Thus, in contrast to I-IV, N-methylisatin α-anils display the ability to exist in the form of a mixture of syn and anti isomers; this is due to the presence in the 3 position of the heteroring of a C=O group, which has a greater volume than the oxygen and sulfur atoms and the methylene group. In this case syn–anti isomerization at the C=N bond in the V molecules is realized via an inversion mechanism.

EXPERIMENTAL

The PMR spectra of deuterochloroform solutions of the compounds were recorded with a Jeol C-60HL spectrometer with tetramethylsilane as the standard. In the calculations of the kinetic parameters the temperature was determined with respect to a standard sample of methanol. The accuracy in the determination of the temperatures was ±1°C, and the isomer ratio ranged from 3 to 5%. With allowance for these errors, the accuracy in the determination of the $\Delta G^{\neq}$ values was ±0.3 kcal/mole.

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SPECTROSCOPIC AND QUANTUM-CHEMICAL STUDY OF 5-ALKOXYPYRIDINE-2- AND 6-ALKOXYPYRIDINE-3-CARBOXYLIC ACIDS

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The peculiarities of the structures of 5-alkoxypyridine-2- and 6-alkoxypyridine-3-carboxylic acids were studyed by experimental (IR, UV, and PMR spectroscopy) and quantum-chemical methods. It was established that both types of compounds exist in the form of dimers in the crystalline state, whereas in CCl_4 the first type exist in the form of monomers, while the second type exist in the form of dimers and monomers in dynamic equilibrium. The ability to form an intramolecular hydrogen bond and the interaction of the unshared pairs of electrons of the ring nitrogen atom and the oxygen atom of the C=O group are among the reasons for the absence of liquid-crystal properties in 5-alkoxypyridine-2-carboxylic acids as compared with 6-alkoxypyridine-3-carboxylic acids, which have such properties. From the point of view of the electronic structures, 6-alkoxypyridine-3-carboxylic acids differ from 5-alkoxypyridine-2-carboxylic acids in that in the former the ring nitrogen atom and the COOH and OAlk groups have an identical effect on the sign of the π-electron charges of the ring carbon atoms, and their π-dipole moments are directed virtually along the longitudinal axis of the molecule.

In liquid-crystal compounds replacement of a benzene ring by a pyridine ring in a number of cases leads to a substantial change in the mesomorphic properties [1]. Of the simplest potentially mesomorphic 5-alkoxypyridine-2- (I) and 6-alkoxypyridine-3-carboxylic acid (II) derivatives that we synthesized, which can be regarded as analogs of liquid-crystal p-alkoxybenzoic acids (III), only II have liquid-crystal properties. At the same time, a decrease in the melting point as compared with the corresponding III is observed for both series I and II. It is known that the liquid-crystal properties of aromatic carboxylic acids are due to the formation of dimers through intermolecular hydrogen bonds of the carbonyl groups [2].

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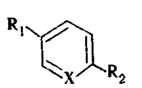
TABLE 1. Frequencies (ν, cm^{-1}) of the Characteristic Vibrations of the O—H and C=O Bonds in the IR Spectra of Compounds of the



Type

X	R$_1$	R$_2$	In CCl$_4$		In KBr	
			ν_{OH}	$\nu_{C=O}$	ν_{OH}	$\nu_{C=O}$
N	COOH	OC$_4$H$_9$	2400—3600 2556, 2680, 3555	1693, 1740	2400—3600 2545, 2660	1694
N	COOH	OC$_5$H$_{11}$	2400—3600 2555, 2680, 3560	1693, 1740	2400—3600 2545, 2655	1695
N	COOH	OC$_6$H$_{13}$	2400—3600 2556, 2680, 3555	1693, 1740	2400—3600 2550, 2655	1695
N	COOH	OC$_7$H$_{15}$	2400—3600 2556, 2680, 3560	1693, 1740	2400—3600 2545, 2660	1694
CH	COOH	OC$_4$H$_9$	2400—3600 2568, 2680, 3560	1697, 1745	2400—3600 2570, 2680	1697
CH	COOH	OC$_6$H$_{13}$	2400—3600 2568, 2680, 3560	1697, 1745	2400—3600 2570, 2680	1697
CH	COOH	OC$_7$H$_{15}$	2400—3600 2565, 2680, 3560	1697, 1745	2400—3600 2570, 2680	1698
N	OC$_4$H$_3$	COOH	3363 br. int	1700	2400—3600 2555, 2630	1700
N	OC$_5$H$_{11}$	COOH	3363 br. int	1700	2400—3600 2560, 2720	1700
N	OC$_6$H$_{13}$	COOH	3363 br. int	1700	2400—3600 2560, 2700	1700
N	OC$_7$H$_{15}$	COOH	3363 br.int	1700	2400—3600 2555, 2700	1700

The introduction of a nitrogen atom in the ring expands the possibilities for the formation of different types of hydrogen bonds. The aim of the present research was to make a comparative study of the structures of I-III (Table 1) by experimental (IR, UV, and PMR spectroscopy) and quantum-chemical methods and to ascertain the effect of hydrogen bonds and the peculiarities of the structures on the change in their mesomorphic properties.

IR Absorption Spectra

A broad absorption band at 2400-3600 cm^{-1} with two weak maxima in the region of stretching vibrations of the O—H bond and a band at 1693-1700 cm^{-1} in the region of the stretching vibrations of the C=O bond are observed in the IR spectra of crystalline I-III in KBr pellets (Table 1). It is known that spectra of this type are characteristic for dimers of carboxylic acids [3, 4]. Consequently, in the crystalline state these compounds exist in the form of dimers connected by a strong intermolecular hydrogen bond through the carbonyl and hydroxyl groups of two molecules.

It follows from an analysis of the IR spectra of solutions of benzoic acid that in CCl$_4$ it exists in the form of both a dimer ($\nu_{C=O}$ 1699 cm^{-1}) and a monomer ($\nu_{C=O}$ 1745 cm^{-1}), and that the absorption of the C=O bond that characterizes the dimer is considerably more intense than the absorption for the monomer [5].

The vibration of the O—H bond in the spectra of II and III (Table 1) in dilute CCl$_4$ solution shows up in the form of a broad absorption band at 2400-3500 cm^{-1} and a low intensity maximum at a 3560 cm^{-1}, close to the frequency of the stretching vibration of the nonassociated O—H group [3]. The absorption of the C=O bond in the spectra of these compounds is characterized by two bands — an intense band at 1693-1697 cm^{-1} and a weak band at 1740-1745 cm^{-1} (Table 1 and Fig. 1). Consequently, in CCl$_4$ solution the indicated compounds exist in two forms in dynamic equilibrium — the dimer ($\nu_{C=O}$ 1693-1697, ν_{OH} 2400-3500 cm^{-1}), with an intermolecular hydrogen bond of the —C=O...HO— type, and the monomer ($\nu_{C=O}$ 1740-1745, ν_{OH} 3560 cm^{-1}).

It follows from an analysis of the IR spectra that I exists in CCl_4 (Table 1) in the form of monomers with an intramolecular hydrogen bond between the hydrogen atom of the carboxyl group and the ring nitrogen atom; this is characteristic for picolinic acid and its derivatives [4]. The absence in the spectra of I of a broad absorption band at 2400-3600 cm^{-1} and the presence of an intense absorption band at 3363 cm^{-1} (Table 1) constitute evidence in favor of this. The position and intensity of these bands in the spectra do not change in the case of successive dilution to $5 \cdot 10^{-4}$ M.

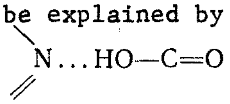
The band of stretching vibrations of the C=O group of the monomers of compounds of the I type at 1770 cm^{-1} is also shifted 30 cm^{-1} with respect to the $\nu_{C=O}$ band at 1740 cm^{-1} of the monomers of II and III. This is in agreement with the formation of an intramolecular hydrogen bond that includes the unshared pair of electrons of the oxygen atom in a six-membered chelate ring, which should lead to weakening of the conjugation of the unshared pair of electrons with the C=O group and reinforcement of the inductive effect and, consequently, to a 30 cm^{-1} shift in the $\nu_{C=O}$ band.

It is interesting to note that one absorption band of a C=O bond is observed in the spectra of ethyl esters II at 1722 cm^{-1}, whereas there are two bands in the spectra of I — an intense band at 1719 cm^{-1} and a weak band at 1745 cm^{-1} (Fig. 1, spectrum b). This constitutes evidence for the existence of two rotational isomers for ethyl esters I because of interaction of the unshared pair of electrons of the oxygen atom of the carboxyl C=O bond with the unshared pair of electrons of the nitrogen atom.

Thus the ability to form an intramolecular hydrogen bond and the interaction of the unshared pair of electrons of the ring nitrogen atom and the oxygen atom of the C=O group are among the reasons for the absence of liquid-crystal properties in the I molecules as compared with the II and III molecules, which have liquid-crystal properties.

It follows from the UV absorption spectra of compounds of the I and II type in neutral (ethanol), alkaline, and acidic media that ionization of the COOH group has virtually no effect on the maximum of the long-wave λ_{max} band and that protonation of the ring nitrogen atom gives rise to 10 and 13 nm bathochromic shifts of λ_{max}, in the spectra of I and II, respectively (Table 2).

The UV spectra of II in water are virtually identical to the spectra of II in ethanol, and the UV spectra of I in water are almost identical to the spectra in acidic media (Table 2). Consequently, I exist primarily in the dipolar form (with a protonated ring atom and a COO^- group) in aqueous media, whereas II exist primarily in the neutral form.

The difficulty in the formation of the dipolar form of II in aqueous media as compared with I can evidently be explained by the presence of an intermolecular hydrogen bond of the $-C{=}O\ldots HO$ type in the dimers of II. On the other hand, the ease of formation of the dipolar form of I in aqueous media can be explained by the existence in these compounds of an intramolecular hydrogen bond of the  $N\ldots HO{-}C{=}O$ type, which promotes the addition of a proton to the ring nitrogen atom with ionization of the COOH group.

Thus the UV spectroscopic data confirm the conclusions regarding the difference in the structures of molecules of the I and II types that were drawn on the basis of an analysis of the IR spectra of these compounds.

Let us examine the peculiarities of the electronic structures of compounds of the I-III type.

A criterion for the reliability of the calculation of the distribution of the π-electron density (g_r) in I-III is the qualitative agreement between the order of the chemical shifts of the ring protons and the order of the g_r values for the corresponding carbon atoms.

In fact, it is apparent from a comparison of the chemical shifts of the H_3, H_4, and H_6 protons in the PMR spectra of I-III (Table 3) and the g_3, g_4, and g_6 values for the C_3, C_4, and C_6 atoms in these compounds (Table 4) that the orders of increasing chemical shifts for compounds of the I-III type ($H_3 < H_4 < H_6$, $H_4 < H_3 > H_6$, and $H_3 < H_4$, respectively) are basically similar to the orders of decreasing g_r values ($g_3 > g_4 > g_6$; $g_4 > g_3, g_6$; $g_3 > g_4$) of the corresponding carbon atoms in I-III.

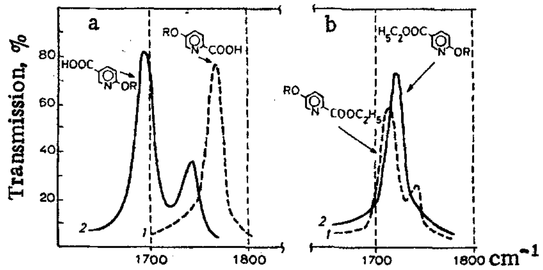
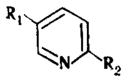


Fig. 1. Absorption of the C=O bond in the IR spectra (CCl_4 solutions): a) compounds of the I (1) and II (2) type; b) their ethyl esters.

TABLE 2. UV Spectroscopic Data for Compounds of the Type



Type	R_2	R_1	Solvent	λ_{max_n}, nm	$\varepsilon_{max_n} \cdot 10^{-3}$
II	OC_4H_9	COOH	Ethanol	243 273,5	13,00 6,25
			25% Ethanol	240,5 275	11,50 6,25
			H_2O	240 275	10,85 6,00
			1 N HCl	235,5 283,5	10,20 8,95
			1 N KOH	238 275	11,00 5,66
II	OC_6H_{13}	COOH	Ethanol	243,5 273,5	12,80 6,26
			25% Ethanol	240 275	11,65 6,26
			H_2O	240 275	10,20 5,90
			1 N HCl	235,5 283,5	10,90 9,36
			1 N KOH	238 275	11,55 6,05
I	COOH	OC_4H_9	Ethanol	248 282	12,55 7,16
			25% Ethanol	245 289	9,40 6,70
			H_2O	245 290	8,66 7,16
			1 N HCl	254 295	7,75 10,78
			1 N KOH	242 282	10,92 6,28
I	COOH	OC_6H_{13}	Ethanol	248,5 282	12,59 7,25
			25% Ethanol	245 289	9,45 6,65
			H_2O	245 290	8,96 7,18
			1 N HCl	254,5 295,5	79,5 11,70
			1 N KOH	242,5 281,5	10,60 6,10

TABLE 3. PMR Spectroscopic Data Relative to Tetramethylsilane: Chemical Shifts of the Ring Protons, Multiplicities, and Spin-Spin Coupling Constants for I-III

Compound	Solvent	H_3	H_4	H_6
I	CD_3OD	8,11, d, 9,0	7,46, q, 9,0 3,0	8,27, d, 3,0
II	CD_3OD	6,80, d, 9,0	8,17, q, 9,0, 3,0	8,63 d, 3,0
III	CD_3OD	7,00, m, 2H	8,00, m, 2H	8,00, m, 2H

The carboxyl group in I-III has an electron-acceptor effect on the distribution of π-electron charge (Δg_r) in the aromatic ring, while the alkoxy group (OAlk) has an electron-donor effect. The COOH group gives rise to accumulation of positive π-electron charge in the ortho and para positions and negative π-electron charges in the meta position, whereas the OAlk group, on the other hand, causes the accumulation of negative π-electron charge in the ortho and para position and positive π-electron charge in the meta position. The inductive effect of the ring nitrogen atom leads to the accumulation of negative π-electron

TABLE 4. Distribution of the π-Electron Charges (Δg_r) in the Neutral Forms of I-III in the Ground State

Compound	Heteroring atoms						COOH group			OAlk
	$N(C_1)$	C_2	C_3	C_4	C_5	C_6	$O^{\cdot\cdot}$	C	$O^{\cdot}$	$O^{\cdot\cdot}$
I	−0,209	+0,012	+0,044	−0,047	+0,023	+0,021	+0,254	+0,221	−0,515	+0,197
II	−0,301	+0,109	−0,090	+0,089	−0,084	+0,111	+0,246	+0,220	−0,521	+0,222
III	−0,090	+0,034	−0,083	+0,054	−0,071	+0,010	+0,246	+0,220	−0,520	+0,200

TABLE 5. Calculated Dipole Moments (D) and Heats of Atomization (eV) for Compounds of the I-III Type

Compound	μ_π	$\alpha_\mu{}^0$	μ_x	μ_y	ΔH
II	4,91	112	−1,86	4,54	80,58
I	5,32	5	5,30	0,42	75,94
III	5,58	107	−1,65	5,33	80,96

charge on the nitrogen atom and in the meta positions and positive π-electron charge in the ortho and para positions.

The orientation of the COOH and OAlk groups and the ring nitrogen atom in II and III is such that their effects on the Δg_r values of the ring are of the same sign. As a result of this, the direction of the calculated π-dipole moment (μ_π) in II and III virtually coincides (α_μ = 107-112° relative to the x axis) with the direction of the longitudinal axis of these compounds (Table 5).

On the other hand, in compounds of the I type the orientation of the ring nitrogen atom is such that its effect on the Δg_r values of the ring is the opposite of the effects on the Δg_r values of the COOH and OAlk groups (Table 3). Because of this, the direction of the calculated π-dipole moment of molecules of the I type (Table 5) virtually coincides with the direction of the transverse axis of these molecules (α_μ = 4.5° relative to the x axis).

Thus from the point of view of the electronic structures, the liquid crystals of the II and III type differ from I, which do not have liquid-crystal properties, in that the ring nitrogen atom and the COOH and OAlk groups in the former have identical effects on the Δg_r values of the ring (with respect to the sign of the charge), and their π-dipole moments are directed virtually along the longitudinal axis of the molecule.

We calculated the heats of atomization (ΔH), which are the most reliable quantum-chemical values for evaluation of the stabilities of compounds, for compounds of the I-III type (Table 5). It follows from an analysis of the ΔH values that compounds of the II and III type have close stabilities and are more stable than compounds of the I type.

The difference in the electronic structures of II, III, and I is also manifested in the peculiarities of the nature of the absorption bands in the electronic spectra of these compounds. In fact, it follows from a comparison of the experimental ΔE_n^{max} values and the calculated transition energies (ΔE_n), as well as from an analysis of the coefficients $[A_n(i \to j)]$ of the configuration interaction matrixes (Table 6) that in the electronic spectra of compounds of the I type both absorption bands (ΔE_{max_1} and ΔE_{max_2}) are due to an almost identical extent to the $\pi \to \pi^*$ singlet—singlet transitions from the upper occupied molecular orbital (UOMO) to the lower-vacant MO (LVMO) and to the second vacant MO (VMO), whereas in the UV spectra of II and III the second absorption band with ΔE_{max_2} is due primarily to a $\pi \to \pi^*$ transition ($6 \to 7$) from the UOMO to the LVMO, and the long-wave band with ΔE_{max_1} is due primarily to a $\pi \to \pi^*$ transition from the UOMO to the second VMO (Table 6).

EXPERIMENTAL

The IR spectra of KBr pellets and CCl_4 solutions ($3 \cdot 10^{-3}$-$5 \cdot 10^{-4}$ M) of I-III at 400-4000 cm^{-1} were recorded with a UR-20 spectrophotometer (Table 1). The accuracy in the determination of the frequencies in the range of an NaCl prism was ±2 cm^{-1}, as compared with ±4 cm^{-1} in

TABLE 6. Calculated and Experimental Data on the Electronic Absorption Spectra of the Neutral Forms of Compounds of the I-III Type (eV)

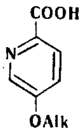
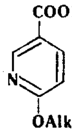
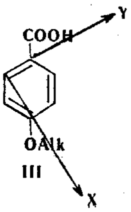
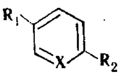
Compound	Calculated				Experimental	
	ΔE_n	f_n	$\alpha_n{}^\circ$	$A_n(i \rightarrow j)$	$\Delta E_{\max_n}$	$\varepsilon_{\max_n} \cdot 10^{4}$
 I	4,34	0,186	11	0,66 (6—7); 0,63 (6—8)	4,40	0,72
	4,86	0,560	−32	0,71 (6—7); 0,65 (6—8)	4,97	1,26
 II	4,49	0,124	9,3	0,81 (6—8); 0,39 (6—7)	4,52	0,63
	5,03	0,664	−47	0,89 (6—7); 0,38 (6—8)	5,07	1,28
 III	4,38	0,036	79	0,83 (6—8); 0,51 (5—7)	4,41	0,176
	4,86	0,654	−34	0,96 (6—7); 0,19 (5—8)	4,88	1,56

TABLE 7. Transition Temperatures of Compounds of the Type



No.	X	R₁	R₂	T_{lc}[a]	T_i[b]	Found, %			Empirical formula	Calc., %			Yield, %
						C	H	N		C	H	N	
1	N	C_4H_9O	COOH	95.0	—	61,6	6,7	6,8	$C_{10}H_{13}O_3$	61,5	6,7	7,2	20
2	N	COOH	C_4H_9O	98,6	86,7[c]	61,9	6,6	6,9	$C_{10}H_{13}O_3$	61,5	6,7	7,2	44,7
3	CH	C_4H_9O	COOH	147,0	160,0[d]	—	—	—	—	—	—	—	—
4	N	$C_5H_{11}O$	COOH	94,5	—	63,1	7.1	6,6	$C_{11}H_{15}O_3$	63,1	7,2	6,7	18,1
5	N	COOH	$C_5H_{11}O$	95,4	—	63,5	7,1	6,3	$C_{11}H_{15}O_3$	63,1	7,2	6,7	43,0
6	CH	$C_5H_{11}O$	COOH	124,0	151,0	—	—	—	—	—	—	—	—
7	N	$C_6H_{13}O$	COOH	80,3	—	64.3	7,3	6,0	$C_{12}H_{17}O_3$	64.5	7,7	6,3	23,2
8	N	COOH	$C_6H_{13}O$	93,2	90,8	64,2	8,0	6,3	$C_{12}H_{17}O_3$	64,5	7,7	6,3	53,3
9	CH	$C_6H_{13}O$	COOH	105,0	153,0	—	—	—	—	—	—	—	—
10	N	$C_7H_{15}O$	COOH	95,0	—	65,4	7,6	5,7	$C_{13}H_{19}O_3$	65,8	8,1	5,9	28,5
11	N	COOH	$C_7H_{15}O$	88,5	89.5	65,8	8,0	5,6	$C_{13}H_{19}O_3$	65,8	8,1	5,9	40.2
12	CH	$C_7H_{15}O$	COOH	92,0	146,0	—	—	—	—	—	—	—	—
13	N	COOH	$C_8H_{17}O$	87,8	93,3	66.9	8.0	5,6	$C_{14}H_{21}O_3$	66,9	8,4	5,6	56,4
14	CH	$C_8H_{17}O$	COOH	101,0	147,0	—	—	—	—	—	—	—	—

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[a] This is the temperature of conversion from the solid state to the liquid-crystal state. [b] This is the temperature of conversion to the isotropic liquid. [c] Monotropic liquid crystals. [d] All compounds III were described in [2].

the range of an LiF prism. The electronic spectra of the compounds were recorded with a Hitachi EPS-3T spectrophotometer. The PMR spectra of CD_3OD solutions of the compounds were recorded with a Varian 100D spectrometer at 20°C with tetramethylsilane as the internal standard. The ring protons of the p-alkoxy derivatives of benzoic acid give a spectrum of AA'BB' type — two two-proton multiplets (m, 2H); the multiplet at weaker field was assigned to the protons attached to C_4 and C_6, which are in the α position relative to the carboxyl group. The assignment of the signals in the spectra of I-II was made on the basis of their multiplicities and their spin—spin coupling constants.

The ground states of the neutral forms of the molecules were calculated by the MO LCAO method within the Pariser—Parr—Pople approximation with allowance for configuration interaction with a program that realizes the Dewar algorithm [6] and optimization of the internuclear distances with respect to the minimum of the atomization energy. The ionization potentials, one-center coulombic integrals, and the parameters for the determination of the σ-bond energies were taken from [6]. In the calculation of the intermolecular distances with respect to the minimum of the atomization energy it was assumed that the planar and valence angles are close to 120°.

5-Alkoxypyridine-2-carboxylic Acids (I). A mixture of 15 ml of 86% alcohol, 0.0095 mole of 5-hydroxypicolinic acid, 0.023 mole of potassium hydroxide, and 0.012 mole of alkyl iodide was refluxed on a water bath for 18-20 h, after which the alcohol was removed by vacuum distillation, and the residue was dissolved in water. The aqueous solution was acidified to pH ∿ 5 with 10% hydrochloric acid, and the precipitate was removed by filtration, dried, and recrystallized from petroleum ether. The petroleum ether-insoluble residue was identified as the starting 5-hydroxypicolinic acid (Table 7).

6-Alkoxypyridine-3-carboxylic Acids (II). A 0.0317-mole sample of 6-chloronicotinic acid was added to a solution of 0.07 mole of sodium metal in 50 ml of the appropriate alcohol and the mixture was refluxed with stirring on an oil bath for ∿10 h. The alcohol was then removed by vacuum distillation, and the residue was dissolved in water. The aqueous solutions was acidified to pH ∿ 5 with 10% hydrochloric acid, and the precipitated acid was removed by filtration, dried, and recrystallized from hexane until it had a constant melting point (Table 7).

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