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STRUCTURE OF SALTS OF SUBSTITUTED 2-ALKYLTHIOTETRAHYDROPYRIMIDINES

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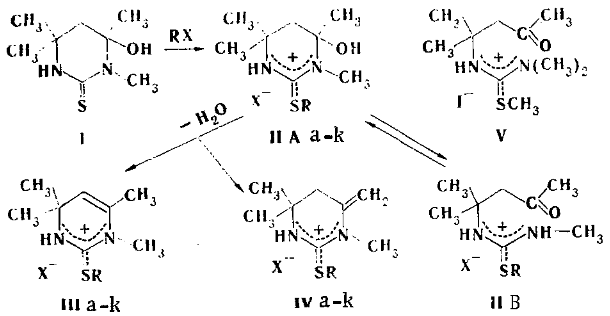
The structure and ring-chain tautomerism of 2-alkylthio-3,4,6,6-tetramethyl-4-hydroxy-3,4,5,6-tetrahydropyrimidine hydrohalides (Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, $CH_2C_6H_5$ Hal = Cl, Br, I) were analyzed by means of UV, IR, and PMR spectroscopy. It is shown that the cations of the salts in the crystalline state and in solutions exist primarily in the cyclic form.

In [1] we reported the synthesis of 2-alkylthio-3,4,6,6-tetramethyl-4-hydroxy-3,4,5,6-tetrahydropyrimidine hydrohalides, the structure of which is discussed in the present communication.



II—IV a R=CH_3, X=I; b R=CH_3, X=Cl; c R=C_2H_5, X=Br; d R=C_2H_5, X=Cl; e R=*n*-C_3H_7, X=Br; f R=p-C_3H_7, X=Cl; g R=*n*-C_4H_9, X=Br; h R=*n*-C_4H_9, X=Cl; i R=*iso*-C_4H_9, X=I; j R=*iso*-C_4H_9, X=Cl; k R=$CH_2C_6H_5$, X=Cl

Compounds IIa-k were obtained by the reaction of 3,4,6,6-tetramethyl-4-hydroxyhexahydropyrimidine-2-thione (I) with alkyl halides in acetone at 20°C. The spectral characteristics of the synthesized compounds are presented in Tables 1 and 2.

The cations of salts IIa-k can exist in two tautomeric forms, viz., the acyclic oxoalkylisothiuronium form (IIB) and the cyclic substituted 2-alkylthio-4-hydroxytetrahydropyrimidinium form (IIA). We have previously observed ring-chain tautomerism in the substituted 4-hydroxyhexahydropyrimidine-2-thione series [2].

The IR spectra of IIa-k in mineral oil do not contain a band corresponding to the stretching vibrations of the C=O group, and this indicates the existence of the cations of the salts in the crystalline state in cyclic form IIA. Broad absorption bands corresponding to the stretching vibrations of N—H and O—H groups connected by intermolecular hydrogen bonds are observed in the 3000-3600 cm^{-1} region.

The cyclic structure of the cations of salts II is also retained in solutions in chloroform, in the IR spectra of which a $\nu_{C=O}$ band is also absent. Slow dehydration of II occurs when the chloroform solutions are allowed to stand, as evidenced by the appearance of absorption bands at 1690 and 1647 cm^{-1}. The first band can be assigned to the stretching vibrations of the C=C bond in 2-alkylthio-3,4,6,6-tetramethyl-3,6-dihydropyrimidine hydrohalides (III), while the second band can be assigned to the $\nu_{C=C}$ band of the isomeric products, viz., 2-alkylthio-3,6,6-trimethyl-4-methylene-3,4,5,6-tetrahydropyrimidine hydro-

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TABLE 1. IR and UV Spectra of 2-Alkylthio-3,4,6,6-tetramethyl-4-hydroxy-3,4,5,6-tetrahydropyrimidine Hydrohalides

Compound	R	X	UV spectrum, λ_{max}, (log ε)			IR spectrum, cm^{-1}	
			water	96% alcohol	dioxane – alcohol (1:1)	3000-3600 region	1500-1700 region
IIa	CH_3	I	225 (4,33)	220 (4,32)	223 (4,34)	3300 s. br 3225 m	1605 s 1540 m
IIb	CH_3	Cl	222 (4,02)	222 (3,98)	222 (4,02)	3150 s br 3100 sh	1595 s 1537 m
IIc	C_2H_5	Br	224 (4,02)	224 (4,02)	224 (4,00)	3255 s. br, 3230 s br 3175 sh	1597 s 1538 s
IId	C_2H_5	Cl	224 (4,01)	224 (4,01)	223 (4,01)	3190 s 3150 sh 3110 m	1592 s 1540 m
IIe	*n*-C_3H_7	Br	—	—	—	3220 s br 3110 sh	1597 s 1535 m
IIf	*n*-C_3H_7	Cl	224 (4,01)	225 (3,98)	224 (4,02)	3170 s. br. 3110 sh	1602 s 1540 m
IIg	*n*-C_4H_9	Br	224 (4,04)	224 (4,02)	224 (3,99)	3200 s. br. 3100 sh	1592 s 1535 m
IIh	*n*-C_4H_9	Cl	—	—	—	3160 s br 3105 sh	1600 s 1540 m
IIi	*iso*-C_4H_9	I	225 (4,23)	220 (4,34)	224 (4,36)	3295 s br 3220 sh	1595 m, 1540 m
IIj	*iso*-C_4H_9	Cl	—	—	—	3180 s. br 3110 sh	1595 s 1538 m
IIk	$CH_2C_6H_5$	Cl	220 (4,02)	207 (4,15), 217 sh	217 (4,11)	3176 s br	1590 s 1535 m
V	—	—	—	221 (4,23), 244 sh	—	3440 s. br 3385 s br 3240 s 3155 s 3070 s	1520 m, 1596 s 1708 s

TABLE 2. Parameters of the PMR Spectra of IIa-k in d_4-Methanol

Compound	Chemical shifts of the protons, δ, ppm			
	6-CH_3^a, 6-CH_3^e	4-CH_3	5-H	S—CH_2
IIa	1,46 br	1,61	2,22	2,71
IIb	1,43. 1,45	1,59	2,15	2,68
IIc	1,44, 1,45	1,59	2,18	3,18—3,30*
IId	1,42, 1,45	1,58	2,18	3,03—3,55*
IIf	1,40, 1,45	1,59	2,16	3,19
IIg	1,40, 1,45	1,60	2,16	3,05—3,43*
IIi	1,45 br	1,63	2,23	3,12
IIk	1,33, 1,35	1,52	2,00, 2,08†	4,53

*The signals are overlapped by the signals from the N—CH_3 group and the solvent.

†Two central signals of the quartet of an AB system.

halides (IV). Two isomeric products were previously observed in the dehydration of substituted 4-hydroxy-4-methylhexahydropyrimidine-2-thiones [3]. These bands are retained after removal of the solvent, which indicates irreversible dehydration, in contrast to the IIA ⇄ IIB tautomeric transformations.

An examination of the PMR spectra of salts IIa-k in solution in CD_3OD also indicates cyclic structure IIA of the cations of the salts. This conclusion follows from a comparison of the chemical shifts of the signals of the protons of the CH_3CO and CH_2CO groups of II and of the signals of the protons of the analogous groups in a model compound, viz., N,N-dimethyl-N'-(4-methyl-2-oxo-4-pentyl)-S-methylisothiourea hydroiodide (V), which has a fixed acyclic structure. The following signals (δ, ppm) are observed in the PMR spectrum of V in CD_3OD: 3.40 [6H, s, $(CH_3)_2N$)], 3.29 (2H, s, CH_2CO), 2.60 (3H, s, SCH_3), 2.23 (3H, s, CH_3CO), and 1.60 [6H, s, $(CH_3)_2C$]. In the PMR spectra of salts II the signals of the protons of the CH_2CO and CH_3CO groups show up at strong field as compared with the analogous signals in the spectrum of V, viz., at 2.16-2.23 and 1.58-1.63 ppm, respectively. The protons of the methyl groups attached to the C_6 atom give two singlet signals in the PMR spectra, which indicates the conformational rigidity of the cations of II. In addition, singlet signals are observed for the protons of the CH_2 group; this is evidently explained by the closeness of the chemical shifts of the indicated protons. The protons of the CH_2 group are nonequivalent only in the spectrum of IIk and give a quartet corresponding to an AB system. In addition, the signals of the protons of the $(CH_3)_2C$, CH_3COH, and CH_2COH groups for IIk were shifted to stronger field as compared with the analogous signals of IIa-i. These facts are probably explained by the shielding effect of the phenyl ring of the S-benzyl group on the indicated protons.

On passing from pyrimidinethione I to hydrohalides IIa-k the UV absorption band of I corresponding to a $\pi\rightarrow\pi^*$ transition [λ_{max} 246 nm (log ε 4.13)] [4-6] experiences a strong hypsochromic shift to 224 nm. This fact constitutes evidence for S alkylation of I [4, 5]. An appreciable shift of the band at 224 nm is not observed on passing to more polar and less polar solvents. An increase in the volume of the alkyl substituent in the alkylthio group does not have a bathochromic effect on this band, which indicates the independence of the position of the transition on steric effects. Similar results for 2-methylthio-1-alkyl-1,4,5,6-tetrahydropyrimidine hydriodides, which were confirmed by calculated data, were presented in [4].

One absorption band at 1525 cm^{-1}, which is a composite band ($\nu_{CN} + \delta_{NH}$) [7-9], is observed in the IR spectrum of crystalline pyrimidinethione I at 1500-1700 cm^{-1}. Alkylated compounds IIa-k in the same region give two absorption bands at 1595 and 1540 cm^{-1}. The high-frequency band can evidently be assigned to the stretching vibrations of the $C=N^+$ group, while the low-frequency band can be assigned to a mixed vibration with a greater contribution from δ_{NH} [10, 11].

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and solutions in $CHCl_3$ (c $8.3 \cdot 10^{-3}$ mole/liter) were recorded with a UR-10 spectrometer. The UV spectra of $6 \cdot 10^{-5}$ mole/liter solutions of the compounds were obtained with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in CD_3OD were obtained with a Bruker WP-60 spectrometer with hexamethyldisiloxane as the internal standard.

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