makes it possible to use the pK_a to establish the structures of methylpyridines.

The change in the nonlinear properties in homologous series of n-alkanes and the effect of the presence of a double bond and OH and SH groups in molecules of the investigated compounds on the spectra of the molecular isostructure were previously investigated [5] by means of acoustic spectra. The nonlinearity (i.e., the nonlinear equation of state) of liquids can be determined from the results of an investigation of the spectrum of the acoustic wave taken on by the liquid. The nonlinearity parameter (N), which is the ratio of the acoustic power of the second harmonic [$(P_2)_{ac}$] in the spectrum of the wave taken on to the power of the first harmonic [$(P_1)_{ac}$], enters into the exponent of this equation and characterizes the nonlinear elasticity of the liquid. The proposed method for the evaluation of changes in N in the investigated group of compounds is based on measurement of the relative change in $(P_2)_{ac}$ for a constant $(P_1)_{ac}$. In connection with the first positive results [5], it seemed expedient to examine the positions set forth above in the case of the link between the structures and nonlinear acoustic properties of methylpyridines and also to evaluate the correlation of the relative changes in N and pK_a for the indicated series of compounds.

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TABLE 1. Nonlinearity Parameters (N and pK_a) of Methylpyridines

Compound	Name	N (rel. units)	pK_a
I	Pyridine	1,000	5,22
II	α-Picoline	1,135	5,94
III	β-Picoline	1,079	5,65
IV	γ-Picoline	1,149	6,03
V	2,3-Lutidine	1,263	6,58
VI	2,4-Lutidine	1,270	6,65
VII	2,6-Lutidine	1,281	6,75

The following compounds were investigated: pyridine (I), 2-methylpyridine (II), 3-methylpyridine (III), 4-methylpyridine (IV), 2,3-dimethylpyridine (V), 2,4-dimethylpyridine (VI), and 2,6-dimethylpyridine (VII). The changes in the nonlinear properties of the methylpyridines were determined from the intensity of $(P_2)_{ac}$ in the acoustic wave spectrum relative to the intensity of $(P_2)_{ac}$ in pyridine. The experimental pK_a and N values (in relative units) for all of the indicated compounds are presented in Table 1. The empirical correlation coefficient ($r = 0.893$) was calculated for the data in Table 1 to evaluate the correlation between the pK_a and N. The existence of a correlation, even though it is not entirely satisfactory in this case, is, in our opinion, a certain experimental basis for the possibility of using the results of measurements of nonlinear elasticity properties for the determination of the number and position of CH_3 groups in methylpyridines, since it is presently supposed [3] that the ionization constants of methylpyridines correlate with their structures and correspond to the known dependences on the inductive and mesomeric effects of substituents.

The reactivities of CH_3 groups in the 2 and 4 positions are expressed in the fact that the hydrogen atoms of these groups react with aldehydes and nitroso compounds. A methyl group in the 3 position does not have this property. This anomalous behavior is also in agreement with the change in N and pK_a in III. The problem of the relative reactivities of CH_3 groups in the 2 and 4 positions has received little study. However, a study of the kinetics of deuterium exchange in the methyl groups of isomeric methyl-N-alkylpyridinium ions has shown that a CH_3 group in the 2 position is more active than one in the 4 position [6]. This is in agreement with the theory of nonlinear properties of condensed systems [7], if it is taken into account that the pK_a values characterize the relative tendency for the addition of a proton. Considering that the energy of the bond of a proton with the molecule in compounds that have strong acidic properties is weaker, it can be assumed that these compounds are less "rigid" (lower N values), and that compounds that are inclined to add a proton are more "rigid"; i.e., their nonlinear elasticity is greater.

The absolute values of the "nonlinearity parameter" of lutidines are higher than the nonlinear elasticity of picolines (see Table 1); this is also in agreement with the increase in the basicity in V, VI, and VII. However, in view of the absence of normalization of the results of measurements of $(P_2)_{ac}$ for acoustic resistances, the change in N in the lutidine series is within the range of experimental error. One can only note the fact that the differences in the nonlinear elasticity properties of the investigated lutidines are just as small as the change in their pK_a values.

Thus the experimental results of an investigation of the change in the nonlinear elasticity properties as a function of the number and position of the CH_3 groups in mono- and dimethylpyridines show that the "nonlinearity parameter," like the ionization constants (pK_a), correlates with the structures and corresponds to the regularities of the inductive and mesomeric effects of substituents.

EXPERIMENTAL

Chromatographically pure substances were used for the analyses. The determinations were accomplished by gas-liquid chromatography (GLC) with a UKh-2 chromatograph with a 3-m long column packed with polyethylene glycol adipate (12%) on Cellite 545 (80-100 mesh fraction) at 140-200° with a nitrogen flow rate of 45 ml/min. The column was packed with SKTV (10%) on Cellite 545 in the case of II, III, and VII.

The spectrophotometric determinations of the pK_a values were made with an SF-4A spectrometer from aqueous solutions ($1 \cdot 10^{-3}$-$4 \cdot 10^{-3}$ M). The mean-square error in each determination did not exceed 0.03 pK_a units.

The apparatus and method for the measurements of the change in the "nonlinearity parameter" of the liquids were examined in [8]. The liquid to be investigated was poured into an 11-cm^3 glass chamber. The temperature in the chamber was maintained at $20 \pm 0.05°$ by means of an ultrathermostat. The sound wave ($f = 3$ kHz) was introduced into the liquid from a magnetostrictive transformer through an acoustic exponential transformer. A TsTS-19 piezoceramic was used as the receiver. The spectrum of the picked-up signal was analyzed with a spectral analyzer – an SK4-13 millivoltmeter. The mean-square error in each determination of the absolute value of the "nonlinearity parameter" did not exceed 0.025 N units.

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