internal standard) at room temperature were obtained with a Brüker WH-90 spectrometer (22.63 MHz) under pulse conditions (with 5 μsec pulses). The error in the shift on the δ scale from tetramethylsilane (with a computer memory of 4 K and a scanning width of 6000 Hz) was ±0.1 ppm. The spectra without decoupling of the protons were recorded at a scanning width of 1200 Hz.

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^{13}C NMR SPECTRA OF PROTONATED S-METHYLQUINOLINES

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The signals in the ^{13}C NMR spectra of protonated 2-, 3-, 4-, 5-, 6-, and 8-S-methylquinolines in solution in 6 N DCl were assigned. The changes in the ^{13}C chemical shifts relative to the neutral molecules were compared with the results of calculations within the CNDO/2 approximation. It is shown that when the molecules are protonated, the shift of the ^{13}C signals is due to changes in the charges and the paramagnetic components of shielding of the nuclei.

The ^{13}C NMR spectra, the increments of the substituents, and the charge distribution in S-methylquinolines were examined in [1]. In the present communication data from the ^{13}C NMR spectra of the cationic forms of quinoline (I) [2] and its 2-S-methyl (II), 3-S-methyl (III), 4-S-methyl (IV), 5-S-methyl (V), 6-S-methyl (VI), and 8-S-methyl (VII) [2] derivatives are presented in order to ascertain the changes in the electronic structure and the character of the coupling of the substituent with the quinoline ring when the nitrogen atom is protonated. The signals were assigned on the basis of the spectra without proton decoupling or with extraresonance suppression of the spin—spin coupling. The ^{13}C chemical shifts of I-VII are presented in Table 1. In Table 2 the increments of the SCH_3 group are compared with the values in the neutral forms of these compounds and the changes in the total charge (Δq) on the atoms and the paramagnetic (σ_{AA}^{P}, σ_{AB}^{P}) and diamagnetic (σ^{d}) components of shielding of the nuclei.

As in the case of quinoline [2], the protonation of S-methylquinolines is accompanied by a shift of the C_2 and C_9 signals to strong field. This is associated with a decrease in the contribution of the σ_{AB}^{P} component to shielding of these nuclei because of a decrease in the order of the CN bond. The latter acts counter to the effect of an increase in the positive charge on these carbon atoms (Table 2). In the case of IV and V the shifts of the C_5 and C_4 signals, respectively, to strong field because of steric hindrance (the γ effect) are similar to the shifts for the neutral forms of these compounds.

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TABLE 1. ^{13}C Chemical Shifts (δ, ppm)[a] of Protonated Quinoline and Its S-Methyl Derivatives

Compound	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_R
I	144,9	122,8	149,4	130,2	131,6	136,9	120,9	137,7	130,0	
II	165,2	121,2	146,2	131,2	131,3	137,3	120,2	139,3	126,4	17,4
III	143,2	138,1	144,5	130,3	133,5	136,8	122,3	136,5	130,9	17,9
IV	142,8	116,4	167,3	125,5	131,8	137,4	122,5	135,8	126,2	17,2
V	146,5	123,9	145,8	142,6	127,6	137,8	118,4	139,9	128,8	17,7
VI	144,6	123,3	147,8	125,1	146,0	136,1	122,0	136,9	131,5	17,2
VII	145,1	123,0	149,0	127,1	130,7	134,5	130,4	134,5	129,3	17,3

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[a] Relative to tetramethylsilane.

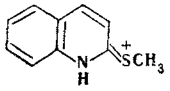
TABLE 2. Changes in the Shielding Parameters, Charges, and ^{13}C Chemical Shifts in the Case of Substitution of Protonated Quinoline

Atom No.	$\Delta\sigma_{AA}^{p}$, ppm	$\Delta\sigma_{AB}^{p}$, ppm	$\Delta q \cdot 10^2$	$\Delta\delta$, ppm
2-S-Methyl;				
C_2	−2,1 (−3,6)	−20,4 (−17,0)	3,1 (5,6)	20,3 (9,7)
C_3	1,3 (1,4)	1,3 (1,0)	−2,3 (−2,3)	−1,6 (−0,5)
C_4	0,3 (−0,9)	0,6 (0,1)	−0,3 (1,2)	−3,2 (−0,9)
C_9	0,3 (−0,5)	0 (−0,4)	−0,3 (0,8)	1,6 (0,1)
C_{10}	0,8 (1,0)	0,2 (0,3)	−1,2 (−1,4)	−3,6 (−2,5)
3-S-Methyl:				
C_2	2,0 (1,4)	1,7 (1,0)	−3,0 (−2,3)	−1,7 (−0,6)
C_3	−3,7 (−4,1)	−15,8 (−15,6)	5,4 (6,1)	15,3 (11,7)
C_4	3,6 (2,8)	0,4 (0,7)	−4,5 (−4,1)	−4,9 (−5,2)
C_9	1,1 1,0)	0,4 (0,6)	−1,6 (−1,5)	−1,2 (−2,6)
C_{10}	−0,6 (−0,8)	−0,3 (−0,3)	1,0 (1,1)	0,9 (−0,1)
4-S-Methyl:				
C_2	−0,3 (−0,9)	0,9 (−0,2)	0,4 (1,3)	−2,1 (−0,9)
C_3	2,2 (2,4)	1,1 (0,7)	−3,7 (−3,9)	−6,4 (−6,5)
C_4	−2,2 (−4,0)	−21,6 (−16,6)	3,1 (5,8)	17,9 (11,2)
C_9	0,1 (−0,5)	0,6 (−0,2)	0,1 (0,8)	−1,9 (0,2)
C_{10}	1,5 (1,5)	0,6 (0,6)	−2,3 (−2,3)	−3,8 (−2,3)
5-S-Methyl:				
C_5	−3,7 (−4,0)	−17,9 (−16,2)	5,5 (6,1)	12,4 (9,1)
C_6	3,3 (2,7)	1,1 (1,1)	−5,0 (−4,2)	−4,0 (−2,5)
C_7	−1,0 (−0,9)	−0,1 (−0,2)	1,4 (1,3)	0,9 (−0,2)
C_8	1,7 (1,4)	0,7 (0,5)	−2,8 (−2,2)	−2,5 (−2,2)
C_9	−0,4 (−0,5)	−0,4 (−0,3)	1,0 (0,9)	2,2 (0,2)
C_{10}	1,6 (1,4)	1,0 (0,8)	−2,4 (−2,1)	−1,2 (−1,1)
6-S-Methyl:				
C_5	3,6 (2,8)	1,4 (1,1)	−5,4 (−4,3)	−5,1 (−5,7)
C_6	−3,6 (−4,0)	−17,0 (−15,8)	5,4 (6,0)	14,4 (11,1)
C_7	0,8 (1,4)	1,7 (0,9)	−2,2 (−2,1)	−0,8 (−0,7)
C_8	−0,6 (−0,8)	0 (−0,1)	0,9 (1,1)	1,1 (0,2)
C_9	1,1 (0,8)	0,8 (0,4)	−1,6 (−1,3)	−0,8 (−1,9)
C_{10}	−0,7 (−0,7)	−0,3 (−0,3)	1,1 (0,9)	1,5 (0,4)
8-S-Methyl:				
C_5	1,8 (1,5)	0,7 (0,7)	−2,6 (−2,2)	−3,1 (−4,5)
C_6	−0,9 (−0,9)	−0,2 (−0,3)	1,3 (1,3)	−0,9 (0,2)
C_7	3,4 (2,8)	0,8 (1,1)	−4,8 (−4,0)	−2,4 (−6,7)
C_8	−3,9 (−4,4)	−16,3 (−16,2)	6,0 (6,4)	9,5 (10,7)
C_9	1,7 (1,3)	1,3 (0,9)	−2,6 (−2,0)	−3,2 (−3,0)
C_{10}	−0,6 (−0,7)	−0,3 (−0,2)	0,9 (1,0)	−0,7 (−0,3)

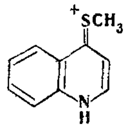
The increments of the SCH_3 group in S-methylquinolines (particularly $\Delta\delta_\alpha$ in the II and IV molecules; see Table 2) change when the quinoline ring is protonated. The increase in the latter can be linked with the substantial increase in the contribution of the σ_{AB}^{p} component to shielding of the C_α nucleus (the positive charge on the C_α atom in II and IV decreases as compared with the neutral forms, in which the $\Delta\delta_\alpha$ value of the SCH_3 group is smaller). It follows from this that resonance structures A and B, respectively, make a substantial contribution to the ground states of these compounds.

For the same reason, in the case of the IV molecule the signals of the C_2 and C_9 atoms undergo a strong-field shift (Table 2) when I is substituted. The stabilization of the ground states of the II and IV molecules as a consequence of contribution of structures

A and B is in agreement with the higher protonation energy as compared with the other S-methylquinolines [3]. The significant decreases in the $\Delta\delta_\alpha$ value of the SCH_3 group in VII



A



B

is associated with steric hindrance to coupling of the SCH_3 group with the quinoline ring. The hindrance arises as a result of protonation of 8-S-methylquinoline, in connection with which the $\Delta\delta_\alpha$ value of the SCH_3 group, in contrast to II-VI, is less than the value in the neutral form of VII (this effect is substantially smaller on the part of the unshared pair of electrons of the nitrogen atom).

EXPERIMENTAL

The ^{13}C NMR spectra of S-methylquinolines synthesized by the method in [4] in solution in 6 N DCl were obtained by the method in [1]. The electron densities on the atoms and the shielding parameters were calculated within the CNDO/2 approximation. The geometry of the molecules and the parametrization of the atoms were taken from [3].

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PREPARATION, MOLECULAR-CRYSTAL STRUCTURE, AND CHEMICAL PECULIARITIES OF THE POTASSIUM SALT OF 3,3,6,6-TETRAMETHYL-1,8-DIOXO-1,2,3,4,5,6,7,8,9,10-DECAHYDROACRIDINE-9-CARBOXYLIC ACID

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It was established by x-ray diffraction analysis that the crystalline title compound exists as a dimer formed by two paired potassium ions bonded to the oxygen atoms of the carboxy group and the coordinated oxygen atoms of the carbonyl groups. The solvate of the dimer with the composition $2C_{18}H_{22}NO_4K \cdot 3H_2O \cdot CH_3COCH_3$ is the crystallochemically independent structural unit. A shift of the electron density toward the carbonyl groups and the formation of a strong hydrogen bond between NH and the oxygen atom of the carboxylate group are observed.

It is known that the dark-brown 10,12-dioxo-5,10,11,12-tetrahydrodiindeno[1,2-b;2',1'-e]pyridine-9-carboxylic acid (Ia), which is a polycyclic derivative of 1,4-dihydropyridine, forms a green salt that contains one equivalent of sodium ions [1]. The characteristic pronounced change in color in this group of compounds constitutes evidence for dissociation of the N–H bond of the 1,4-dihydropyridine ring [2]; however, it is difficult to conceive that this takes place more readily than dissociation of the carboxy group. The possibility

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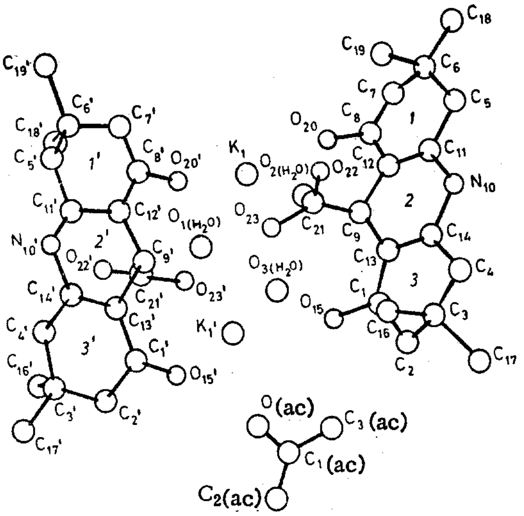
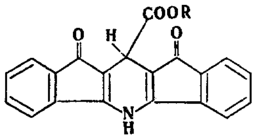
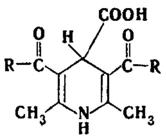


Fig. 1. Model and designations of the atoms of the solvated dimer of the IIIb molecule.

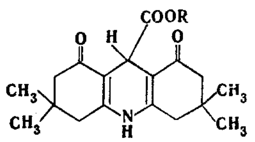
of the 1,4-dihydropyridine-4-carboxylate ⇄ 4-carboxy-1,4-dihydropyridine anion equilibrium state can be conceived of only under the condition of the existence of a strong hydrogen bond between NH and the carboxy group. The instability of salt Ib limits the possibility of its study, and IIa,b and III, which are related with respect to their chemical properties, were therefore examined. Monocyclic β-acetyl- and β-ethoxycarbonyl-1,4-dihydroisonicotinic acids IIa,b display only a small bathochromic shift in their UV spectra in the presence of a small excess of alkali [3]. A more suitable model compound for the study of the properties of Ia,b is the three-ring 3,3,6,6-tetramethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,-10-decahydroacridine-9-carboxylic acid (IIIa) system [4], which can be regarded as an analog of dihydropyridine IIa with β-carbonyl substituents fixed in the s-trans conformation. The more facile (as compared with IIa,b) dissociation of the N—H bond increases the similarity between Ia and IIIa. The addition of NaOH to a solution of salts of acids IIa,b up to a concentration of $4 \cdot 10^{-2}$ mole/liter does not affect their UV spectra (for a dihydropyridine concentration of $5 \cdot 10^{-5}$ mole/liter), whereas in the case of IIIb a change in the spectrum undoubtedly indicates reversible dissociation of the N—H bond and the formation of dihydropyridine anions in a concentration of ∿20% of the starting amount of salt IIIb.



Ia, b



IIa, b



IIIa-c

I a R=H; b R=Na; II a R=CH_3; b R=OC_2H_5; III a R=H; b R=K; c R=NH_4

In order to determine the geometry of the molecule, the coordination of the potassium ions, and the packing of the molecules in the unit cell of the crystal, which reveals the character of the intermolecular interaction, we made an x-ray diffraction study of salt IIIb obtained by crystallization from alcohol—water—acetone. It was established that crystalline IIIb exists as a dimer formed by two paired potassium ions bonded to the oxygen atoms of the carboxy groups and the coordinated oxygen atoms of the carbonyl groups of two molecules of IIIb. The packing of the dimeric molecules in the crystal is loose; the vacancies in the crystal space are filled with solvent molecules, viz., with three molecules of water and one molecule of acetone. Thus the crystallochemically independent structural unit is the solvate of the dimer, viz., triaquoacetonebis(potassium 3,3,6,6-tetramethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydroacridine-9-carboxylate). The model and the symbols of the atoms (equivalent atoms of the two molecules of IIIb in the dimer are designated by ordinal numbers with and without apostrophes) of the solvated dimer are given in Fig. 1. The averaged (over two molecules of the IIIb dimer) interatomic distances and bond angles are presented in Tables 1 and 2. The standard deviations of the interatomic distances do not exceed 0.02 Å, while the standard deviations of the bond angles do not exceed 1 deg.

TABLE 1. Interatomic Distances

Bond	Distance, Å	Bond	Distance, Å
In the IIIb molecules of the dimer:*		C_{21}—O_{23}	1,25
O_{15}—C_1	1,24	In the acetone molecule:	
C_1—C_2	1,52	C_1—C_2	1,53
C_1—C_{13}	1,44	C_1—C_3	1,39
C_2—C_3	1,54	C_1—O	1,29
C_3—C_{16}	1,56	In the coordination polyhedron of the K_1 ion:	
C_3—C_{17}	1,53		
C_3—C_4	1,53	K_1—O_{20}	2,73
C_4—C_{14}	1,50	K_1—$O_{20'}$	2,62
C_{14}—N_{10}	1,38	K_1—O_{23}	2,73
C_{14}—C_{13}	1,37	K_1—$O_{23'}$	2,91
N_{10}—C_{11}	1,39	K_1—$O_{1\,(H_2O)}$	2,92
C_{11}—C_5	1,51		
C_{11}—C_{12}	1,36	K_1—$O_{2\,(H_2O)}$	2,91
C_5—C_6	1,53	K_1—O_3 (H_2O)	2,97
C_6—C_{18}	1,55	In the coordination polyhedron of the K_1'ion:	
C_6—C_{19}	1,54		
C_6—C_7	1,54		
C_7—C_8	1,51	$K_{1'}$—O_{15}	2,71
C_8—O_{20}	1,24	$K_{1'}$—$O_{15'}$	2,62
C_8—C_{12}	1,46	$K_{1'}$—O_{23}	2,67
C_{12}—C_9	1,53	$K_{1'}$—$O_{23'}$	2,84
C_9—C_{13}	1,52	$K_{1'}$—$O_{3\,(H_2O)}$	2,73
C_9—C_{21}	1,56		
C_{21}—O_{22}	1,26	$K_{1'}$—Oac	2,85

---

*The averaged (over two IIIb molecules in the dimer) values are presented.

TABLE 2. Bond Angles

Angle	Value, deg	Angle	Value, deg
In the IIIb molecules of the dimer:*		C_5—C_6—C_{19}	110
C_2—C_1—O_{15}	119	C_5—C_6—C_{18}	110
C_2—C_1—C_{13}	121	C_{18}—C_6—C_{19}	110
C_{13}—C_1—O_{15}	120	C_6—C_7—C_{18}	111
C_1—C_2—C_3	112	C_7—C_{18}—C_{12}	121
C_2—C_3—C_4	110	C_7—C_8—O_{20}	120
C_2—C_3—C_{17}	109	C_{12}—C_8—O_{20}	120
C_2—C_3—C_{16}	109	C_8—C_{12}—C_{11}	117
C_{16}—C_3—C_{17}	110	C_8—C_{12}—C_9	119
C_4—C_3—C_{16}	110	C_{11}—C_{12}—C_9	123
C_4—C_3—C_{17}	109	C_{12}—C_9—C_{13}	110
C_3—C_4—C_{14}	111	C_{12}—C_9—C_{21}	108
C_4—C_{14}—C_{13}	125	C_{13}—C_9—C_{21}	109
C_4—C_{14}—N_{10}	114	C_9—C_{21}—O_{22}	118
C_{13}—C_{14}—N_{10}	120	C_9—C_{21}—O_{23}	118
C_{14}—N_{10}—C_{11}	122	C_9—C_{13}—C_{14}	123
N_{10}—C_{11}—C_{12}	120	C_9—C_{14}—C_1	120
N_{10}—C_{11}—C_5	115	C_{14}—C_{13}—C_1	117
C_{12}—C_{11}—C_5	125		
C_{11}—C_5—C_6	112	In the acetone molecule:	
C_5—C_6—C_7	108	O—C_1—C_2	111
C_7—C_6—C_{19}	109	O—C_1—C_3	123
C_7—C_6—C_{18}	109	C_2—C_1—C_3	126

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*The averaged (over two IIIb molecules of the dimer) values are presented.

The results of an analysis of the configurations of the individual rings of both molecules of IIIb in the dimer are presented in Table 3.

The C—O bonds of the carboxy groups are equalized completely, and their length is 1.26 Å. Partial equalization of the bonds is observed in the conjugated aminobis(vinylcarbonyl) system. The C=O bonds of the carbonyl groups are somewhat lengthened (up to 1.24 Å) as compared with the length of the bond in ketone molecules (1.20 Å) but are close to the bond length (1.23 Å) in 2,6-dimethyl-4-(3-pyridyl)-3,5-diacetyl-1,4-dihydropyridine [5], as well as to the length (1.23 Å) calculated for the $(O{=}C{-}C{=}C{-})_2NH$ model system [6]. The C=C bonds (average value 1.36 Å) are also somewhat elongated as compared with the standard double bond (1.33 Å) and are close to the calculated value (1.37 Å) [6]. The inter-

TABLE 3. Equations of the Average Planes of the Individual Fragments of Both IIIb Molecules in the Solvated Dimer and Deviations of the Atoms from Them

Plane	Atoms of the plane	Deviations of the atoms from the plane, Å	Equation of the plane: Ax + By + Cz − D = 0			
			A	B	C	D
1	C_5	0,02	0,4320	−0,8287	−0,3558	−3,0797
	C_7	−0,02				
	C_8	0,02				
	C_{11}	−0,02				
	C_6*	0,66				
	C_{12}*	−0,04				
	O_{20}*	0,08				
2	C_{11}	0,00	0,3098	−0,8697	−0,3842	−4,1580
	C_{12}	0,00				
	C_{13}	0,00				
	C_{14}	0,00				
	C_9*	0,21				
	N_{10}*	0,09				
	C_1*	−0,24				
	O_{15}*	−0,25				
	C_8*	−0,10				
	O_{20}*	−0,03				
3	C_1	0,04	0,1182	−0,9043	−0,4102	−5,1096
	C_2	−0,04				
	C_4	0,04				
	C_{14}	−0,04				
	C_3*	0,64				
	C_{13}*	0,00				
	O_{15}*	0,08				
1′	$C_{5'}$	−0,03	0,0759	0,1324	−0,9883	−1,5052
	$C_{7'}$	0,03				
	$C_{8'}$	−0,03				
	$C_{11'}$	0,03				
	$C_{6'}$*	−0,67				
	$C_{12'}$*	0,02				
	$O_{20'}$*	−0,09				
2′	$C_{11'}$	0,00	0,1381	0,1493	−0,9791	−1,0720
	$C_{12'}$	0,00				
	$C_{13'}$	0,00				
	$C_{14'}$	0,00				
	$C_{9'}$*	−0,10				
	$N_{10'}$*	−0,03				
	$C_{1'}$*	0,08				
	$O_{15'}$*	0,20				
	$C_{8'}$*	0,04				
	$O_{20'}$*	−0,01				
3′	$C_{1'}$	0,02	0,1644	0,1438	−0,9759	−0,9362
	$C_{2'}$	−0,01				
	$C_{4'}$	0,01				
	$C_{14'}$	−0,15				
	$C_{3'}$*	−0,65				
	$C_{13'}$*	−0,02				
	$O_{15'}$*	0,12				

*These are the atoms that were disregarded in the calculation of the corresponding plane.

atomic C_1—C_{13}, $C_{1'}$—$C_{13'}$, C_8—C_{12}, and $C_{8'}$—$C_{12'}$ distances (average value 1.45 Å) are considerably shorter than the single bond (1.54 Å). The C—N bond is 0.04 Å longer than the corresponding bonds in the acridine molecule [7] and its derivatives [8] and is equal to the C—N bond in pyrrole [9].

The potassium ions, which are located at a distance of 3,76 Å, are coordinated with the oxygen atoms of the carboxy and carbonyl groups of two monomeric molecules of IIIb and water and acetone molecules. The sum of the van der Waals radii of the O atom (1.40 Å) and the K^+ ion (1.33 Å) is 2.73 Å. The immediate environment of the K_1 atom contains seven oxygen atoms (Table 1) at a distance within the limits of 2.62 and 2.97 Å (average value 2.83 Å), and the coordination polyhedron is a pentagonal bipyramid. The coordination polyhedron of the $K_{1'}$ ion is a distorted octahedron formed by six oxygen atoms at a distance of 2.62 to 2.85 Å (average value 2.74 Å). The water molecules form the following hydrogen bonds with the oxygen atoms of the carboxy groups: $O_{22}\ldots O_1(H_2O)$ (2.67 Å), $O_{22'}\ldots O_2(H_2O)$ (2.77 Å), and $O_{23'}\ldots O_1(H_2O)$ (2.75 Å).

TABLE 4. Coordinates of the Nonhydrogen Atoms of the Solvated Dimer and Their Standard Deviations (in Parentheses)*

Atom	x	y	z
K_1	0,5271 (2)	0,2529 (2)	0,1529 (2)
$K_{1'}$	0,2292 (2)	0,2087 (2)	0,0883 (2)
O_{15}	0,1769 (7)	0,3192 (5)	−0,0030 (5)
$O_{15'}$	0,1935 (6)	0,0690 (5)	0,0720 (5)
O_{20}	0,5982 (7)	0,3627 (5)	0,0777 (5)
$O_{20'}$	0,6214 (7)	0,1300 (5)	0,1293 (5)
O_{22}	0,4685 (7)	0,2473 (4)	−0,0735 (4)
$O_{22'}$	0,4299 (7)	0,0257 (4)	0,2269 (4)
O_{23}	0,4042 (7)	0,2261 (4)	0,0251 (4)
$O_{23'}$	0,3875 (7)	0,1359 (4)	0,1879 (4)
N_{10}	0,4063 (8)	0,4268 (5)	−0,1446 (5)
$N_{10'}$	0,4751 (8)	−0,1063 (5)	0,0838 (5)
C_1	0,1872 (11)	0,3497 (7)	−0,0582 (8)
$C_{1'}$	0,2233 (10)	0,0045 (7)	0,0717 (6)
C_2	0,0871 (10)	0,3711 (8)	−0,1093 (7)
$C_{2'}$	0,1335 (9)	−0,0535 (6)	0,0559 (7)
C_3	0,1104 (10)	0,3695 (8)	−0,1840 (7)
$C_{3'}$	0,1752 (9)	−0,1294 (6)	0,0826 (7)
C_4	0,2112 (9)	0,4175 (6)	−0,1902 (6)
$C_{4'}$	0,2844 (9)	−0,1456 (6)	0,0576 (7)
C_5	0,5981 (9)	0,4684 (6)	−0,1102 (6)
$C_{5'}$	0,6753 (9)	−0,0887 (6)	0,1012 (6)
C_6	0,7062 (10)	0,4412 (7)	−0,0679 (7)
$C_{6'}$	0,7645 (9)	−0,0426 (6)	0,1448 (7)
C_7	0,6956 (10)	0,4399 (7)	0,0097 (7)
$C_{7'}$	0,7503 (9)	0,0368 (6)	0,1178 (7)
C_8	0,5961 (10)	0,3962 (6)	0,0219 (7)
$C_{8'}$	0,6349 (10)	0,0644 (7)	0,1186 (6)
C_9	0,3973 (9)	0,3498 (6)	−0,0170 (6)
$C_{9'}$	0,4238 (8)	0,0459 (6)	0,1044 (6)
C_{11}	0,4994 (10)	0,4272 (6)	−0,0928 (6)
$C_{11'}$	0,5622 (9)	−0,0561 (7)	0,0968 (6)
C_{12}	0,4971 (9)	0,3942 (6)	−0,0313 (7)
$C_{12'}$	0,5393 (9)	0,0159 (6)	0,1056 (6)
C_{13}	0,2972 (9)	0,3681 (6)	−0,0713 (6)
$C_{13'}$	0,3381 (9)	−0,0133 (6)	0,0833 (5)
C_{14}	0,3043 (10)	0,4020 (6)	−0,1330 (7)
$C_{14'}$	0,3663 (9)	−0,0848 (6)	0,0760 (6)
C_{16}	0,1349 (12)	0,2885 (8)	−0,2039 (8)
$C_{16'}$	0,1921 (11)	−0,1306 (8)	0,1631 (8)
C_{17}	0,0098 (11)	0,3988 (8)	−0,2340 (8)
$C_{17'}$	0,0878 (10)	−0,1853 (7)	0,0519 (8)
C_{18}	0,8001 (10)	0,4958 (7)	−0,0765 (7)
$C_{18'}$	0,7560 (10)	−0,0453 (8)	0,2228 (6)
C_{19}	0,7365 (11)	0,3638 (7)	−0,0912 (8)
$C_{19'}$	0,8769 (9)	−0,0701 (7)	0,1338 (7)
C_{21}	0,4254 (9)	0,2662 (6)	−0,0215 (7)
$C_{21'}$	0,4137 (9)	0,0709 (7)	0,1784 (7)
$O_1(H_2O)$	0,4734 (10)	0,2314 (5)	0,2915 (5)
$O_2(H_2O)$	0,5153 (9)	0,3835 (5)	0,2359 (6)
$O_3(H_2O)$	0,3147 (9)	0,3162 (6)	0,1780 (7)
$O(ac)$	0,0172 (10)	0,2408 (8)	0,1213 (6)
$C_1(ac)$	−0,0416 (18)	0,2950 (15)	0,1334 (10)
$C_2(ac)$	−0,1555 (14)	0,2727 (11)	0,1465 (11)
$C_3(ac)$	−0,0033 (20)	0,3673 (12)	0,1331 (16)

*The temperature factors can be obtained from the authors.

Dihydropyridine rings 2 and 2' have a boat form (Table 3) similar to that of the previously investigated 2,6-dimethyl-4-phenyl-3,5-diethoxycarbonyl-1,4-dihydropyridine (IV) [10] and 2,6-dimethyl-4-(3-pyridyl)-3,5-diacetyl-1,4-dihydropyridine (V) [5]. However, the boat conformation in this case is weakly expressed and approaches the half-chair form. The deflections of the "angles" formed by the C_9—C_{12}—C_{13}, $C_{9'}$—$C_{12'}$—$C_{13'}$, N_{10}—C_{11}—C_{14}, and $N_{10'}$—$C_{11'}$—$C_{14'}$ atoms from the average 2 and 2' planes are 13.8, 6.4, 7.5, and 2.5°, respectively. The difference in the deviations of the C_9 and $C_{9'}$ and N_{10} and $N_{10'}$ atoms from the average 2 and 2' planes (Table 3), i.e., the distortion of the boat conformation of the dihydropyridine rings, which is manifested as an increase in their planarity, is evidently due to the different (in magnitude) interactions of the potassium ions with the carbonyl groups of both IIIb molecules (see the interatomic distances in Table 1) and the participation of the N_{10} and $N_{10'}$ atoms in the formation of intermolecular hydrogen bonds. A comparison of the x-ray diffraction data for the dimeric IIIb molecules and dihydropyridines IV and V makes it possible to assert that the conformation of the 1,4-dihydropyridine ring can vary over wide limits.

As compared with the 2 and 2' planes, the deviations of the atoms from the 1 and 1' and 3 and 3' average planes formed by them in the side (with respect to the dihydropyridine fragment) six-membered rings are an order of magnitude greater (Table 3). The side six-membered rings have a half-chair conformation, and the carbon atoms bonded to two methyl groups each, viz., the C_3 and $C_{3'}$ and C_6 and $C_{6'}$ atoms, the deviations of which from the 1 and 1' and 3 and 3' planes are within the limits of the deviations of the atoms that form the given average planes, form the upper point of the "edge." The dimer of the molecules of IIIb is nonplanar. The dihedral angle between the average planes formed by the $C_2—C_3—C_{14}—C_{13}—C_{11}—C_{12}—C_7—C_6$ and $C_{2'}—C_{3'}—C_{14'}—C_{13'}—C_{11'}—C_{12'}—C_{7'}—C_{6'}$ atoms is 108°.

The facilitation (as compared with dihydropyridines II) of the dissociation of the proton of the NH group in III, which is confirmed by the UV spectra, can be explained by the high degree of polarization of the fixed (in the s-trans conformation) carbonyl groups and the entire bis(ketovinyl)amine system, which leads to weakening of the N—H bond. This is in good agreement with the results of an x-ray diffraction study of salt IIIb, viz., the planar character of the molecule and the interatomic $K...O_{carbonyl}$ distances, which in one molecule of the dimer were found to be even shorter (by 0.1 Å) as compared with $K...O_{carboxy}$ distance. This indicates significant redistribution of the electron density, leading to the development of a negative charge on the oxygen atoms of the carbonyl groups, which is additionally intensified by the intermolecular $N—H...O_{carboxy}$ hydrogen bond and is manifested in the more planar (than in IV and V) dihydropyridine ring. The slight deviation from planarity of the $(C{=}C—C{=}C—)_2NH$ systemdoes not hinderits conjugation, since the maximum deviation of the individual atoms from the plane does not exceed 0.2 Å. Since salt Ib represents the 3,5-dicarbonyl-1,4-dihydropyridine system with a longer conjugation chain, the electron density distribution observed in the IIIb molecule convincingly confirms the probability of the existence of salt Ib in the form of the 4-carboxy-1,4-dihydropyridine anion.

As regards the coordination-bonded cation, a great similarity between salt IIIb and the known membranotropic substance of another class of compounds, viz., the sodium salt of lasolacid A [11], is observed.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in D_2O were recorded with a Bruker WH-90 spectrometer with tetramethylsilane as the external standard. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The IR spectra were obtained with a UR-20 spectrometer.

The x-ray diffraction study of salt IIIb was made with a Syntex $P2_1$ diffractometer. The intensities of 4957 independent reflections were measured by $\theta/2\theta$ scanning ($2\theta_{max}$ = 100°) in copper emission (with a graphite monochromator). The IIIb crystals were monoclinic with the following parameters of the unit cell: a = 12.294(1), b = 18.413(4), c = 19.504 Å (3), β =99.76°(1), V= 4351.2 Å³, M = 823.08, d_{calc} = 1.26 g/cm³, $z = 4 \cdot C_{39}H_{56}N_2O_{12}K_2$, $\mu(CuK_\alpha)$ = 24.3 cm⁻¹, space group $P2_1/c$, and F_{000} = 1752. A total of 3785 reflections with $J \geqslant 2\sigma_J$ was used. Absorption was disregarded. A model of the IIIb molecule was found from E synthesis from the best of 16 variants of the phases calculated from a MULTAN program [12] (R = 0.42). Refinement of the nonhydrogen atoms by the method of least squares within the total matrix approximation and then within the anisotropic approximation with allowance for the coordinates of the hydrogen atoms led to a final R value of 0.093. The coordinates of the nonhydrogen atoms are presented in Table 4.

Potassium 3,3,6,6-Tetramethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydroacridine-9-carboxylate (IIIb). The method in [4] for the preparation of ammonium salt IIIc was modified somewhat. A solution of 20 g (0.06 mole) of 2,2'-didimedonylacetic acid in 40 ml of ethanol and 50 ml (0.75 mole) of 25% ammonium hydroxide was heated in a steel autoclave at 120°C for 5 h, after which the mixture was cooled and worked up to give 17 g (85%) of the yellow crystalline ammonium salt IIIc. The latter was dissolved in water, an equimolar amount of KOH was added, and the mixture was evaporated to dryness in vacuo. The residue was dissolved in 100 ml of 50% ethanol, and 100 ml of acetone was added. The mixture was stored for a long time in the cold, after which it was worked up to give 8.1 g (29%) of the bright-yellow crystalline potassium salt IIIb.

PMR spectrum, δ: 4.35 (1H, s, 9-H), 2.38 (4H, s, 4-H, 5-H), 2.27 (4H, s, 2-H, 7-H), 2.22 (3H, s, 0.5 mole of CH_3COCH_3), and 1.05 ppm (12H, s, 3- and 6-CH_3). IR spectrum (in Nujol): 1720 (acetone C=O) and 1615-1650 cm^{-1} (COO^-, C=C, and C=O).* UV spectrum, λ_{max} (log ε): in ethanol, 253 (4.28) and 388 nm (3.84); in an ethanol solution of sodium hydroxide ($4 \cdot 10^{-4}$ mole/liter NaOH), 253 (4.22) and 392 nm (3.81); in an ethanol solution of sodium hydroxide ($4 \cdot 10^{-2}$ mole/liter NaOH), 257 (4.22), 268 sh (4.18), 402 (3.67), and 475 nm (3.79). Found: C 56.9; H 6.9; N 3.4%. $2C_{18}H_{22}NO_4K \cdot 3H_2O \cdot (CH_3)_2CO$. Calculated: C 56.9; H 6.9; N 3.4%. The crystallization solvents can be removed by heating salt IIIb at 110°C. A sample dried at 20°C was used for x-ray diffraction analysis.

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*The difficulties involved in the interpretation of the IR spectra of 1,4-dihydropyridines are demonstrated in [13].

SUBSTITUTED 2- AND 4-BENZYLPYRIDINES IN THE SYNTHESIS OF BENZO[g]QUINOLINES AND BENZO[g]ISOQUINOLINES

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Nitrogen-containing heterocyclic analogs of anthracene, viz., benzo[g]isoquinolines and benzo[g]quinolines, were obtained by dehydrocyclization on a K-16 catalyst of mixtures of methyl-substituted 2- and 4-benzylpyridines with methyl groups in various positions of the pyridine and benzyl rings, which are formed by benzylation of β-picoline, as well as pyridine, by the Ladenburg method. The spectral characteristics of the synthesized compounds are presented.

In numerous investigations involving the study of the electrophysical properties of anthracene the latter has been regarded as a standard with which to compare the electrophysical properties of other organic compounds. In this respect, extremely little study has been devoted to nitrogen-containing heterocyclic analogs of anthracene because of the limited number of methods for their preparation.

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