RESEARCH IN THE PYRIMIDINE SERIES

XX*. CALCULATION OF THE NORMAL VIBRATIONS OF URACIL AND ITS DEUTERO DERIVATIVES

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UDC 547.854.4+543.422.4

The normal vibrations of one of the bases of nucleophilic acids – uracil and its di- and tetradeutero derivatives – were calculated for the C_s symmetry point group. On the basis of an analysis of the forms of the normal vibrations and the shifts of the atoms in Cartesian coordinates the fundamental frequencies observed in the IR and Raman spectra of these compounds were assigned with respect to the types of vibrations, and the potential energy constants were determined.

Continuing our study of methods for the synthesis of and of the structure and properties of oxo-hydroxypyrimidines we calculated the in-plane normal vibrations of one of the bases of nucleic acids – uracil, which is the precursor of a large number of physiologically active compounds. In the present paper we report the results of a calculation of the in-plane normal vibrations of uracil itself and of several of its deutero derivatives, which served as the basis for subsequent calculations of the vibrational spectra of substituted "hydroxy"-pyrimidines. The calculation of the matrixes of the kinematic coefficients, the reduction of the matrixes with respect to symmetry, allowance for supplementary expressions, and the construction and solution of the secular equations were accomplished with a Minsk-22 computer with a program developed by L. A. Gribov and co-workers [2]. The anharmonicity of the vibrations was taken into account by introduction of the "spectroscopic" atomic masses. The geometrical parameters of the uracil molecule used for the calculations were taken from [3]. The uracil molecule has a planar conformation, C_s symmetry group, and 30 normal vibrations of the following symmetry types: $\Gamma_V = 21A' + 9A''$. The natural coordinates of the molecules are presented in Fig. 1.

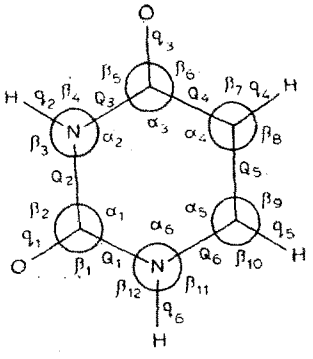

Fig. 1. Designation of the natural vibrational coordinates in the uracil molecule.

The force constants of the C=O, C–N, and C–C bonds, determined from correlation of the force constants with the π-bond order [4, 5], were used for the calculations within the zero approximation. The force constants of the interaction of the coordinates of the bonds and the valence angles and the force constants of interaction of the angular coordinates were taken from [6]. In addition, the force constants of the ortho and meta interactions of the ring bonds were introduced. In the calculations the force field was refined by the method of least squares in conformity with the derivatives of the frequencies with respect to the force constants. The potential energy constants were varied until there was satisfactory agreement between the calculated frequencies and the experimental values. The force field of uracil obtained in this way was then used for the calculation of the frequencies and forms of the normal vibrations and the shifts of the atoms in Cartesian coordinates of 1,3- and 5,6-dideutero- and 1,3,5,6-tetradeuterouracils. The agreement between the calculated frequencies of

* See [1] for communication XIX.

Lensovet Leningrad Technological Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 98-104, January, 1975. Original article submitted July 20, 1973; revision submitted July 8, 1974.

the vibrations of the deuterouracils and the experimental values constitutes evidence for the correct selection of the force field of uracil (Table 1). The final set of force constants for the uracil molecule is presented below.

Force Constants of Uracil (in $10^6 \cdot cm^{-2}$ units)

$K_{Q_1}=K_{Q_2}=K_{Q_3}=K_{Q_6}=10{,}30$	$H_{Q_1q_1}=1{,}10$	$A_{\beta_1}^{q_1}=A_{\beta_2}^{q_1}=A_{\beta_3}^{q_3}=A_{\beta_6}^{q_3}=A_{\beta_9}^{q_5}=$ $=A_{\beta_{10}}^{q_5}=A_{\beta_{11}}^{q_6}=A_{\beta_{12}}^{q_6}=0{,}80$	$l_{\beta_2}^{\beta_1}=0{,}45$
$K_{Q_4}=9{,}50$	$H_{Q_1Q_2}=1{,}20$	$A_{\beta_3}^{q_2}=A_{\beta_4}^{q_2}=A_{\beta_7}^{q_4}=A_{\beta_8}^{q_4}=0{,}20$	$l_{\beta_4}^{\beta_3}=l_{\beta_{10}}^{\beta_9}=0{,}22$
$K_{Q_5}=14{,}30$	$H_{Q_1Q_3}=0{,}50$	$A_{\beta_1}^{Q_1}=A_{\beta_{11}}^{Q_1}=A_{\beta_2}^{Q_2}=A_{\beta_3}^{Q_2}=A_{\beta_4}^{Q_3}=$ $=A_{\beta_8}^{Q_3}=A_{\beta_5}^{Q_4}=A_{\beta_7}^{Q_5}=A_{\beta_{10}}^{Q_5}=$ $=A_{\beta_1}^{Q_6}=A_{\beta_2}^{Q_6}=0{,}50$	$l_{\beta_6}^{\beta_5}=0{,}40$
$K_{q_1}=18{,}20$	$H_{Q_1Q_6}=1{,}20$	$A_{\beta_7}^{Q_4}=A_{\beta_8}^{Q_5}=A_{\beta_9}^{Q_5}=A_{\beta_{10}}^{Q_6}=0{,}80$	$l_{\beta_8}^{\beta_7}=0{,}14$
$K_{q_2}=7{,}98$	$H_{Q_2q_1}=1{,}80$	$A_{\alpha_1}^{Q_1}=A_{\beta_8}^{Q_5}=A_{\beta_9}^{Q_5}=A_{\beta_{10}}^{Q_6}=0{,}80$	$l_{\beta_{12}}^{\beta_{11}}=0{,}38$
$K_{q_3}=16{,}50$	$H_{Q_2Q_3}=2{,}60$		
$K_{q_4}=K_{q_5}=8{,}80$	$H_{Q_2Q_4}=0{,}20$	$A_{\alpha_1}^{Q_1}=A_{\alpha_4}^{Q_2}=A_{\alpha_5}^{Q_3}=1{,}80$	$l_{\beta_1}^{\alpha_1}=l_{\beta_2}^{\alpha_1}=-0{,}01$
$K_{q_6}=9{,}04$	$H_{Q_2Q_6}=0{,}10$	$A_{\alpha_2}^{Q_2}=A_{\alpha_2}^{Q_3}=A_{\alpha_3}^{Q_4}=A_{\alpha_6}^{Q_6}=A_{\alpha_7}^{Q_1}=1{,}50$	$l_{\beta_3}^{\alpha_2}=l_{\beta_4}^{\alpha_2}=-0{,}25$
$K_{\alpha_1}=2{,}00$	$H_{Q_3q_3}=1{,}50$		
$K_{\alpha_2}=1{,}80$	$H_{Q_3Q_4}=1{,}60$	$A_{\alpha_4}^{Q_5}=A_{\alpha_5}^{Q_5}=1{,}70$	$l_{\beta_5}^{\alpha_3}=l_{\beta_6}^{\alpha_3}=-0{,}15$
$K_{\alpha_3}=2{,}30$	$H_{Q_3Q_5}=0{,}10$	$A_{\alpha_7}^{Q_6}=1{,}20$	$l_{\beta_7}^{\alpha_4}=l_{\beta_8}^{\alpha_4}=-0{,}02$
$K_{\alpha_4}=2{,}10$	$H_{Q_4q_3}=1{,}50$	$A_{\alpha_1}^{q_1}=-0{,}70$	$l_{\beta_9}^{\alpha_5}=l_{\beta_{10}}^{\alpha_5}=-0{,}10$
$K_{\alpha_5}=K_{\alpha_6}=1{,}90$	$H_{Q_4Q_5}=1{,}40$		
$K_{\beta_1}=K_{\beta_2}=K_{\beta_5}=K_{\beta_6}=2{,}00$	$H_{Q_4Q_6}=0{,}40$	$A_{\alpha_3}^{q_3}=-0{,}80$	$l_{\beta_{11}}^{\alpha_6}=l_{\beta_{12}}^{\alpha_6}=-0{,}15$
$K_{\beta_3}=K_{\beta_4}=0{,}80$	$H_{Q_5Q_6}=1{,}30$	$A_{\alpha_2}^{q_2}=A_{\alpha_4}^{q_4}=A_{\alpha_5}^{q_5}=A_{\alpha_6}^{q_6}=-0.15$	
$K_{\beta_7}=K_{\beta_8}=0{,}70$			
$K_{\beta_9}=K_{\beta_{10}}=0{,}81$			
$K_{\beta_{11}}=K_{\beta_{12}}=0{,}75$			

A complex broad band with most intense maxima at 3130 and 2935 cm^{-1} is observed in the IR spectrum of uracil in the region of stretching vibrations of N–H and C–H bonds. It has been established [7, 8] that the lower of these frequencies corresponds to stretching vibrations of the $N_{(3)}$–H bond, which forms a stronger hydrogen bond with the $C_{(4)}=O$ carbonyl group than the $N_{(1)}$–H group [9]. The stretching vibrations of the N–H bonds are characteristic in form (Table 2), and their frequencies are determined by the magnitude of the force constants of the bonds. Using the $N_{(1)}$–H and $N_{(3)}$–H frequencies obtained in [10] in an investigation of the IR spectra of chloroform solutions of 1-methyl- and 3-methyluracils, we calculated the force constants for nonassociated N–H bonds. It was found that the potential energy constant of the $N_{(3)}$–H bond is reduced by $2.7 \cdot 10^6$ cm^{-2} during the formation of a hydrogen bond, whereas that of the $N_{(1)}$–H bond is reduced by $1.93 \cdot 10^6$ cm^{-2} [under the condition that the $N_{(1)}$–H frequency at 3432 cm^{-1} and the $N_{(3)}$–H frequency at 3394 cm^{-1} correspond to the vibrations of free NH groups]. Analysis of the forms of the normal vibrations for the $C_{(5)}$–H and $C_{(6)}$–H bonds showed that the frequencies corresponding to νC–H vibrations (3110 and 3092 cm^{-1}) are actually the frequencies of the synphase and antiphase vibrations of the CH bonds of the $H-C_{(5)}=C_{(6)}-H$ fragment.

TABLE 1. Observed and Calculated Frequencies of the In-Plane Normal Vibrations of Uracil and Its Deutero Derivatives

Uracil			1,3-Dideuterouracil			5,6-Dideuterouracil			Tetradeuterouracil		
observed	calc.	assignment	observed	calc.	assignment	observed	calc.	assignment	observed	calc.	assignment
3130 m	3126	$\nu N_{(1)}$—H	2265 s	2324	$\nu N_{(1)}$—D	3120 s	3125	$\nu N_{(1)}$—H	2265	2324	$\nu N_{(1)}$—D, $\nu C_{(5)}$—D
2930 s	2930	$\nu N_{(3)}$—H	2135 s	2186	$\nu N_{(3)}$—D	2940 s	2930	$\nu N_{(3)}$—H	2135 s	2186	$\nu N_{(3)}$—D
3105 s	3110	$\nu C_{(5)}$—H, $\nu C_{(6)}$—H	3065 m	3110	$\nu C_{(5)}$—H, $\nu C_{(6)}$—H	2315 s	2351	$\nu C_{(5)}$—D, $\nu C_{(6)}$—D	2315	2352	$\nu C_{(5)}$—D, $\nu C_{(6)}$—D
3092 s	3092	$\nu C_{(5)}$—H, $\nu C_{(6)}$—H	3065 m	3088	$\nu C_{(5)}$—H, $\nu C_{(6)}$—H	2300 s	2305	$\nu C_{(5)}$—D, $\nu C_{(6)}$—D	2300 s	2301	$\nu C_{(5)}$—D, $\nu C_{(6)}$—D, $\nu N_{(1)}$—D
1730 vs	1724	$\nu C_{(2)}$=O, $\delta N_{(1)}$—H; $\nu C_{(2)}$—$N_{(1)}$	1712 vs	1714	$\nu C_{(2)}$=O, $\nu C_{(2)}$—$N_{(1)}$	1720 s	1723	$\nu C_{(2)}$=O; $\nu C_{(2)}$—$N_{(1)}$	1710 s	1713	$\nu C_{(2)}$=O, $\nu C_{(2)}$—$N_{(1)}$
1666 vs	1667	Synphase $\nu C_{(4)}$=O, νC=C, $\delta C_{(6)}$—H	1680 vs	1663	Synphase $\nu C_{(4)}$=O, νC=C, $\delta C_{(6)}$—H	1680 vs	1658	Synphase $\nu C_{(4)}$=O, νC=C	1650 vs	1654	Synphase $\nu C_{(4)}$=O, νC=C
1623 sh	1616	Antiphase $\nu C_{(4)}$=O, νC=C, $\delta C_{(6)}$—H	1590 m	1609	Antiphase $\nu C_{(4)}$=O, νC=C, $\delta C_{(6)}$—H	1590 m	1585	Antiphase $\nu C_{(4)}$=O, νC=C	1571 s	1580	Antiphase $\nu C_{(4)}$=O, νC=C
1454 s	1465	ν ring, $\delta C_{(5)}$—H, $\delta C_{(6)}$—H	1460 s	1437	ν ring, $\delta C_{(5)}$—H, $\delta C_{(6)}$—H	1460 s	1464	ν ring	1457 m	1433	ν ring
1425 m	1427	ν ring, $\delta N_{(3)}$—H	1400 m	1393	ν ring, $\delta N_{(1)}$—D, $\delta C_{(5)}$—H	1417 m	1422	ν ring, $\delta N_{(3)}$—H	1410 m	1374	ν ring
1418 s	1419	$\delta C_{(5)}$—H	1400 m	1417	$\delta C_{(5)}$—H, $\delta N_{(1)}$—D	1370 w	1367	ν ring, $\delta N_{(3)}$—H, $\delta N_{(1)}$—H	1330 vw	1302	ν ring, $\delta C_{(5)}$—D, $\delta N_{(1)}$—D
1390 m	1374	$\delta N_{(3)}$—H, ν ring	1238 s	1239	ν ring	1290 m	1309	ν ring, $\delta N_{(1)}$—H, $\delta N_{(3)}$—H	1220 vw	1178	ν ring, $\delta N_{(3)}$—D
1240 s	1252	ν ring, $\delta N_{(1)}$—H	1200 w	1189	$\delta C_{(5)}$—H, $\delta C_{(6)}$—H	1235 m	1196	ν ring, $\delta N_{(1)}$—H,	1060 vw	1062	$\delta N_{(3)}$—D, $\delta C_{(5)}$—D, $\delta C_{(6)}$—D, $\delta N_{(1)}$—D
1218 sh	1205	$\delta C_{(6)}$—H	1140 s	1148	$\delta N_{(3)}$—D	1000 w	1010	ν ring, $\delta C_{(6)}$—D, $\delta N_{(1)}$—H	970 w	960	ν, δ ring
1095 w	1090	$\delta N_{(1)}$—H, $\delta C_{(5)}$—H	1000 m	979	ν, δ ring	990 vw	956	ν, δ ring	890 vw	874	$\delta C_{(5)}$—D, $\delta C_{(6)}$—D, $\delta N_{(1)}$—D
1005 m	1000	ν, δ ring	988 m	923	ν, δ ring	—	914	δ ring, $\delta C_{(6)}$—D	840 w	855	ν ring, $\delta N_{(1)}$—D, $\delta N_{(3)}$—D, $\delta C_{(6)}$—D
994 m	963	ν, δ ring	820 s	818	$\delta N_{(1)}$—D	860 m	872	$\delta C_{(5)}$—D, $\delta C_{(6)}$—D, $\delta N_{(1)}$—H	790 w	808	$\delta N_{(1)}$—D, δ ring
782 w	776	ν, δ ring	770 w	743	ν ring, $\delta N_{(1)}$—D	780 m	757	ν, δ ring	720 w	730	ν ring, $\delta N_{(1)}$—D
722 w	702	δ ring	740 m	680	δ ring	670 vw	689	δ ring	670 vw	677	δ ring
—	665	δ ring	620 w	659	δ ring	630	652	δ ring	—	652	δ ring
575 m	584	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O	560	559	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O	560	563	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O	560	545	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O
422 m	408	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O	430	406	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O	430	406	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O	430	405	$\delta C_{(2)}$=O, $\delta C_{(4)}$=O

* Note: the IR spectra of crystalline 5,6-di- and 1,3,5,6-tetradeuterouracils were taken from [7].

TABLE 2. Frequencies and Forms of the Normal Vibrations of Uracil in Natural Coordinates*

Frequency, cm^{-1}	Q_1	Q_2	Q_3	Q_4	Q_5	Q_6	q_1	q_2	q_3	q_4	q_5	q_6	α_1	α_2	α_3	α_4	α_5	α_6	β_1	β_2
3126	−2,4	—	—	—	—	—	—	+70,0	—	—	—	—	−3,2	+6,9	−3,4	—	—	—	−0,4	+3,6
2930	—	−2,7	−2,5	—	—	—	—	—	—	—	—	+71,4	—	−0,1	−3,2	+3,8	+2,8	−3,3	—	+0,2
3110	—	—	—	−2,3	−6,1	−1,5	+0,1	−0,6	—	+56,0	+49,0	—	−3,2	−0,1	—	−0,3	−2,8	+6,5	+3,5	−0,2
3092	+0,1	+0,1	—	—	−0,3	−2,1	−0,1	+0,2	—	−49,0	+56,0	—	—	−0,1	−3,2	+3,8	+2,8	−3,3	+0,2	—
1724	+24,2	+5,9	+3,1	+2,1	−1,3	−3,9	−34,4	+0,6	−6,2	+0,4	−0,1	+1,2	−27,6	+19,2	−5,6	+1,7	+6,0	+6,2	+5,7	+21,8
1667	+3,3	+3,8	−9,7	−18,6	+25,5	−13,0	−5,3	−0,9	+27,5	+1,7	−1,3	−0,4	−6,8	−11,5	−32,0	−20,6	−4,6	+11,5	+4,4	+2,3
1616	−3,3	+0,2	+5,6	+6,6	+29,9	−12,5	+0,9	+0,4	−25,0	+0,5	+0,3	+2,3	−0,5	+9,5	−1,1	−3,2	−7,7	+12,8	+4,1	−3,6
1465	+24,9	−22,2	−7,0	−0,9	+4,5	−9,3	−15,2	−1,2	−3,4	−0,2	+0,1	−0,3	+3,5	+14,9	−4,8	−1,0	+7,0	−19,5	−28,4	+24,9
1427	+4,2	−9,8	−18,9	+24,7	−4,1	−3,2	−2,4	−1,0	+7,1	+0,6	−0,1	−0,2	−5,5	−17,2	−0,9	−19,4	+9,8	−11,8	−3,9	+9,4
1419	+6,6	−0,8	+7,2	+6,8	−4,1	−24,5	+5,1	+0,3	+0,9	−0,1	−1,4	−0,8	−1,2	−6,1	−2,4	−10,3	+19,6	+0,5	+4,4	−3,1
1374	+7,1	−8,2	+23,1	−18,7	+3,4	−7,8	+3,4	+0,5	+1,8	−0,6	−0,2	—	+7,1	−12,8	+0,6	+9,8	—	−0,3	+2,3	−9,4
1252	−5,2	+28,7	−15,9	+12,0	−2,1	−13,6	+2,1	+0,7	−3,8	+0,4	−0,6	−0,3	−2,5	−10,0	+11,0	−14,8	+13,8	+8,3	+29,0	−20,1
1205	−1,2	−2,1	−6,5	+3,5	+8,6	+1,6	−2,8	−0,3	+0,8	+0,6	+0,6	+0,1	−2,2	+6,5	+2,5	−6,0	−4,6	+3,9	−2,9	+5,1
1090	+2,6	−6,9	+6,1	+1,9	−8,8	−23,5	−2,7	−0,2	−1,2	−0,1	−1,4	−1,0	−9,7	+5,2	−11,4	−3,1	+12,9	+6,1	+9,2	+0,5
1000	−1,3	−14,9	+23,3	+21,4	−2,5	+15,8	+2,3	+0,6	+1,4	+1,1	—	—	+20,6	−14,0	+4,5	−18,6	+10,8	−3,3	+4,9	−15,7
963	−18,2	−11,1	+3,2	−3,7	+1,2	−6,6	−2,2	−0,7	—	−0,4	−0,7	−0,4	−14,1	+18,3	−23,1	+15,8	−24,9	+27,9	+21,7	−7,5
776	+11,5	+13,6	−0,5	+10,9	+2,6	−1,2	+1,8	+0,5	—	+0,7	+0,3	+8,1	−13,9	+9,8	−19,7	+31,8	−29,2	+21,8	+11,0	+2,9
702	−5,5	+5,4	+0,8	−0,4	+5,2	−0,3	−1,1	—	—	+0,6	−0,2	—	+16,7	+10,9	−18,2	−44,1	+31,0	+36,2	−0,9	−1,5
665	−1,6	+3,3	+6,8	−1,6	+1,3	+7,1	+4,3	+0,3	+0,8	+0,2	+0,3	+0,1	−31,7	+28,5	−39,2	−18,3	+15,9	+9,5	+9,8	+21,9
584	−1,0	−1,0	−2,6	+7,4	+2,6	−5,3	−1,5	—	—	—	—	—	+9,4	−3,3	−3,6	−3,8	+1,2	+0,9	+34,5	+25,1
408	−3,5	+5,6	+7,6	−3,4	−2,0	−3,1	—	—	—	+7,6	—	—	−2,1	−5,9	−2,5	+6,1	−2,8	+7,2	−23,1	+25,1

TABLE 2. (Continued)

Frequency, cm^{-1}	β_3	β_4	β_5	β_6	β_7	β_8	β_9	β_{10}	β_{11}	β_{12}
3126	−3,4	−3,5	+3,7	−0,2	—	—	—	—	—	—
2930	−0,3	+3,5	−4,0	+0,2	+1,1	−4,0	+3,5	−2,6	—	—
3110	—	—	—	—	—	—	—	+3,4	+3,2	−2,9
3092	—	—	+0,1	−2,6	+2,2	+5,9	+5,9	−2,9	+13,4	−0,4
1724	−24,5	+5,3	+1,7	+3,9	−5,1	+3,3	+3,5	−9,6	+31,5	−37,7
1667	−14,4	+26,0	−13,9	−18,1	+41,0	−20,0	−23,4	+27,9	−6,2	−5,3
1616	+16,2	−25,7	+13,6	−2,7	+17,0	−13,7	−36,3	+44,0	−22,2	+9,5
1465	−39,6	+24,6	+11,1	−6,3	+22,0	−21,0	+16,9	−23,9	+51,0	−31,5
1427	+66,6	−83,8	+29,4	−28,5	+4,3	+15,0	−25,6	−15,7	+4,6	−3,5
1419	−7,0	+13,2	−8,4	+10,9	−83,9	+94,1	−6,4	+4,4	+26,5	−27,1
1374	+97,9	−85,1	−15,8	+16,4	+3,2	−13,0	+35,0	−35,1	+41,1	−37,5
1252	−12,2	+22,3	+2,8	−13,8	+24,8	−10,3	+31,6	−45,0	+61,6	−69,9
1205	−5,9	−0,5	+7,6	−10,2	−66,3	+72,3	+79,8	−75,1	−45,7	+41,8
1090	−6,6	+1,4	+2,6	+8,7	+38,3	−35,1	+9,4	−22,0	−74,8	+68,7
1000	−4,1	+18,2	+3,7	−8,2	+17,7	+0,9	+8,8	−19,7	+13,0	−9,7
963	−20,6	+2,2	+19,2	+3,8	−9,7	−6,0	+15,8	+9,0	+49,0	+7,6
776	−7,3	−1,9	+3,3	+16,4	−14,9	−16,8	+14,2	+15,0	−28,0	+6,8
702	+10,0	−0,8	+15,7	+2,5	+3,9	+0,4	−15,6	−15,6	+21,9	+14,2
665	−10,2	−18,3	−8,4	+12,1	+12,4	+5,8	−5,2	−10,6	−7,1	−2,3
584	+5,4	−2,1	−26,1	+29,8	+6,6	−2,8	+4,7	−5,9	+2,0	−2,0
408	+3,4	+2,5	+25,7	−23,2	−3,0	−3,0	+1,0	+1,7	+1,2	−8,4

* The coordinates of stretching of the bonds are presented in angstrom units · 10^{-3}, and the coordinates of the changes in the angles are presented in radians · 10^{-3}.

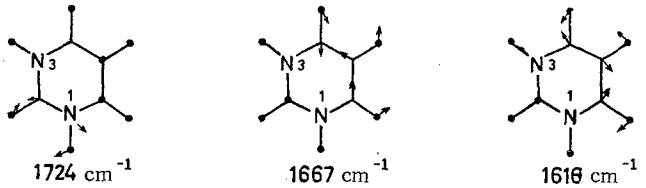

Fig. 2. Shift of the atoms of the uracil molecule in the case of vibrations corresponding to 1724, 1667, and 1616 cm^{-1}.

The highest frequency in the region of multiple bond absorption was previously [7, 8, 11] assigned to $\nu C_{(2)}=O$ (1730 cm^{-1}). The unusually high (as compared with acyclic amides) frequency of this vibration is explained by Horac and Gut [12] by interaction of the vibrations of the $C_{(2)}=O$ and $C_{(4)}=O$ groups, just as was observed for 1,3-dicarbonyl compounds. Other investigators have studied the IR spectra of 1,3-dideuterouracil and the Raman spectra of 1-methyl- and 1-methyl-3-deuterouracil and have proposed that the frequencies of the in-plane deformation vibrations of N–H bonds are also found in the region of $\nu C_{(2)}=O$ vibrations [7, 11]. Lord and Thomas [11] assumed that the increase in $\nu C_{(2)}=O$ occurs as a result of interaction of $\delta N-H$ and $\nu C_{(2)}=O$. In their opinion, the decrease in $\nu C_{(2)}=O$ in the Raman spectra of 1-methyl- (1680 cm^{-1}) and 1-methyl-3- deuterouracils (1694 cm^{-1}) is a confirmation of this. The data that we obtained from our calculation of the forms of the normal vibrations and the shifts of the atoms in Cartesian coordinates (Table 2 and Fig. 2) show that interaction of the vibrations of the carbonyl groups is absent, and the band at 1730 cm^{-1} is due to $\nu C_{(2)}=O$, $\nu C_{(2)}-N_{(1)}$, and $\delta N_{(1)}-H$ vibrations of the $O-C_{(2)}-N_{(1)}-H$ fragment. The frequency of this vibration depends mainly on the magnitude of the $KC_{(2)}=O$ force constant and the force constants of the $C_{(2)}-N_{(1)}-H$ and $C_{(6)}-N_{(1)}-H$ angles. Below 1700 cm^{-1} the IR spectrum of crystalline uracil contains an intense band at 1666 cm^{-1}, and a band at 1624 cm^{-1} appears as a shoulder on it. A band at 1620 cm^{-1} corresponding to the shoulder at 1624 cm^{-1} in the IR spectrum is clearly distinguished in the Raman spectrum of crystalline uracil [11]. The band at 1666 cm^{-1} was assigned to $\nu C_{(4)}=O$ vibrations, whereas the band at 1620 cm^{-1} was assigned to $\nu C_{(5)}=C_{(6)}$ vibrations [8, 11]. According to the calculations, the frequencies of two normal 1667 and 1616 cm^{-1} vibrations should be found in this region of the spectrum. In the case of each of them, there is a change in the $C_{(4)}=O$ and $C_{(5)}=C_{(6)}$ bond lengths and also a change in the inner $C_{(4)}-C_{(5)}-H$, $C_{(6)}=C_{(5)}-H$, $C_{(5)}=C_{(6)}-H$, and $N_{(1)}-C_{(6)}-H$ angles (Table 2 and Fig. 2). These two vibrations might have been termed synphase (1667 cm^{-1}) and antiphase (1616 cm^{-1}) vibrations of the conjugated $O=C_{(4)}-C_{(5)}=C_{(6)}-H$ system. It should be noted that, in contrast to $\delta N_{(1)}-H$, the $N_{(3)}-H$ deformation vibrations do not appear above 1600 cm^{-1}. As one should have expected, the frequencies corresponding to the stretching vibrations of the ring bonds are found at 1200-1500 cm^{-1} and to a certain degree characterize the vibrations of all of the ring bonds but not of each taken individually. In addition, the $\delta N-H$ and $\delta C-H$ in-plane deformation vibrations contribute to practically all of the vibrations whose frequencies are found at 1000-1750 cm^{-1}. Bands corresponding primarily to the in-plane deformation vibrations of N–H and C–H bonds are found in this same region. It is precisely this fact that may explain the shifts and changes in the intensities of a large number of bands in the spectra of partially and completely deuterated uracils and the sharp decrease in the intensities of all of the bands at 1000-1400 cm^{-1} in the IR spectra of tetradeuterouracil.

In the course of this research, data from calculations of the in-plane normal vibrations of uracil and its deutero analogs were published [13]. Susi and Ard used a different approach to the selection of the force field of uracil within the zero approximation – namely, from correlations of the force constants with the bond lengths rather than with the π-bond orders, as in our approach. We did not introduce a coefficient for the interaction between the $C_{(4)}=O$ and $C_{(5)}=C_{(6)}$ bonds, and the overall number of force constants used in our variant of the calculation does not coincide with the number used in [13]. Despite this, with certain exceptions [the $\delta N_{(1)}-H$ vibrations and some ring vibrations], good agreement is observed between the frequencies and forms of the normal vibrations of uracil and its deutero analogs calculated by the different methods. The force constants of the C=O, C=C, C–N, and C–C bonds and the angles obtained as a result of refinement of the force field within the zero approximation are in good agreement with the values presented in [13]. All of this, in our opinion, constitutes evidence for the correctness of our approach to the selection of the force field of such complex heterocyclic molecules as uracil and its derivatives.

The authors sincerely thank Professor B. V. Gidaspov, V. V. Mel'nikov, and V. V. Stolpakova for enabling us to carry out the present research and for their constant interest.

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