LITERATURE CITED

1. Yu. D. Kanaskova, Yu. A. Pentin, and B. I. Sukhorukov, Optika i Spektroskopiya, 29, 679 (1970).
2. R. C. Lord, A. L. Marston, and F. A. Miller, Spectrochim. Acta, 9, 113 (1957).
3. I. A. Brownlie, J. Chem. Soc., 3062 (1950).
4. L. N. Short and H. W. Thompson, J. Chem. Soc., 168 (1952)..
5. A. J. Lafaix and J. M. Lebas, Spectrochim. Acta, 26A, 1243 (1970).
6. O. P. Shkurko, V. F. Sedova, and I. K. Korobeinicheva, Atlas of the Spectra of Aromatic and Hetero-cyclic Compounds [in Russian], No. 4, Novosibirsk (1974), p. 4.
7. O. P. Shkurko and I. K. Korobeinicheva, Zh. Prirodn. Soedin., 0000 (1975).
8. Atlas of the Spectra of Aromatic and Heterocyclic Compounds, [in Russian], No. 8, Novosibirsk (1975).

RESEARCH IN THE PYRIMIDINE SERIES

XXV.* CALCULATION OF THE NORMAL VIBRATIONS OF BARBITURIC AND 2-THIOBARBITURIC ACIDS

N. A. Smorygo and B. A. Ivin   UDC 547.854.5 : 543.422.4

The frequencies and forms of the in-plane normal vibrations of the tricarbonyl forms of barbituric and 2-thiobarbituric acids and their tetradeutero derivatives were calculated. The calculations were made for the C_{2V} (or C_{2v} and C_S for barbituric acid) symmetry point group. The principal frequencies observed in the IR spectra of these compounds were assigned with respect to the types of vibrations on the basis of an analysis of the forms of the normal vibrations.

Continuing our investigation of the vibrational spectra of polyhydroxypyrimidines, we calculated the in-plane normal vibrations of barbituric and 2-thiobarbituric acids. The IR and Raman spectra of barbituric acid and its derivatives were investigated previously in [2-13]. Principal attention was directed to an interpretation of the spectra in the region of the stretching vibrations of the NH and C = O bonds. Two intense bands at ~3200 and ~3080 cm^{-1} are observed in the spectra of most of the investigated compounds in the ν_{NH} region (for example, see Fig. 1) [6]. The intensity of the first band is somewhat higher than that of the second. These same bands are also present in the spectra of the mono-N-methyl derivatives. For example, two intense bands at 3208, 3098, and 3230, 3130 cm^{-1} are observed in the spectra of 1-methylbarbituric acid and 1-methylbarbital [9]. These same bands were also detected in the spectra of other cyclic amides [14]. Miyazawa [14] feels that the band at 3200 cm^{-1} is due to ν_{NH} and that the band at 3080 cm^{-1} is due to a combination of $\nu_{C=O}$ and δ_{NH} and is reinforced by Fermi resonance. However, there are a number of examples [10] in which the intensity of the band at 3080 cm^{-1} is higher than that of the band at 3200 cm^{-1}. According to x-ray diffraction data [15], crystalline barbituric acid exists in the tricarbonyl form and only two of its carbonyl groups participate in the formation of hydrogen bonds. The $C_{(2)} = O$ carbonyl group forms a hydrogen bond with the NH group (R = 2.909 Å). Two acid molecules form a dimer by means of these hydrogen bonds, and the $C_{(4)} = O...H-N$ hydrogen bonds (r = 2.855 Å) crosslink the dimers in ribbons. The third $C_{(6)} = O$ carbonyl group does not participate in the formation of hydrogen bonds. Bolton [15] determined the bond lengths and the valence angles in the barbituric acid molecule.

The hydrogen bonds are also retained in solutions of barbituric acid and its derivatives in chloroform and dimethyl sulfoxide (DMSO), but a band at 3400 cm^{-1}, which can be assigned to the vibrations of

*See [1] for communication XXIV.
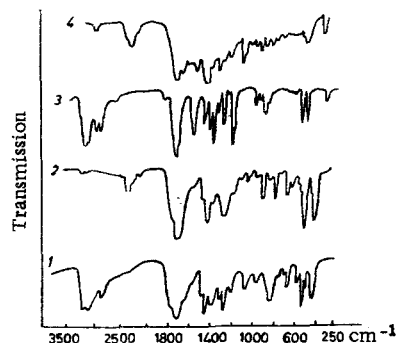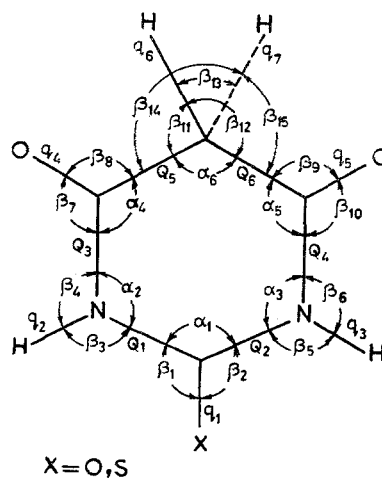
Fig. 1. IR spectra of crystalline samples (suspensions in mineral oil and perfluorinated oil): 1) barbituric acid; 2) 1,3,5,5-tetradeutero barbituric acid; 3) 2-thiobarbituric acid (recrystallized from acetic acid); 4) 1,3,5,5-tetradeutero-2-thiobarbituric acid (recrystallized from D_2O and containing an appreciable amount of the enol form).

Fig. 2. Designations of the natural vibrational coordinates of the barbituric and 2-thiobarbituric acid molecules (the tricarbonyl forms).

the nonbonded NH groups [2], appears in the IR spectra of solutions of the barbiturates in $CHCl_3$. If one takes into account the fact that barbituric acid forms hydrogen bonds of two types, the band at ~ 3200 cm^{-1} can be assigned to the vibrations of the NH groups bonded to $C_{(2)} = O$, and the band at ~ 3080 cm^{-1} can be assigned to the vibrations of the NH group bonded to $C_{(4)} = O$ by hydrogen bonds. The hydrogen bonds between NH and $C_{(4)} = O$ are probably broken when the compounds are dissolved in DMSO, and barbituric acid exists in the dimer form in DMSO solution. In fact, in the IR spectra of such solutions the band at 3200 cm^{-1} is retained, and the $\nu_{C_{(2)}=O}$ frequency is not shifted on dissolving, whereas the $\nu_{C_{(4)}=O}$ and $\nu_{C_{(6)}=O}$ frequencies increase by 30 cm^{-1} [9]. Thus the appearance of two bands in the region of the stretching vibrations of the NH bonds can be explained either by the presence in this region of a band of the corresponding combination of $\nu_{C=O}$ and δ_{NH} or by the fact that each type of association has its own ν_{NH} absorption band.

Several very intense overlapped bands are observed in the region of stretching vibrations of carbonyl groups in the IR spectra of the barbituric acids (Fig. 1). Intense bands at 1755, 1740, and 1710 cm^{-1} are present in the spectrum of a solution of barbituric acid in diethyl ether [3]. These same bands are also observed in the IR spectra of crystalline samples of N-alkyl- and 5-alkyl(aryl) derivatives of barbituric acid and in the spectra of their solutions in $CHCl_3$ [1-5]. These investigators [1-5] feel that the $C = O$ groups can be considered to be interacting oscillators. The lowest of the frequencies was assigned to $\nu_{C_{(2)}=O}$, and the bands at 1740 and 1755 cm^{-1} were assigned to symmetrical and asymmetrical vibrations of $C_{(4)} = O$ and $C_{(6)} = O$ bonds. Another interpretation of these three frequencies is presented in [7, 8]. As a result of a study of the IR spectra of solutions of barbituric acid and its ^{15}N analog in DMSO it was observed that the highest-frequency band is most sensitive to isotopic substitution and that it can be assigned to the stretching vibrations of the $C_{(2)} = O$ group included between the two nitrogen atoms. When the oxygen atom attached to $C_{(2)}$ is replaced by sulfur, this band vanishes and, as already mentioned above, is not shifted in the spectra of solutions of barbituric acid in DMSO.

An intense band at 1762 cm^{-1}, a band of low intensity at 1737 cm^{-1}, and an intense band at 1692 cm^{-1} are present in the Raman spectra of crystalline barbital and phenobarbital [12]. The ratio of the intensities of the second and third bands in the IR spectra of these compounds is the inverse of the ratio observed in the Raman spectra. This constitutes yet another proof that the first band corresponds to $\nu_{C_{(2)}=O}$ whereas the two other bands are asymmetrical and symmetrical vibrations of the bonds of the β-dicarbonyl fragment.

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

Barbituric acid			Tetradeuterobarbituric acid			2-Thiobarbituric acid			Tetradeutero-2-thiobarbituric acid		
observed	calc. C_{2v} / C_s	type of vibration	observed	calc.	type of vibration	observed*	calc.	type of vibration	observed†	calc.	type of vibration
3192 s	3190 A_1 / 3186	ν_{NH}	2320 vs	2327 A	ν_{ND}	3150 s	3154 A_1	ν_{NH}	2340	2354 A_1	ν_{ND}
3110 s	3186 B_1 / 3111	ν_{NH}	2320 vs	2319 B_1	ν_{ND}	3100 s	3099 B_1	ν_{NH}	2300	2310 B_1	ν_{ND}
2880 m	2878 B_2 / 2878	$\nu_{as\,CH_2}$	2132 s	2173 B_2	$\nu_{as\,CD_2}$	2905 m	2896 A_2	$\nu_{as\,CH_2}$	2230	2199 B_2	$\nu_{as\,CD_2}$
2828 m	2833 A_1 / 2833	$\nu_{s\,CH_2}$	2132 s	2086 A_1	$\nu_{s\,CD_2}$	2855 m	2850 A_1	$\nu_{s\,CH_2}$	2110	2090 A_1	$\nu_{s\,CD_2}$
1758 s	1756 A_1 / 1753	$\nu_{C_2=O}$	1740 m	1745 A_1	$\nu_{C_2=O}$	1708 vs	1708 B_1	$\nu_{as\,C_{4(6)}=O}$, δ_{CH_2}	1700	1687 B_1	$\nu_{as\,C_{4(6)}=O}$
1717 vs	1714 B_1 / 1713	$\nu_{as\,C_{4(6)}=O}+\delta_{CH_2}$	1710 vs	1681 B_1	$\nu_{as\,C_{4(6)}=O}$	1685 s	1686 A_1	$\nu_{s\,C_{4(6)}=O}$	1668	1671 A_1	$\nu_{s\,C_{4(6)}=O}$
1696 vs	1685 A_1 / 1686	$\nu_{s\,C_{4(6)}=O}$	1681	1681 A_1	$\nu_{s\,C_{4(6)}=O}$	—	1611 B_1	ν_{ring}, δ_{NH}, δ_{CH_2}	1560	1547 B_1	ν_{ring}, δ_{CD_2}
1629 sh	1640 B_1 / 1646	$\nu_{ring}+\delta_{NH}$	1562	1565 B_1	ν_{ring}	1540 s	1533 B_1	ν_{ring}, δ_{ND}, δ_{CH}	1495	1503 A_1	ν_{ring}, $\nu_{C=S}$
1543 w	1532 B_1 / 1517	$\nu_{ring}+\delta_{NH}$	1469	1484 B_1	ν_{ring}	1530 s	1527 A_1	ν_{ring}, $\nu_{C=S}$	1462	1452 B_1	ν_{ring}
1462 m	1473 A_1 / 1473	$\delta_{s\,CH_2}+\nu_{ring}$	1158	1141 A_1	$\delta_{s\,CD_2}$	1424 m	1415 A_1	ν_{ring}, δ_{CH_2}	1272	1286 A_1	ν_{ring}, δ_{ND}
1428 s	1441 A_1 / 1447	$\nu_{ring}+\delta_{s\,CH_2}$	1412 s	1427 A_1	ν_{ring}	1377 m	1382 A_1	$\delta_{s\,CH_2}$	1232	1236 B_1	ν_{ring}, δ_{CD_2}, δ_{ND}
1388 s	1379 B_1 / 1378	$\delta_{as\,CH_2}+\nu_{ring}$	1266	1258 B_1	$\delta_{CD_2}+\nu_{ring}$	1342 s	1356 B_1	ν_{ring}, δ_{NH}	1150	1157 A_1	ν_{ring}, $\nu_{C=S}$
1370 s	1369 A_1 / 1398	δ_{NH}	1041	1036 A_1	δ_{ND}	1312	1309 B_1	δ_{NH}, δ_{CH_2}	1080	1077 B_1	δ_{NH}, δ_{CH_2}
1340 s	1318 B_1 / 1327	δ_{NH}	1084	1084 B_1	δ_{ND}	1282 m	1282 A_2	δ_{CH_2}	1048	1046 A_1	δ_{CD_2}, $\nu_{C=S}$
1282 m	1282 A_2 / 1282	δ_{CH_2}	878 m	890 A_2	δ_{CD_2}	1247 m	1251 A_1	ν_{ring}	—	991 A_1	δ_{ND}, δ_{CD_2}, $\nu_{C=S}$
1255 s	1254 A_1 / 1255	ν_{ring}	1279	1275 A_1	ν_{ring}	1155 s	1135 A_1	ν_{ring}, $\nu_{C=S}$	888	890 B_2	δ_{CD_2}
1050 m	1055 A_1 / 1056	ν, δ ring	923 w	924 A_1	ν, δ_{ring}, δ_{ND}	917 w	910 B_1	ν_{ring}, δ_{CH_2}	825	818 A_1	$\nu_{C=S}$, ν_{ring}, δ_{CD_2}
955 m	979 B_1 / 979	ν, δ ring	804	813 B_1	ν, δ_{ring}, δ_{CD_2}	898 w	889 A_1	$\nu_{C=S}$, ν_{ring}	778	766 B_1	ν_{ring}, δ_{CD_2}
763	771 A_1 / 770	ν_{ring}	758	738 A_1	ν_{ring}, δ_{CD_2}		752 B_1	ν, δ_{ring}	722	732 B_1	ν, δ_{ring}
725 w	744 B_1 / 747	ν, δ_{ring}	729	729 B_1	ν, δ_{ring}		705 A_1	ν, δ_{ring}		692 A_1	ν, δ_{ring}
660 w	654 A / 654	$\delta_{C_2=O}$	654	642 A_1	$\delta_{C_2=O}$	645 m	638 B_1	$\delta_{C=S}$, $\delta_{C_{4(6)}=O}$	578	588 B_1	$\delta_{C=S}$, $\delta_{C_{4(6)}=O}$
—	704 B_1 / 702	ν, δ_{ring}	—	696 B_1	ν, δ_{ring}	450 m	468 A_1	$\nu_{C=S}+\nu_{ring}$	472	461 A_1	$\delta_{C=S}$, $\delta_{C_{4(6)}=O}$
470	434 B_1 / 433	$\delta_{C_{4(6)}=O}$	—	433 B_1	$\delta_{C_{4(6)}=O}$	390 vs	389 A_1	$\nu_{C=S}+\delta_{C_{4(6)}=O}$	—	389 A_1	$\nu_{C=S}$, $\delta_{C_{4(6)}=O}$
410	413 A_1 / 413	$\delta_{C_{4(6)}=O}$	—	413 A_1	$\delta_{C_{4(6)}=O}$	270 m	283 A_1	$\delta_{C=S}$	—	281 B_1	$\delta_{C=S}$

*The spectrum of the pure desmotrope of 2-thiobarbituric acid, which has a thionedicarbonyl structure, was obtained from a sample obtained by recrystallization of the acid from CH₃COOH.

†The spectral frequencies pertaining to the absorption of the tautomer having the thionedicarbonyl structure are presented.

TABLE 2

Force constants of barbituric and 2-thiobarbituric acids $(K \cdot 10^6 \text{ cm}^{-2})$

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

$K_{Q_3} = K_{Q_4} = 10,50$

$K_{Q_5} = K_{Q_6} = 9,00$

$K_{q_1} = 16,40$

$K_{q_2} = K_{q_3} = 9,00$

$K_{q_4} = K_{q_5} = 16,00$

$K_{q_6} = K_{q_7} = 7,50$

$K_{\alpha_1} = 3,80$

$K_{\alpha_2} = K_{\alpha_3} = 3,00$

$K_{\alpha_4} = K_{\alpha_5} = 3,50$

$K_{\alpha_6} = 2,50$

$K_{\beta_1} = K_{\beta_2} = 2,50$

$K_{\beta_3} = K_{\beta_4} = K_{\beta_5} = K_{\beta_6} = 0,85$

$K_{\beta_7} = K_{\beta_8} = K_{\beta_9} = K_{\beta_{10}} = 2,00$

$K_{\beta_{11}} = K_{\beta_{12}} = K_{\beta_{13}} = K_{\beta_{14}} = 0,80$

$K_{\beta_{13}} = 0,70$

$H_{Q_1 Q_2} = 2,70$

$H_{Q_1 Q_3} = H_{Q_2 Q_4} = 0,30$

$H_{Q_1 Q_4} = H_{Q_2 Q_3} = 0,40$

$H_{Q_1 Q_5} = H_{Q_2 Q_6} = 0,80$

$H_{Q_3 Q_5} = H_{Q_4 Q_6} = 1,00$

$H_{Q_3 Q_6} = H_{Q_4 Q_3} = 0,60$

$H_{Q_5 Q_6} = 1,50$

$H_{Q_1 q_1} = H_{Q_2 q_1} = 1,80$

$H_{Q_3 q_4} = H_{Q_4 q_5} = 0,80$

$H_{Q_5 q_4} = H_{Q_6 q_5} = 1,50$

$H_{Q_5 q_6} = H_{Q_5 q_7} = H_{Q_6 q_6} = H_{Q_6 q_7} = 0,03$

$H_{q_1 q_4} = H_{q_1 q_5} = 0,45$

$H_{q_4 q_5} = 0,95$

$H_{q_6 q_7} = 0,05$

$A_{\alpha_1}^{Q_1} = A_{\alpha_1}^{Q_2} = A_{\alpha_4}^{Q_3} = A_{\alpha_5}^{Q_4} = 1,80$

$A_{\alpha_2}^{Q_1} = A_{\alpha_3}^{Q_2} = 1,00$

$A_{\beta_2}^{Q_1} = A_{\beta_1}^{Q_2} = A_{\beta_4}^{Q_1} = A_{\beta_6}^{Q_2} = A_{\beta_3}^{Q_3} = A_{\beta_5}^{Q_4} = A_{\beta_9}^{Q_3} = A_{\beta_{10}}^{Q_4} = 0,50$

$A_{\beta_1}^{Q_1} = A_{\beta_2}^{Q_2} = 1,20$

$A_{\beta_3}^{Q_1} = A_{\beta_5}^{Q_2} = A_{\beta_7}^{Q_3} = A_{\beta_9}^{Q_4} = 1,50$

$A_{\beta_4}^{Q_3} = A_{\beta_6}^{Q_4} = A_{\beta_8}^{Q_5} = A_{\beta_{10}}^{Q_6} = 0,90$

$A_{\beta_7}^{Q_5} = A_{\beta_9}^{Q_6} = 0,80$

$A_{\alpha_1}^{q_1} = -1,20$

$A_{\beta_1 \beta_2}^{q_1} = A_{\beta_7 \beta_8}^{q_4} = A_{\beta_9 \beta_{10}}^{q_5} = 0,80$

$A_{\beta_3}^{q_2} = A_{\beta_4}^{q_2} = A_{\beta_5}^{q_4} = A_{\beta_6}^{q_3} = A_{\beta_{11}}^{q_6} = A_{\beta_{12}}^{q_3} = A_{\beta_{15}}^{q_7} = A_{\beta_{13}}^{q_7} = A_{\beta_{11}}^{Q_5} =$

$= A_{\beta_{12}}^{Q_5} = A_{\beta_{14}}^{Q_5} = A_{\beta_{15}}^{Q_6} = A_{\beta_{11}}^{Q_6} = A_{\beta_{12}}^{Q_6} = A_{\beta_{14}}^{Q_6} = A_{\beta_{15}}^{Q_6} = 0,20$

$A_{\beta_{13}}^{q_6} = A_{\beta_{14}}^{q_7} = 0,50$

$l_{\beta_2}^{\beta_1} = l_{\beta_8}^{\beta_7} = l_{\beta_{10}}^{\beta_9} = 0,40$

$l_{\beta_4}^{\beta_3} = l_{\beta_6}^{\beta_5} = 0,25$

$l_{\beta_{12}}^{\beta_{11}} = l_{\beta_{14}}^{\beta_{11}} = l_{\beta_{15}}^{\beta_{11}} = l_{\beta_{14}}^{\beta_{12}} = l_{\beta_{15}}^{\beta_{12}} = l_{\beta_{15}}^{\beta_{14}} = -0,02$

$l_{\alpha_1}^{\beta_1} = l_{\alpha_1}^{\beta_2} = l_{\alpha_4}^{\beta_7} = l_{\alpha_4}^{\beta_8} = l_{\alpha_5}^{\beta_9} = l_{\alpha_5}^{\beta_{10}} = -0,30$

$l_{\alpha_2}^{\beta_3} = l_{\alpha_2}^{\beta_4} = l_{\alpha_3}^{\beta_5} = l_{\alpha_3}^{\beta_6} = -0,25$

$l_{\alpha_6}^{\beta_{11}} = l_{\alpha_6}^{\beta_{12}} = l_{\alpha_6}^{\beta_{14}} = l_{\alpha_6}^{\beta_{15}} = -0,04$

$l_{\beta_{13}}^{\beta_{11}} = l_{\beta_{13}}^{\beta_{12}} = l_{\beta_{13}}^{\beta_{14}} = l_{\beta_{13}}^{\beta_{15}} = -0,35$

$l_{\alpha_2}^{\alpha_6} = l_{\alpha_3}^{\alpha_6} = -1,20$

$l_{\alpha_2}^{\alpha_1} = l_{\alpha_3}^{\alpha_1} = l_{\alpha_1}^{\alpha_2} = l_{\alpha_4}^{\alpha_5} = l_{\alpha_4}^{\alpha_6} = l_{\alpha_5}^{\alpha_5} = l_{\alpha_4}^{\alpha_1} = l_{\alpha_5}^{\alpha_1} = -0,40$

TABLE 2 (continued)

Some force constants of 2-thiobarbituric acid $(K \cdot 10^6 \ cm^{-2})*$

$K_{Q_3}=K_{Q_4}=9{,}50$

$K_{q_1}=4{,}80$

$K_{q_2}=K_{q_3}=9{,}10$

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

$H_{Q_1q_1}=H_{Q_2q_1}=1{,}20$

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

$H_{Q_3Q_5}=H_{Q_4Q_6}=0{,}50$

$H_{q_1q_4}=H_{q_1q_5}=0{,}30$

$H_{q_2q_3}=0{,}15$

$A^{q_1}_{\beta_1}=A^{q_1}_{\beta_2}=0{,}40$

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

$A^{Q_1}_{\alpha_2}=A^{Q_2}_{\alpha_3}=1{,}30$

$A^{Q_5}_{\alpha_4}=A^{Q_6}_{\alpha_5}=1{,}80$

$A^{Q_1}_{\beta_4}=A^{Q_2}_{\beta_6}=0{,}80$

$A^{Q_1}_{\beta_1}=A^{Q_2}_{\beta_2}=1{,}35$

$A^{Q_3}_{\beta_5}=A^{Q_4}_{\beta_5}=0{,}80$

$A^{Q_3}_{\beta_7}=A^{Q_4}_{\beta_9}=2{,}00$

$A^{q_4}_{\alpha_4}=A^{q_5}_{\alpha_5}=-1{,}20$

$A^{q_6}_{\beta_{13}}=A^{q_7}_{\beta_{13}}=0{,}60$

$A^{q_6}_{\beta_{11}}=A^{q_7}_{\beta_{11}}=A^{q_6}_{\beta_{12}}=A^{q_7}_{\beta_{12}}=0{,}02$

$l^{\alpha_6}_{\alpha_2}=l^{\alpha_6}_{\alpha_3}=-0{,}8$

*The remaining force constants are the same as those obtained for barbituric acid.

Characteristic series of bands of medium intensity are observed below 1600 cm^{-1} in the IR and Raman spectra of barbituric acid (Fig. 1) and its derivatives. The precise assignment of these bands with respect to the types of vibrations on the basis of an analysis of the experimental data has not been made. A weak band, which probably corresponds to vibrations of the bonds of the $O=C-N-H$ fragment [10], is observed at 1515-1540 cm^{-1} [10]. This band is absent in the Raman spectra. The IR spectra of most of the barbiturates have a band at 1425-2430 cm^{-1} (1447 cm^{-1} in the Raman spectra), which is frequently accompanied by a shoulder at 1400 cm^{-1}. All of the investigators assign the several bands at 1300-1400 cm^{-1} to ν_{C-N} ring vibrations [10]. Some of them vanish when the hydrogen atom attached to the nitrogen atom is replaced by deuterium and are probably related to the deformation vibrations of the N-H groups. The band at 1360-1389 cm^{-1} was assigned to the deformation vibrations of the methylene group and is shifted to 1050 cm^{-1} on deuteration [9]. One weak band at 1320 cm^{-1} is observed in this region in the Raman spectra. It is assumed that the band at 1200 cm^{-1}, which is absent in the Raman spectra, corresponds to vibrations of the ring C-C bonds. The band at 1050 cm^{-1} (1053 cm^{-1} in the Raman spectrum) can be assigned to ring skeletal vibrations. The broad band at 840-860 cm^{-1}, which is frequently accompanied by a band at ~815 cm^{-1} and is shifted to the low-frequency region on deuteration, is ascribed to γ_{NH}. A narrow intense band, which is absent in the Raman spectra, is present at ~760 cm^{-1} in the IR spectra of barbituric acid and its derivatives. The band at 670 cm^{-1} probably corresponds to $\delta_{C_{(2)}=O}$, inasmuch as it is not present in the spectrum of 2-thiobarbituric acid. The band at 629 cm^{-1} was assigned to ring symmetrical breathing vibrations [12]. The IR spectra of barbituric acids below 600 cm^{-1} have not been investigated. Four bands of medium intensity and a weak band at ~200 cm^{-1} are observed in the Raman spectrum of barbituric acid in this region. Two bands at 599 and 416 cm^{-1}, common to both compounds, are found here in the Raman spectra of barbiturates.

It is clear from what has been stated above that for complex cyclic amides, specifically, barbituric acids, it is difficult to make an accurate assignment of the observed frequencies with respect to the types of vibrations using only experimental data, and we therefore calculated the in-plane normal vibrations of the tricarbonyl forms of barbituric acid and its 1,3,5,5-tetradeutero and 2-thio- and 2-thio-1,3,5,5-tetra-

deutero derivatives. All of the atoms of the molecule except the hydrogens of the methylene group are situated in a single plane. The hydrogen atoms of the methylene group lie in a plane perpendicular to the plane of the ring above and below it. Inasmuch as, according to x-ray diffraction data, the differences in the $N_{(1)}-C_{(2)}$, and $N_{(3)}-C_{(2)}$, $N_{(3)}-C_{(4)}$ and $N_{(1)}-C_{(6)}$, $C_{(4)}-C_{(5)}$ and $C_{(5)}-C_{(6)}$, $C_{(4)}=O$ and $C_{(6)}=O$, and $N_{(3)}-H$ and $N_{(1)}-H$ bond lengths and the internal and external angles included between these bonds are small, a model with C_{2v} symmetry was selected. The plane of symmetry coincides with the plane of the ring, while the axis of symmetry passes through the $O=C_{(2)}$ and $C_{(5)}$ atoms. The model has 33 normal vibrations that break down as follows with respect to symmetry types: $12A_1 + 4A_2 + 10B_1 + 7B_2$. For 2-thiobarbituric acid all of the geometrical parameters were taken to be the same as those for barbituric acid, whereas the $C=S$ bond length was assumed to be equal to the $C_{(2)}=S$ bond length in 2,4-dithiouracil [16]. The natural coordinate that we selected for the calculations are presented in Fig. 2.

For calculations within the zero approximation, the force constants of a series of fragments of the barbituric acid molecule were assumed to be equal to the force constants of the corresponding structural elements of uracil, which we have previously calculated [17]. The force constants of the methylene group were taken from [18]. The constants of the potential energy of the $C=S$ bond and its interaction with the adjacent bonds and angles of the $N-C(=S)-N$ fragment are equal to the corresponding force constants of thiourea [19]. During the calculation, the force field was refined by the method of least squares (MLS) in conformity with the derivatives of the frequencies with respect to the force constants. The potential energy constants were varied until the calculated frequencies coincided satisfactorily with the experimental values. The frequencies (Table 1) and forms of the in-plane normal vibrations were determined. The final set of force constants is presented in Table 2.

As one should have expected, most of the vibrations of barbituric acid and its derivatives are complex. An analysis of the forms of the normal vibrations shows that the band at 1756 cm^{-1} corresponds to $\nu_{C_{(2)}=O}$ and the bands at 1717 and 1696 cm^{-1} are asymmetrical and symmetrical stretching vibrations of the $C_{(4)}=O$ and $C_{(6)}=O$ groups, as was previously assumed. The ring bonds participate in these vibrations. The 1640 cm^{-1} frequency, which appears in the IR specra as a shoulder on the intense band at 1696 cm^{-1}, and the 1523, 1441, 1254, 1057, and 768 cm^{-1} frequencies correspond to ring stretching vibrations. Primarily the $C-N$ bonds rather than the $C-C$ bonds participate in the vibration at 1254 cm^{-1}. As in the case of uracil, the deformation vibrations of the NH and CH groups contribute to the ring vibrations. The 1300-1400-cm^{-1} region is the region of absorption of the in-plane deformation vibrations of the NH bonds and the methylene group. Bands of very low intensity are found in this region in the IR spectra of tetradeuterobarbituric acid and its 2-thiotetradeutero derivative, and intense bands corresponding to δ_{ND} and δ_{CD_2} vibrations appear at 1000-1200 cm^{-1}.

Replacement of the oxygen atom attached to $C_{(2)}$ by sulfur also changes the force field of the molecule. The force constants of the $C-N$ bonds are increased, whereas the coefficients of interaction of the ring bonds and the $C-S$ group with the ring decrease. This constitutes evidence for a decrease in the degree of delocalization of the electrons in the ring when oxygen is replaced by sulfur. The increase in the frequencies of the ring vibrations, to which the stretching vibrations of the thiocarbonyl group contribute, is also associated with this. There are three such vibrations at 1527, 1135, and 889 cm^{-1}. The band at 458 cm^{-1} corresponds to the vibrations to which the $C_{(2)}=S$ group makes the primary contribution.

Thus our calculations of the in-plane normal vibrations of the model of barbituric acid, 2-thiobarbituric acid, and their deutero analogs with C_{2v} symmetry satisfactorily describe their experimental vibrational spectra. Replacement of the $C_{(2)}=O$ group by a $C_{(2)}=S$ group brings about redistribution of the electron density in the ring, and this is reflected in changes in the frequencies and forms of the normal vibrations of the ring and the force field of the molecule. However, we did not obtain a completely definite interpretation of the spectrum in the region of NH stretching vibrations. In the calculated spectrum of barbituric acid, 3190 cm^{-1} corresponds to ν_{asNH}, and 3186 cm^{-1} corresponds to ν_{sNH}. From this it can be concluded that in the experimental spectra only one frequency corresponds to ν_{NH} (3200 cm^{-1}), and the other is a combination of $\nu_{C=O}$ and δ_{NH}. It might be assumed that this was a result of the selection of the symmetry type (C_{2v}) for the calculations, inasmuch as the barbituric acid molecule actually more likely has C_S symmetry. Its symmetry relative to the axis of symmetry is disrupted because of the nonequivalence of the $C=O$ and NH bond lengths due to the formation of hydrogen bonds with different strengths. We therefore calculated the normal vibrations of a model with C_S symmetry. The bond lengths and valence angles correspond to those presented in [15]. All of the force constants except the force constants of the NH bonds coincide with the values that we obtained in the calculations with allowance for C_{2v} symmetry. The K_{N_1H} and K_{N_3H} force

constants are $9.44 \cdot 10^6$ and $8.9 \cdot 10^6$ cm^{-2}, respectively. The $\nu_{N_1 H}$ and $\nu_{N_3 H}$ bands at 3186 cm^{-1} and 3111 cm^{-1} correspond to them. A more rigorous conclusion relative to the origin of the bands in the region of the stretching vibrations of the NH bonds might have been drawn after a more detailed experimental investigation of the spectroscopic manifestation of the hydrogen bonds formed by barbituric acid (this is markedly hindered by the extremely low solubility of barbituric acid in solvents suitable for such investigations) and calculations of mdoels that more rigorously take into account the presence of hydrogen bonds.

EXPERIMENTAL

The calculations were made with a Minsk-22 computer with programs developed by L. A. Gribov and co-workers [20]. The spectra of mineral oil and perfluorinated mineral oil suspensions of the compounds were recorded with a Perkin-Elmer 457 spectrometer. Barbituric and 2-thiobarbituric acids were obtained by known methods, recrystallized to obtain samples with constant extinction in their UV spectra, and dried at 100-130° (1 mm, mercury gage). Inasmuch as 2-thiobarbituric acid may take on different desmotropic forms depending on the nature of the solvent used for recrystallization [21], it was recrystallized from acetic acid in order to have the pure thionedicarbonyl form in the crystalline sample. The deuterated samples were obtained by repeated crystallization from D_2O at pD ~ 1.

LITERATURE CITED

1. B. A. Ivin, A. I. D'yachkov, I. M. Vishnyakov, and E. G. Sochilin, Zh. Organ. Khim., 11, 2182 (1975).
2. J. Unberger and G. Adams, Anal. Chem., 24, 1302 (1952).
3. W. C. Price, J. E. S. Bradley, R. D. B. Fraser, and Y. P. Qulliam, J. Pharm. Pharmacol., 6, 522 (1954).
4. L. Levi and C. E. Huby, Anal. Chem., 28, 1591 (1956).
5. L. Levi and P. M. Laughton, Agricultural and Food Chem., 7, 850 (1959).
6. B. Cleverley and P. P. Williams, Tetrahedron, 7, 277 (1959).
7. S. Goenechea, Z. anal. Chem., 218, 416 (1966).
8. S. Pinchas, Spectrochim. Acta, 22, 1889 (1966).
9. V. A. Slesarev, B. A. Ivin, N. A. Smorygo, I. Yu. Tsereteli, and E. G. Sochilin, Zh. Organ. Khim., 6, 1313 (1970).
10. R. Y. Mesley, Spectrochim. Acta, 26A, 1427 (1970).
11. R. Jankow and Y. N. Willis, J. Mol. Spectr., 41, 412 (1972).
12. J. N. Willis, R. B. Cook, and R. Jankow, Anal. Chem., 44, 1228 (1972).
13. A. Sucharda-Sobczyk, Roczn. Chem., 46, 517 (1972).
14. T. Miyazawa, J. Mol. Spectr., 4, 155 (1960).
15. W. Bolton, Acta.Cryst., 16, 166 (1963).
16. . Shefter [sic] and H. Mautner, J. Amer. Chem. Soc., 89, 1249 (1967).
17. N. A. Smorygo and B. A. Ivin, Khim. Geterotsikl. Soedin., 98, 105 (1975).
18. G. F. Vlasova and Yu. N. Sheinker, Zh. Prirodn. Soedin., 14, 657 (1971).
19. Yu. Ya. Kharitonov, V. D. Brega, and A. V. Ablov, Zh. Neorgan. Khim., 15, 3163 (1970).
20. M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich, and B. I. Stepanov, Molecular Vibrations [in Russian], Nauka, Moscow (1972), p. 400.
21. B. A. Ivin, V. I. Slesarev, and N. A. Smorygo, Zh. Org. Khim., 10, 1968 (1974).