RESEARCH IN THE PYRIMIDINE SERIES

XXVI.* CALCULATION OF THE IN-PLANE NORMAL VIBRATIONS OF THE "ENOL" FORMS OF BARBITURIC ACIDS

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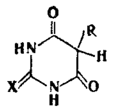
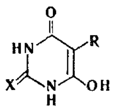
UDC 547.854.5 : 543.422.4

The frequencies and forms of the in-plane normal vibrations of the "enol" forms of barbituric and 5-chloro- and 2-thiobarbituric acids and their deutero derivatives were calculated for the C_s symmetry point group. On the basis of an analysis of the forms of the normal vibrations, the principal frequencies observed in the IR spectra of 5-substituted (methyl, chloro, and bromo) and 2-thiobarbituric acids were assigned with respect to the types of vibrations. The force constants were also determined. The results of the calculations also confirm and refine the previously proposed interpretation of the IR spectra of crystalline samples of the investigated compounds and make it possible to form a judgment regarding the presence of tautomers in the crystalline state and in solutions from the IR spectra.

Barbituric acid and its C- and N-alkyl and 5-halo and 2-thio derivatives exist in the tricarbonyl form (A) in solutions in aprotic solvents of low polarity [2, 3]. According to the data from the UV and PMR spectra of solutions of these compounds in hydroxyl-containing solvents, these compounds undergo enolization. The amount of the "enol" form (B) in solution is determined, on the one hand, by the polarizability of the β-dicarbonyl fragment of the molecule and, on the other, depends on the nature of the solvent (it increases on passing from water to methanol and subsequently to ethanol). Intense bands, which we assigned to the absorption of the monoenol form of the barbituric acids (B), are observed in the IR spectra of these solutions at 1500-1800 cm^{-1} in addition to frequencies corresponding to the absorption of the tricarbonyl form (A), which are readily identified from the IR spectra of nonpolar solutions and the results of calculations [1]. Bands of this sort are also retained in the IR spectra of crystalline samples of some derivatives (II-V) of barbituric acid (Fig. 1). We therefore assumed that they also exist as a mixture of two desmotropic forms in the crystalline state. However, this conclusion cannot be considered to be a rigorous one, inasmuch as the appearance of new intense bands and a shift of the frequencies of the stretching vibrations of the carbonyl groups may be due to a change in the types of hydrogen bonds in the crystalline barbituric acids. In order to calculate the vibrational spectra of the tricarbonyl forms of some barbituric acids [1], it was necessary to isolate those absorption bands in the IR spectra of the barbituric acids that can be used for the identification of this tautomer. The calculation of the frequencies and forms of the normal vibrations of the monoenol forms (B) of the barbituric acids would make it possible to determine whether the bands that appear in the spectra of the compounds in water, alcohol, and other solvents, which do not pertain to the vibrations of form A, are really associated with the vibration of form B in solution, i.e., it would enable one to form a judgment regarding the presence of one or several tautomers of the barbituric acids.



IA–VA



IIB–VB

I–IV X=O; V X=S; I, V R=H; II R=CH_3; III R=Cl; IV R=Br

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*See [1] for communication XXV.

Lensovet Leningrad Technological Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1411-1419, October, 1975. Original article submitted December 31, 1974.

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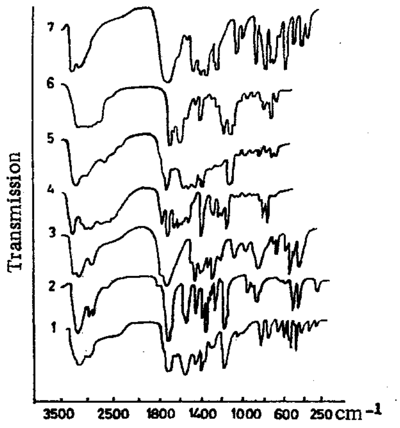

Fig. 1

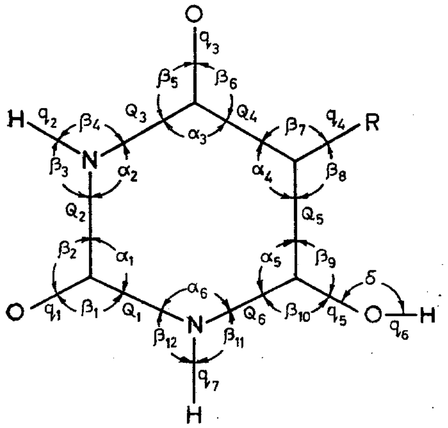

Fig. 2

Fig. 1. IR spectra of crystalline samples (suspensions in mineral oil and perfluorinated mineral oil): 1) 2-thiobarbituric acid, recrystallized from acetic acid (form A); 2) 2-thiobarbituric acid, recrystallized from water (a mixture of forms A and B); 3) barbituric acid; 4) 5-methylbarbituric acid; 5) 5-bromobarbituric acid; 6) 5-chlorobarbituric acid; 7) 5,5-dichlorobarbituric acid.

Fig. 2. Designation of the natural vibrational coordinates of the monoenol forms of barbituric acid.

The monoenol forms of the barbituric acids are none other than 6-hydroxyuracils. For the calculation we therefore used the same bond lengths and valence angles as in the calculation of the vibrational spectra of uracil [4] and its derivatives [5]. In so doing, it was assumed that the hydroxyl group is situated in the plane of the pyrimidine ring and that the molecule has C_s symmetry. The force constants of uracil and its 5-chloro derivative were used for the calculations of the force field within the zero approximation. The most convenient compounds for the calculation of the spectra of the enol forms of barbituric acid are 5-chloro- and 2-thiobarbituric acids (III, V).* The former exists in the crystalline state almost entirely in the "enol" form [2], whereas the latter after recrystallization from water exists almost entirely in the form of a mixture of the thionedicarbonyl (VA) and monoenol (VB) forms [3]. Their spectra differ most markedly from the spectra of their tricarbonyl forms (model IIIA is 5,5-dichlorobarbituric acid), and we were able to obtain pure desmotrope VA by recrystallization from CH_3COOH.

The designations of the natural vibrational coordinates are presented in Fig. 2. In the calculations the force field was refined in conformity with the derivatives of the frequencies with respect to the force constants. As a result we obtained the optimum sets of force constants that satisfactorily described the experimental spectra of the monoenol forms (B) of 5-chloro- and 2-thiobarbituric acids and their trideutero analogs. The results of the calculation of the frequencies of the normal vibrations are presented in Tables 1-3, and the force constants are presented in Table 4.

The force field obtained as a result of the calculation of the in-plane normal vibrations of IIIB was used to calculate the frequencies and forms of the normal vibrations of the monoenol form of barbituric acid (IB). It is evident from a comparison of the frequencies (Table 1) and forms of the normal vibrations of IA and IB that they differ considerably from one another and attest to the absence of the enol in crystals and solutions of barbituric acids.

The forms of the normal vibrations with the participation of multiple bonds and ring bonds of isomers B differ markedly from the forms of the corresponding vibrations of isomers A. For these vibrations there is greater similarity to the vibrations of the multiple bonds and the ring bonds of uracil and its 5-substituted derivatives [4, 5]. The frequencies corresponding to the stretching and stretching-deformation vibrations of the ring are elevated as compared with A. Moreover, the contribution of the vibration of the $C_2=O$ bond

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*The $C=S$ bond length and force constants of the bonds of the thiourea fragment necessary for the calculation of the spectra of the "enol" form of 2-thiobarbituric acid were taken from [1], and the bond lengths and $C_{(6)}-O-H$ angle were assumed to be the same as those for 5-nitrobarbituric acid [6].

TABLE 1. Observed and Calculated Frequencies of the In-Plane Normal Vibrations in the IR Spectra of Barbituric Acids (cm^{-1})

IA		IB	II	IV	III		5,5-Dichlorobarbituric acid	Type of vibrations	Tautomer
observed	calc.	calc.	observed	observed	observed	calc. (B)	observed		
1	2	3	4	5	6	7	8	9	10
3192	3186	—	3264	3200	—	—	3170	ν_{NH}	A
—	—	3169	—	3156	3168	3169	—	$\nu_{N_{(1)}H}$	B
3110	3111	—	3096	—	—	—	3130	ν_{NH}	A
—	—	3089	—	3088	3088	3090	—	$\nu_{N_{(3)}H}$	B
—	—	2958	—	—	2964	2960	—	ν_{OH}	B
2880	2878	—	—	—	2898	—	—	$\nu_{as}CH_2$	A
2828	2833	—	—	—	—	—	—	$\nu_s CH$	A
1758	1753	—	1756	1746	—	—	1748	$\nu_{C_2=O}$	A
1717	1713	—	1726	1719	—	—	1720	$\nu_{as}C_{(4,6)}=O$	A
1696	1686	—	—	—	—	—	—	$\nu_s C_{(4,6)}=O$	A
—	—	1700	1696	1690	1697	1703	—	$\nu_{C_{(2)}=O}, \nu_{C_{(2)}-N_1}, \delta_{NH}$	B
—	—	1689	1655	1658	1665	1667	—	$\nu_{C_{(4)}=O}, \nu_{C=C}$	B
1629	1646	—	1628	—	—	—	1610	ν_{ring}	A
—	—	1616	1610	—	1618	1616	—	$\nu_{C=C}$	B
—	—	1593	1586	1568	1589	1598	—	ν_{ring}	B
1543	1527	—	1520	1526	1537	—	1525	ν_{ring}	A
1462	1473	—	1477	1498	—	—	—	$\delta_{CH_2}, \delta_{ring}$	A
—	—	1507	1464	1457	1448	1453	—	ν_{ring}	B
1428	1447	—	—	—	—	—	1412	$\delta_{ring}, \delta_{CN_3}$	A
—	—	1390	1389	1382	1396	1389	—	$\delta_{N_{(3)}H}$	B
1370	1398	—	—	—	1374	—	1388	δ_{NH}	A
1340	1318	—	—	—	—	—	1348	δ_{NH}	A
1388	1379	—	—	—	—	—	—	$\delta_{CH_2}, \nu_{ring}$	A
		1322	—	—	1351	1350		$\nu_{ring}, \nu_{C_{(6)}-O}$	B
1282	1282	—	—	—	—	—	—	δ_{CH_2}	A
—	—	1355	—	—	—	—	—	$\delta_{C_{(5)}H}$	B
1255	1254	—	1270	1279	—	—	1238	ν_{ring}	A
—	—	1229	1228	1244	1233	1222	—	$\delta_{N_{(1)}H}, \nu_{ring}$	B
—	—	1168	1177	1152	1165	1167	—	δ_{OH}	B
		1116	1140	1120	1114	1116	—	$\nu_{ring}, \delta_{NH}, \delta_{CH}$	B
		1046	1080	1110	1086	1090	—	ν, δ_{ring}	B
1050	1056	1017	1050	1020	1025	1066	1034	ν, δ_{ring}	A, B
955	979	—	955	970	965	—	985	ν, δ_{ring}	A
763	770	—	—	—	—	—	764	ν_{ring}	A
—	—	—	—	—	744	740	—	ν_{C-Cl}	B
725	747	—	721	—	—	—	715	δ_{ring}	A
—	—	715	717	710	712	707	—	δ_{ring}	B
—	702	—	—	—	—	—	690	ν, δ_{ring}	A
660	654	637	—	—	—	670	—	$\delta_{C=O}$	A, B
		665	—	—	—	584	—	δ, ν_{ring}	B
470	433	388				381	—	$\delta_{C=O}$	A, B
410	413	—	—	—	—	—	—	$\delta_{C=O}$	A
—	—	279	—	—	—	274	—	$\delta_{C_{(6)}-O}$	B
—	—	—	—	—	—	166	—	δ_{C-Cl}	

TABLE 2. Observed and Calculated Frequencies of the In-Plane Normal Vibrations of the Monoenol Form (B) of Trideutero Derivatives of Barbituric Acids III and IV (cm^{-1})

IV	III		Type of vibration
observed	observed	calculated	
2408	2366	2363	$\nu_{N_{(1)}D}$
2336	2338	2300	$\nu_{N_{(3)}D}$
2140	2190	2198	ν_{OD}
1713	1685	1694	$\nu_{C_{(2)}=O}$
1696	1669	1664	$\nu_{C_{(4)}=O}$
1616	1609	1594	$\nu_{C=C}$
1555	1586	1576	ν_{ring}
1478	1488	1449	ν_{ring}
—	1346	1336	ν_{C-O}, ν_{ring}
—	1260	1265	$\delta_{N_{(3)}D}$
1168	1167	1162	ν_{ring}
1089	1082	1084	ν_{ring}, δ_{ND}
970	992	994	ν_{ring}, δ_{ND}
890	904	908	δ_{OD}
—	880	851	$\delta_{N_{(1)}D}$
—	720	723	ν_{C-Cl}
704	705	696	δ_{ring}
—	—	620	$\delta_{ND}, \delta_{ring}$
—	—	584	ν, δ_{ring}
—	—	372	$\delta_{C=O}$
—	—	262	δ_{C-O}
—	—	155	δ_{C-Cl}

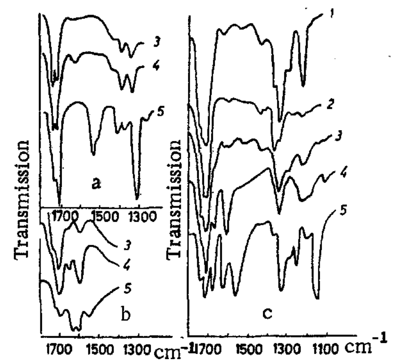

Fig. 3. IR spectra of dioxane (a), dimethyl sulfoxide (b), and methanol (c) solutions of: 1) barbituric acid; 2) 5-methylbarbituric acid; 3) 5-bromobarbituric acid; 4) 5-chlorobarbituric acid; 5) 2-thiobarbituric acid.

to the highest-frequency ring vibration increases. The increase in the intensity of the band corresponding to this vibration observed in the IR spectrum of B is associated with this to some degree. The $\nu_{C_2=O}$ frequency of the B isomers is lower than the $\nu_{C_2=O}$ frequency of the A isomers, whereas the form is close to the form of $\nu_{C_2=O}$ of uracil.

The intense band at ~1350 cm^{-1} observed in the spectra of the investigated compounds (II-V) corresponds to the ring stretching vibration and $\nu_{C_{(6)}}-O$. In addition, δ_{NH} and δ_{CH} contribute to it. The frequency of this vibration is very sensitive to a change in the magnitude of force constant K_{C_6-C}. In place of the frequencies corresponding to $\nu_{as}C_{4(6)}=O$ and $\nu_{s}C_{4(6)}=O$ of forms A, the spectrum of B contains frequencies corresponding to the antiphase and synphase vibrations of the $C_4=O$ and $C=C$ bonds in the spec-

TABLE 3. Observed and Calculated Frequencies of the In-Plane Normal Vibrations in the IR Spectra of 2-Thiobarbituric Acid and Its Deutero Derivatives (cm^{-1})

2-Thiobarbituric acid*				Deutero-2-thiobarbituric acid*			
observed	calc.	type of vibration	tautomer	observed	calc.	type of vibration	tautomer
3145	3143	ν_{NH}	A, B	2340	2340	ν_{ND}	A, B
3100	3089	ν_{NH}	A, B	2300	2300	ν_{ND}	A, B
2945	2950	ν_{OH}	B	2170	2190	ν_{OD}	B
2900	2896	$\nu_{as}CH_2$	A	—	—	—	—
2840	2850	$\nu_{s}CH_2$	A A	—	—	—	—
1700	1708	$\nu_{as}C_{(4,6)}=O$	B	1700	1687	$\nu_{as}C_{(4,6)}=O$	A
1680	1678	$\nu_{C_{(4)}=O}$, δ_{CH}	B	1675	1674	$\nu_{C_{(4)}=O}$	B
1630	1633	$\nu_{C=C}$	B	1668	1671	$\nu_{s}C_{(4,6)}=O$	A
1562	1566	ν_{ring}	A	1622	1621	$\nu_{C=C}$	B
1545	1533	ν_{ring}, $\nu_{C=S}$	A	1560	1556	ν_{ring}	A, B
1525	1526	ν_{ring}	A, B	1512	1515	ν_{ring}	B
1424	1415	δ_{CH_2}	A	1495	1503	ν_{ring} $\nu_{C=S}$	A
1378	1372	$\delta_{N_{(3)}H}$	A, B	1462	1452	ν_{ring}	A
1357	1356	ν_{ring}, δ_{NH}	B A	1385	1391	ν_{ring}	B
1345	1335	ν_{ring}, $\nu_{C_{(6)}-O}$	B	1345	1328	ν_{ring}, ν_{C-O}, δ_{ND}	B
1298	1309	$\delta_{N_{(1)}H}$	B	1272	1276	ν_{ring}, δ_{ND}, δ_{CD_2}	A
1245	1245	ν_{ring}, δ_{NH}	A	1260	1248	ν_{ring}, $\delta_{N_{(3)}D}$	B
1155	1155	δ_{OH}	B	1232	1236	ν_{ring}, δ_{ND}, δ_{CD_2}	A
1145	1135	ν_{ring}, $\nu_{C=S}$	B	1150	1157	ν_{ring}, $\nu_{C=S}$	A
—	1117	ν, δ_{ring}	B	—	—		
1038	1055	ν, δ_{ring}	A	1080	1077	δ_{ND}, δ_{CD_2}	A
995	1009	ν, δ_{ring}	A	1018	1018	ν, δ_{ring}	B
928	910	ν_{ring} δ_{CH_2}	B	962	964	$\delta_{N_{(1)}D}$, $\delta_{N_{(3)}D}$	B
898	889	$\nu_{C=S}$, ν_{ring}	B	888	890	δ_{CD_2}	A
725	721	$\delta_{C=O}$	A	830	845	$\delta_{N_{(1)}D}$, $\delta_{N_{(3)}D}$, δ_{OD}	B
—	686	$\nu_{C=S}$, δ_{ring}	A	825	818	$\nu_{C=S}$, δ_{ring}	A
635	638	$\delta_{C=O}$	A	778	766	ν_{ring} δ_{CD_2}	A
628	622	$\nu_{C=S}$, δ_{ring}	A, B	722	715	$\nu_{C=S}$, δ_{ring}	B
520	514	δ_{ring}	B	650	666	δ_{ring}, $\nu_{C=S}$	B
470	468	$\nu_{C=S}$	A, B	578	588	$\delta_{C=S}$, $\delta_{C=O}$	A, B
—	329	$\delta_{C=O}$, δ_{C-O}		515	504	δ_{ring}	B
278	262	$\delta_{C=S}$, δ_{C-O}		472	461	$\nu_{C=S}$	A, B
				—	320	$\delta_{C=O}$, δ_{C-O}	B
				—	255	$\delta_{C=S}$, δ_{C-O}	B

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*Recrystallized from H_2O and D_2O, respectively.

trum of uracil. However, in the case of B, in contrast to uracil, the contribution of the $C_4=O$ bond to the antiphase vibration decreases and that of the $C=C$ bond increases. Three frequencies – δ_{OH} (1160 cm^{-1}) and two frequencies of the stretching-deformation vibrations of the ring (at 1080-1120 cm^{-1}) – are found at 1100-1200 cm^{-1} in the calculated spectrum of B. Frequencies corresponding to the vibrations of A are absent in this region. Intense overlapped bands are observed in this region in the IR spectra of crystalline samples of the barbituric acid derivatives.

In a study of the IR spectra of crystalline samples of 2-thiobarbituric acid (V) and solutions of it in various solvents [3] we isolated frequencies corresponding to the vibrations of $C=S$ bonds and ring bonds of VA and VB and presented a preliminary interpretation of them. An analysis of the forms of the normal vibrations made it possible to refine this interpretation. The band at 1540 cm^{-1} in the spectra of VA [1] corresponds to ring stretching vibrations with participation of the $C=S$ bond, and the band at 1562 cm^{-1} in

TABLE 4

Force constants of the "enol" form of 5-chlorobarbituric acid (in units of 10^6 cm^{-2})

$K_{Q_1}=K_{Q_2}=12{,}00$

$K_{Q_3}=9{,}50$

$K_{Q_4}=10{,}50$

$K_{Q_5}=11{,}50$

$K_{Q_6}=9{,}80$

$K_{q_1}=17{,}30$

$K_{q_2}=8{,}87$

$K_{q_3}=15{,}60$

$K_{q_4}=7{,}40$

$K_{q_5}=9{,}80$

$K_{q_6}=8{,}14$

$K_{q_7}=9{,}35$

$K_{\alpha_1}=2{,}00$

$K_{\alpha_2}=1{,}80$

$K_{\alpha_3}=2{,}30$

$K_{\alpha_4}=2{,}10$

$K_{\alpha_5}=2{,}00$

$K_{\alpha_6}=1{,}90$

$K_{\delta}=1{,}05$

$K_{\beta_1}=K_{\beta_2}=K_{\beta_5}=K_{\beta_6}=2{,}00$

$K_{\beta_3}=K_{\beta_4}=0{,}78$

$K_{\beta_7}=K_{\beta_8}=0{,}74$

$K_{\beta_9}=K_{\beta_{10}}=1{,}00$

$K_{\beta_{11}}=K_{\beta_{12}}=0{,}71$

$H_{Q_1q_1}=H_{Q_2q_1}=1{,}80$

$H_{Q_1Q_2}=2{,}00$

$H_{Q_1Q_3}=0{,}40$

$H_{Q_1Q_5}=0{,}20$

$H_{Q_1Q_6}=0{,}80$

$H_{Q_2Q_3}=0{,}30$

$H_{Q_2Q_6}=0{,}40$

$H_{Q_3Q_4}=1{,}50$

$H_{Q_4Q_6}=0{,}40$

$H_{Q_5Q_6}=0{,}10$

$H_{q_3Q_4}=1{,}50$

$H_{q_3Q_3}=0{,}80$

$H_{Q_5q_5}=0{,}80$

$H_{Q_5q_6}=1{,}30$

$H_{Q_5Q_6}=0{,}30$

$A^{Q_2}_{\beta_1}=A^{Q_1}_{\beta_1}=A^{Q_2}_{\beta_4}=A^{Q_3}_{\beta_5}=A^{Q_3}_{\beta_6}=A^{Q_4}_{\beta_7}=A^{Q_6}_{\beta_{10}}=$

$=A^{q_5}_{\alpha_5}=A^{Q_6}_{\beta_{12}}=0{,}5$

$A^{Q_1}_{\alpha_1}=A^{Q_4}_{\alpha_4}=A^{Q_5}_{\alpha_4}=A^{Q_6}_{\alpha_5}=A^{Q_1}_{\beta_{11}}=1{,}20$

$A^{Q_4}_{\beta_8}=A^{Q_6}_{\beta_9}=0{,}40$

$A^{Q_2}_{\alpha_1}=A^{Q_3}_{\alpha_3}=1{,}80$

$A^{Q_2}_{\beta_2}=A^{Q_2}_{\beta_3}=A^{Q_3}_{\beta_4}=A^{Q_3}_{\beta_5}=A^{Q_4}_{\beta_6}=A^{Q_5}_{\beta_{10}}=A^{q_5}_{\beta_{10}}=0{,}90$

$A^{Q_2}_{\alpha_2}=A^{Q_3}_{\alpha_2}=A^{Q_4}_{\alpha_3}=A^{Q_6}_{\alpha_5}=A^{q_5}_{\beta_9}=1{,}50$

$A^{Q_6}_{\delta}=A^{q_5}_{\delta}=0{,}40$

$A^{q_1}_{\beta_1}=A^{q_1}_{\beta_2}=A^{q_3}_{\beta_5}=A^{q_3}_{\beta_6}=0{,}80$

$A^{q_1}_{\alpha_1}=A^{q_3}_{\alpha_3}=-0{,}80$

$A^{q_2}_{\beta_3}=A^{q_2}_{\beta_4}=A^{q_7}_{\beta_{11}}=A^{q_7}_{\beta_{12}}=0{,}20$

$A^{q_2}_{\alpha_2}=A^{q_7}_{\alpha_6}=-0{,}15$

$l^{\alpha_1}_{\beta_1}=l^{\alpha_1}_{\beta_3}=-0{,}01$

$l^{\beta_2}_{\beta_1}=l^{\beta_6}_{\beta_5}=0{,}10$

$l^{\alpha_2}_{\beta_3}=l^{\alpha_2}_{\beta_4}=-0{,}25$

$l^{\beta_4}_{\beta_3}=0{,}22$

$l^{\alpha_3}_{\beta_5}=l^{\alpha_3}_{\beta_6}=-0{,}15$

$l^{\alpha_4}_{\beta_7}=l^{\alpha_4}_{\beta_8}=-0{,}02$

$l^{\beta_{10}}_{\beta_9}=0{,}04$

$l^{\alpha_5}_{\beta_9}=l^{\alpha_5}_{\beta_{10}}=-0{,}10$

$l^{\beta_{11}}_{\beta_{12}}=0{,}30$

$l^{\alpha_6}_{\beta_{11}}=l^{\alpha_6}_{\beta_{12}}=-0{,}15$

$l^{\alpha_2}_{\alpha_1}=0{,}35$

$l^{\alpha_6}_{\alpha_1}=0{,}55$

$l^{\alpha_3}_{\alpha_2}=0{,}25$

$l^{\alpha_5}_{\alpha_2}=l^{\alpha_6}_{\alpha_2}=-0{,}40$

$l^{\alpha_4}_{\alpha_3}=0{,}15$

$l^{\alpha_5}_{\alpha_3}=-0{,}05$

$l^{\alpha_5}_{\alpha_4}=0{,}60$

TABLE 4 (continued)

$l^{\beta_6}_{\beta_5}=0,10$

$l^{\beta_8}_{\beta_7}=0,11$

$l^{\alpha_3}_{\alpha_1}=-0,50$

$l^{\alpha_5}_{\alpha_1}=-0,35$

$l^{\alpha_6}_{\alpha_4}=-0,7$

Force constants of the "enol" form of 2-thiobarbituric acid*

$K_{Q_1}=11,50$

$K_{q_1}=4,9$

$K_{q_3}=15,60$

$K_{q_4}=8,80$

$K_{Q_5}=12,00$

$K_{q_6}=8,10$

$K_{q_7}=9,20$

$K_{\beta_1}=K_{\beta_2}=1,85$

$K_{\beta_3}=K_{\beta_4}=0,79$

$K_{\beta_7}=K_{\beta_8}=0,74$

$K_{\beta_{11}}=K_{\beta_{12}}=0,71$

$K_{\delta}=1,00$

$H_{Q_1Q_3}=1,40$

$H_{Q_1q_1}=H_{Q_3q_1}=1,20$

$H_{Q_3Q_4}=2,00$

$H_{Q_5Q_6}=0,50$

$A^{\beta_1}_{Q_1}=1,35$

$A^{\alpha_1}_{Q_1}=1,50$

$A^{\alpha_1}_{q_1}=-1,80$

$A^{\alpha_2}_{Q_3}=1,65$

$A^{\beta_5}_{Q_3}=0,50$

$A^{\beta_8}_{Q_4}=0,80$

$A^{\beta_7}_{q_4}=A^{\beta_8}_{q_4}=0,20$

$A^{\alpha_4}_{q_4}=-0,15$

$A^{\beta_9}_{Q_5}=0,90$

$A^{\delta}_{q_5}=0,50$

$A^{\beta_{11}}_{Q_6}=0,80$

$A^{\beta_9}_{Q_5}=0,80$

$A^{\alpha_5}_{Q_5}=1,00$

$A^{\beta_5}_{\beta_6}=0,10$

$l^{\beta_9}_{\beta_{10}}=0,04$

$l^{\alpha_6}_{\beta_{11}}=l^{\alpha_6}_{\beta_{12}}=-0,05$

Force constants of the "enol" form of barbituric acid*

$H^{\beta_8}_{Q_4}=0,80$

$K_{q_4}=8,80$

$A^{\beta_7}_{q_4}=A^{\beta_8}_{q_4}=0,02$

$A^{\alpha_4}_{q_4}=-0,15$

$K_{\beta_7}=K_{\beta_8}=0,74$

$K_{\delta}=1,00$

$K_{\beta_{11}}=K_{\beta_{12}}=0,71$

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* The remaining force constants are the same as those for 5-chlorobarbituric acid.

the spectrum of VB corresponds to ring stretching vibrations but without participation of the C=S bond. Vibrational frequencies with the participation of the thiocarbonyl group are absent in the IR spectrum of VB above 700 cm^{-1} (Table 3).

Using the results of the calculations of the vibrational spectra of IB and IIIB, we assigned the frequencies with respect to the types of vibrations observed in the IR spectra of crystalline samples of 5-methyl- and 5-bromobarbituric acids (II, IV) and isolated frequencies related to each of the forms (Table 1).

Frequencies characteristic for forms A and B are also observed in the spectra of solutions. Thus in the IR spectrum of a solution of 2-thiobarbituric acid in DMSO the frequencies corresponding to the ring stretching vibrations of isomers VA and VB coincide completely with the corresponding frequencies in the spectrum of a crystalline sample of 2-thiobarbituric acid recrystallized from water [3]. The IR spectra of solutions of 5-bromo-, 5-chloro-, and 2-thiobarbituric acids in dioxane contain the frequencies of the stretching vibrations of the carbonyl groups and the ring bonds only of isomers A, whereas the spectra of solutions of III and IV in methanol contain primarily frequencies of enols IIIB and IVB (Fig. 3).

The introduction of a hydroxyl group in the 6 position of the uracil molecule markedly changes its polarization. This is reflected in the change in the force field of 6-hydroxyuracil as compared with uracil. The force constants of the $N_{(1)}-C_{(6)}$ and $N_{(3)}-C_{(4)}$ bonds decrease, and the degree of delocalization of the electrons in the $O=C_{(4)}-C_{(5)}-C_{(6)}-OH$ fragment decreases (Table 4).

Thus our calculations of the frequencies and forms of the in-plane normal vibrations and the calculated force field of the model of the monoenol form of 2- and 5-substituted barbituric acids confirm and refine our previously proposed interpretation [2, 3] of the IR spectra of crystalline samples of these compounds, make it possible to isolate the frequencies characterizing the tricarbonyl and dicarbonyl forms of the investigated compound, and, on the basis of IR spectroscopic data, make it possible to form a judgment regarding the structures of the barbituric acids in solutions.

EXPERIMENTAL

The calculations were made with a Minsk-22 computer with programs composed by L. A. Gribov and co-workers [7]. The IR spectra were recorded with IKS-14A and Perkin-Elmer 457 spectrometers. The spectra were obtained from suspensions of crystalline samples in mineral oil and perfluorinated oil on KBr plates. The spectra of solutions of the compounds were recorded in CaF_2 cuvettes.

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FORMAZANS OF THE PYRIMIDINE SERIES

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UDC 547.556.9'854.3

A series of 1-(2'-pyrimidyl)-3,5-diarylformazans was synthesized. Their structures were studied by means of IR and electronic spectroscopy, and assumptions regarding the most probable tautomeric forms of the investigated compounds were made. The ionization constants of the formazans were measured. It was found that 2,5-diphenyltetrazoles are formed instead of the expected tetrazolium salts in the reaction of 1-(2'-pyrimidyl)-3,5-diphenylformazans with N-bromosuccinimide.

Of the formazans of the pyrimidine series, 3-uracilyl-1,5-diphenylformazans are known. A series of 1-(2'-pyrimidyl)-3,5-diphenylformazans (I-VIII, Table 1) was synthesized in order to study the effect on the structures and properties of foramazans of a pyrimidine residue in the 1 position as compared with aryl and benzazole fragments. These compounds were obtained from 2-hydrazinopyrimidines [2] by coupling of the arenediazonium salts with benzaldehyde 2-pyrimidylhydrazones [3] in alcoholic alkali.

The tautomerism of these formazans envisages a large number of possible forms, and the most probable such forms are presented in the scheme below.

One distinct and intense absorption band at 3384-3390 cm^{-1} (Table 1), which can be assigned to the stretching vibrations of both the N—H bond and the O—H bond, is observed in the IR spectra of formazans I-V. In a comparison of the IR spectra of 1-(6'-methyl-4'-hydroxy-2'-pyrimidyl)-3,5-diphenylformazan (I) and 1-(6'-methyl-2'-pyrimidyl)-3,5-diphenylformazan (VII) at 1400-1700 cm^{-1} it was observed that the spectrum of I contains a $\nu_{C=O}$ absorption band at 1665 cm^{-1}, which is absent in the case of formazan VII. This proves the presence of a keto group in the 4 position of the pyrimidine ring of I-V and suggests that

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