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

I. V. Zuika, Z. P. Bruvers,
and M. A. Tsirule

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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

^{a}Relative to tetramethylsilane.

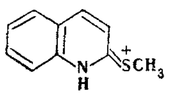
TABLE 2. Changes in the Shielding Parameters, Charges, and ^{13}C Chemical Shifts in the Case of Substitution of Protonated Quinoline

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)

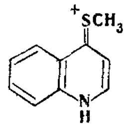
The increments of the SCH_3 group in S-methylquinolines (particularly $\Delta\delta_\alpha$ in the II and IV molecules; see Table 2) change when the quinoline ring is protonated. The increase in the latter can be linked with the substantial increase in the contribution of the $\sigma_{AB}{}^P$ component 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

M. F. Bundule, É. A. Bisenieks,
A. A. Kemme, Ya. Ya. Bleidelis,
G. Ya. Dubur, and Ya. R. Uldrikis

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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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