RESEARCH IN THE PYRIMIDINE SERIES

XXI.* CALCULATION OF THE NORMAL VIBRATIONS OF SUBSTITUTED URACILS

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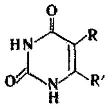
The frequencies and forms of the normal vibrations of thymine, 5-amino-, 5-fluoro-, 5- and 6-chloro-, 5-bromo-, and 5-nitrouracils and their 1,3-dideutero analogs were calculated, and their force constants were determined. The calculated and observed frequencies were assigned with respect to the types of vibrations. The introduction of substituents into the 5 and 6 positions of the uracil ring leads to a change in a whole series of force constants and to redistribution of the forms of the normal vibrations with respect to natural coordinates. Despite this, one can isolate those structural fragments of the investigated molecules whose normal vibrations remain characteristic in form. A linear dependence of the $\nu N_{(1)}H$ and $\nu N_{(3)}H$ frequencies on the force constants of the corresponding bonds was observed.

Continuing our study of the vibrational spectra of hydroxypyrimidines, we turned to a calculation of the frequencies and forms of the normal vibrations of 5-substituted uracils, including thymine – one of the bases of nucleic acids and of a number of compounds that display biological activity or serve as starting materials for the synthesis of physiologically active preparations. We have previously calculated the frequencies and forms of the normal vibrations of the precursor of the investigated series of pyrimidines – uracil [1]. The force field obtained as a result of this calculation was used as a zero approximation for the calculation of the normal vibrations of II-VIII and their 1,3-dideutero derivatives. Unfortunately, the literature does not contain data from x-ray diffraction analyses of most of the investigated compounds, but most of the bond lengths and angles in the thymine [2], 5-fluoro- [3] and 5-nitrouracil [4] molecules differ little from the corresponding parameters of uracil [5]. A model in which the bond lengths and valence angles of the pyrimidine ring, NH and C=O groups, and the corresponding external angles are equal to their values in uracil was therefore used for the calculations. Depending on the type of substituents, only the $C_{(4)}-C_{(5)}-R$ and $C_{(6)}=C_{(5)}-R$ angles changed (Table 1).



I-VIII

I-VII R'=H; VIII R'=Cl; I, VIII R=H;
II-VII R=CH_3, NH_2, F, Cl, Br, NO_2

All of the investigated molecules are planar, and all of the atoms of the substituents, except for the hydrogens of the methyl groups in the thymine molecule, lie in the plane of the ring. For the calculations within the zero approximation, the force constants of the C–Hal bonds and the constants of their interaction with the angles were taken from the calculation of the normal vibrations of monohaloethylenes [6]. The force constants for the CH_3, NO_2, and NH_2 groups were taken from calculations of the normal vibrations of

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[*] See [1] for communication XX.

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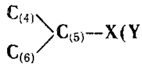
TABLE 1. Bond Lengths (l) and Angles of the


$C_{(4)}, C_{(6)} > C_{(5)}-X(Y)_n$

Fragment of Some 5-Substituted Uracils (II-VIII)

Compound	R	l, Å		Valence angles			
		$C_{(5)}-X$	$X-Y$	$C_{(4)}-C_{(5)}-X$	$C_{(6)}-C_{(5)}-X$	$C_{(5)}-X-Y$	$Y-X-Y$
II	CH_3	1,470	1,090	119°18′	121°54′	109°27′	109°27′
III	NH_2	1,470	1,011	119°18′	121°54′	125°	110°
IV	F	1,294	—	—	—	—	—
V	Cl	1,706	—	—	—	—	—
VI	Br	1,860	—	—	—	—	—
VII	NO_2	1.427	1,230	121°18′	118°54′	119°12′	121°36′

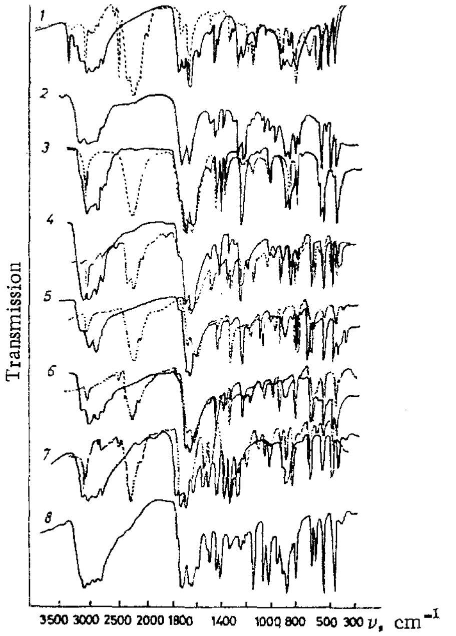


Fig. 1. IR spectra of crystalline samples of substituted uracils (continuous lines) and their deutero analogs (dash lines): 1) 5-aminouracil (III); 2) thymine (II); 3) uracil (I); 4) 5-fluorouracil (IV); 5) 5-chlorouracil (V); 6) 5-bromouracil (VI); 7) 5-nitrouracil (VII); 8) 6-chlorouracil (VIII).

nitromethane [7] and the simplest amines [8]. The remaining force constants were assumed to be equal to the corresponding force constants of uracil [1]. In the course of the calculations, the force constants were refined by the method of least squares in conformity with the derivatives of the frequencies with respect to the force constants. The optimum sets of force constants that satisfactorily describe the experimental spectra of the investigated 5- and 6-substituted uracils and their 1,3-dideutero analogs were obtained in this way. The potential energy constants that underwent changes as compared with their values for uracil [1] are presented in Table 2.

An analysis of the frequencies and forms of the in-plane normal vibrations of 5-substituted uracils made it possible to assign the frequencies observed in the IR spectra (Fig. 1) with respect to the types of vibrations and expose some peculiarities. As in the case of uracil [1], the vibrations of the $N_{(1)}H$ and $N_{(3)}H$ bonds are characteristic with respect to form and frequency. Their frequencies depend mainly on the magnitude of the force constant of the NH bond (Fig. 2).

When substituents with different masses and geometrical and electronic structures are introduced into the uracil molecule, one observes a change not only in the potential energy constants but also a redistribution of the forms of the normal vibrations with respect to the natural coordinates of the molecule. Nevertheless, despite this, one can isolate those vibrations which remain characteristic in form for definite structural fragments of the uracil molecules. As we have previously noted [1], three bands are found at 1600-1750 cm^{-1} – the highest-intensity band corresponds to $\nu C_{(2)}=O$, $\nu C_{(2)}-N_{(1)}$, and $\delta N_{(1)}-H$ vibrations, whereas the lower two are related to the synphase and antiphase vibrations of the multiple bonds of the conjugated $O=C_{(4)}-O_{(5)}=C_{(6)}H$ system. The characteristic nature of these vibrations with respect to form is retained, but the magnitudes of their frequencies depend both on the kinematic and electronic properties of the substituents. Thus, for example, replacement of the hydrogen attached to the $C_{(5)}$ atom of uracil by chlorine or bromine does not have a substantial effect on the force field of the molecule. At the same time, there are changes in the forms of a number of the normal ring vibrations and the deformation vibrations of the C–H and N–H bonds. The normal vibrations corresponding primarily to $\delta C_{(6)}H$ change particularly markedly: the $\delta C_{(6)}H$ frequency increases by more than 100 cm^{-1}. Inasmuch as the force fields of 5-chloro- and 5-bromouracils remain almost unchanged as compared with the force field of uracil, it might be assumed that the observed changes in the frequencies and forms of the vibrations are due to kinematic factors. The fact that the introduction of chlorine and bromine atoms into the 5 position of the pyrimidine ring had a substantial effect on the difference ($\Delta\nu$) in the synphase and antiphase vibrations of the $O=C_{(4)}-C_{(5)}=C_{(6)}$ fragment proved to be extremely interesting: $\Delta\nu$ for uracil is 51 cm^{-1}, whereas $\Delta\nu$ for halouracils is 35 cm^{-1}. Replacement of the hydrogen atom attached to the $C_{(6)}$ atom by chlorine does not affect the $\Delta\nu$ value. This serves as yet another confirmation of the presence of a mechanical resonance interaction between the $C_{(4)}=O$ and $C_{(5)}=C_{(6)}$ group. The changes in

TABLE 2. Some Force Constants (K) of Five-Substituted Uracils (in $10^6 \cdot cm^{-2}$ units)

Compound	I	II	III	IV	V	VI	VII	VIII
K \ R	5-H	5-CH_3	5-NH_2	5-F	5-Cl	5-Br	5-NO_2	6-Cl
K_{Q_1}	10,30	10,30	10,30	10,30	10,30	10,30	10,30	10,30
K_{Q_2}	10,30	9,10	9,10	10,30	10,30	10,30	10,30	10,30
K_{Q_3}	10,30	10,30	10,30	10,30	10,30	10,30	9,80	10,30
K_{Q_4}	9,50	9,50	9,50	9,50	9,50	9,50	10,30	9,50
K_{Q_5}	14,30	14,00	14,60	13,20	14,30	14,30	14,10	14,30
K_{Q_6}	10,30	10,30	10,30	10,30	10,30	10,30	10,30	10,30
K_{q_1}	18,20	18,50	18,20	18,20	17,50	17,50	18,50	18,20
K_{q_2}	7,980	8,55	8,38	7,98	7,980	7,74	8,50	7,98
K_{q_3}	16,50	16,50	16,50	16,50	16,50	16,50	16,50	16,50
K_{q_4}	8,80	6,40	8,80	10,00	5,80	4,10	8,55	8,80
K_{q_5}	8,80	8,65	8,80	8,80	8,80	8,80	8,80	4,70
K_{q_6}	9,04	9,40	9,45	9,48	9,33	9,33	9,04	9,33
K_{q_7}	—	8,40	10,40	—	—	—	14,00	—
K_{q_8}	—	8,40	10,40	—	—	—	14,00	—
K_{q_9}	—	8,40	—	—	—	—	—	—
K_{α_4}	2,10	3,50	3,50	2,10	2,10	2,10	3,00	2,10
K_{β_3}	0,80	0,80	0,83	0,80	0,80	0,80	0,80	0,80
K_{β_4}	0,80	0,80	0,83	0,80	0,80	0,80	0,80	0,80
K_{β_7}	0,70	1,30	1,30	1,60	1,10	0,95	1,20	0,70
K_{β_8}	0,70	1,30	1,30	1,60	1,10	0,95	1,20	0,70
K_{β_9}	0,81	0,81	0,85	0,75	0,81	0,81	0,81	1,10
$K_{\beta_{10}}$	0,81	0,81	0,85	0,75	0,81	0,81	0,81	1,10
$K_{\beta_{11}}$	0,75	0,75	0,85	0,75	0,75	0,75	0,75	0,75
$K_{\beta_{12}}$	0,75	0,75	0,85	0,75	0,75	0,75	0,75	0,75
$H_{Q_1Q_2}$	1,20	1,80	1,10	1,20	1,20	1,20	1,40	1,20
$H_{Q_1Q_3}$	0,50	0,00	0,00	0,50	0,50	0,50	0,00	0,50
$H_{Q_2Q_6}$	0,10	0,02	0,02	0,10	0,10	0,10	0,10	0,10
$H_{Q_3Q_4}$	1,60	1,60	0,80	1,60	1,60	1,60	1,60	1,60
$H_{Q_3Q_5}$	0,10	0,50	0,20	0,10	0,10	0,10	0,10	0,10
$H_{Q_4Q_5}$	1,40	1,40	1,60	1,40	1,40	1,40	1,40	1,40
$H_{Q_4Q_6}$	0,40	0,40	0,40	0,40	0,40	0,40	0,00	0,40
$H_{Q_1q_1}$	1,10	0,80	0,80	1,10	1,10	1,10	1,10	1,10
$H_{Q_4q_4}$	0,00	1,00	1,00	0,00	0,00	0,00	1,50	0,00
$H_{Q_5q_4}$	0,00	1,00	1,00	0,00	0,00	0,00	1,50	0,00
$A^{q_4}_{\beta_{7,8}}$	0,20	0,60	0,40	0,80	0,80	0,65	0,60	0,20
$A^{q_5}_{\beta_{9,10}}$	0,20	0,20	0,20	0,20	0,20	0,20	0,20	0,80
$A^{Q_1}_{\beta_1}$	0,90	0,90	1,10	0,90	0,90	0,90	0,90	0,90
$A^{Q_1}_{\beta_{12}}$	0,50	0,50	1,50	0,60	0,60	0,60	0,50	0,60
$A^{Q_4}_{\beta_7}$	0,80	0,90	0,90	0,80	0,80	0,80	0,96	0,90
$A^{Q_4}_{\beta_8}$	0,40	0,50	0,50	0,40	0,40	0,40	0,58	0,50

TABLE 2. (Continued)

Compound	I	II	III	IV	V	VI	VII	VIII
R K	5-H	5-CH$_3$	5-NH$_2$	5-F	5-Cl	5-Br	5-NO$_2$	6-Cl
$A_{\beta_7}^{Q_5}$	0,50	0,30	0,20	0,50	0,50	0,50	0,30	0,50
$A_{\beta_8}^{Q_5}$	0,80	0,80	0,80	0,80	0,80	0,80	0,85	0,80
$A_{\beta_9}^{Q_6}$	0,40	0,50	0,50	0,40	0,40	0,40	0,30	0,40
$A_{\beta_{10}}^{Q_6}$	0,80	0,98	1,00	0,80	0,80	0,80	0,80	0,80
$A_{\beta_{11}}^{Q_6}$	0,90	0,80	0,80	0,90	0,90	0,90	0,96	0,90
$A_{\beta_{12}}^{Q_6}$	0,50	0,50	0,50	0,50	0,50	0,50	0,30	0,50
$A_{\alpha_6}^{Q_1}$	1,50	1,50	1,90	1,50	1,50	1,50	1,50	1,50
$A_{\alpha_4}^{Q_4}$	1,20	1,80	1,80	1,20	1,20	1,20	0,920	1,2
$A_{\alpha_4}^{Q_5}$	1,70	2,10	2,13	1,70	1,70	1,70	2,10	1,7
$A_{\alpha_5}^{Q_5}$	1,70	1,30	1,30	1,70	1,70	1,70	1,80	1,7
$A_{\alpha_5}^{Q_6}$	1,70	1,20	1,20	1,70	1,70	1,70	1,20	1,7
$A_{\alpha_1}^{q_1}$	−0,70	−1,20	−1,20	−0,70	−0,70	−0,70	−0,70	−0,7
$A_{\alpha_4}^{q_4}$	−0,15	−0,70	−0,70	−0,70	−0,70	−0,55	−0,70	−0,15
$A_{\alpha_5}^{q_5}$	−0,15	−0,15	−0,15	−0,15	−0,15	−0,15	−0,55	−0,15
$l_{\beta_8}^{\beta_7}$	0,14	−0,20	−0,20	0,40	0,14	0,14	−0,30	0,14
$l_{\beta_{12}}^{\beta_{11}}$	0,38	0,38	0,30	0,38	0,38	0,38	0,38	0,38
$l_{\beta_{7,8}}^{\alpha_4}$	−0,02	0,30	0,30	+0,01	+0,01	+0,01	−0,20	0,01
$H_{q_7,q_8}^{q_4}$	—	0,2	0,05	—	—	—	0,94	—
$H_{q_8}^{q_7}$	—	0,05	0,08	—	—	—	1,65	—
$A_{\omega_{1,3}}^{q_4}$	—	0,60	0,45	—	—	—	0,65	—
$A_{\omega_2}^{q_4}$	—	−0,6	−0,45	—	—	—	−0,65	—
$A_{\omega_{1,3}}^{q_{7,8}}$	—	0,35	0,47	—	—	—	0,76	—
$A_{\omega_2}^{q_{7,8}}$	—	0,35	0,40	—	—	—	0,55	—
$K_{\omega_{1,3}}$	—	1,15	1,22	—	—	—	1,54	—
K_{ω_2}	—	0,70	0,30	—	—	—	2,10	—
$l_{\omega_2}^{\omega_3}$	—	−0,03	0,05	—	—	—	0,10	—
$l_{\omega_3}^{\omega_1}$	—	−0,03	0,35	—	—	—	−0,06	—

TABLE 3. Observed (in the IR spectra) and Calculated Frequencies of the In-Plane Normal Vibrations of Substituted Uracils (cm^{-1})

Compound	I		II		III		IV		V		VI		VII		VIII	
R	5-H		5-CH_3		5-NH_2		5-F		5-Cl		5-Br		5-NO_2		6-Cl	
Type of vibration	ob-served	calc.	ob-served	calc.	ob-served	calc.	ob-served	calc.	ob-served	calc.	ob-served	calc.	ob-served	calc.	ob-served	calc.
$\nu N_{(1)}H$	3130	3126	3180	3178	3180	3181	3174	3176	3176	3179	3160	3130	3127	3127	3176	3170
$\nu N_{(3)}H$	2930	2930	3033	3033	2995	3004	3126	3126	2928	2930	2900	2900	3050	3050	2900	2900
$\nu C_{(5)}R$	3092	3092	765	788	1278	1290	818	823		723	715	702	832	818	3090	3101
$\nu C_{(6)}R$	3105	3110	3080	3077	3098	3103	3070	3080	3055	3060	3058	3065	3103	3100	905	889
$\nu C_{(2)}=O$, $\nu C_{(2)}N_{(1)}$, $\delta N_{(1)}H$	1730	1724	1730	1725	1745	1759	1722	1738	1700	1699	1700	1700	1741	1737	1725	1724
$\nu C_{(4)}=O$, $\nu C=C$, $\delta C_{(6)}H$	1666	1667	1675	1676	1715	1707	1660	1661	1665	1670	1665	1669	1700	1701	1670	1673
$\nu C_{(4)}=O$, $\nu C=C$, $\delta C_{(6)}H$	1623	1616	1635	1643	1665	1649	1625	1625	1628	1634	1620	1624	1632	1629	1630	1629
ν ring	1454	1465	1482	1488	1495	1503	1450	1450	1445	1440	1440	1438	1508	1503	1490	1466
ν ring, $\delta N_{(3)}H$	1425	1427	1365	1359	1452	1453	1430	1420	1422	1422	1420	1425	1361	1363	1415	1425
ν ring, $\delta N_{(1)}H$	1240	1252	1211*	1208*	1245*	1234*	1255*	1260*	1233	1270	1253	1253	1257	1257	1233	1264*
ν, δ ring	1005	1000	985	976	965	957	1184*	1187*	1090*	1115*	1060*	1037*	1120*	1106*	1032	1026
ν, δ ring	994	963	1050	1047	860	867	948	955	950	964	944	959	944	959	937	954
ν ring, $\delta C_{(6)}H$, $\delta N_{(1)}H$	1095	1090	1130	1133	1210	1194	—	1115	1125	1127*	1124	1124	1165	1168	1132	1168*
$\delta N_{(3)}H$	1390	1374	1428	1435	1432	1437	1378	1378	1375	1380	1375	1374	1469	1466	1335	1353
$\delta C_{(5)}-R$	1418	1419	—	329	—	331	—	335	—	225	—	173	—	156	1412	1415
$\delta C_{(6)}-R$	1218	1205	1383	1382	1415	1404	1348	1333	1341	1343	1343	1336	1422	1398	—	229
$\delta C=O$	575	584	—	618	605	629	—	600*	645	614	608	608	640	633	625	625
$\delta C=O$	422	408	—	395	435	402	365	382	420	433*	415	413	415	433	—	378
δ ring	782	776	—	863	810	825	757	767	790	799	781	767*	865	868	688	705
δ ring	722	702	695	699		695		694	684	695	692	692*	708	702		670
δ ring		665		557	545	561	545	562*	375*	369*		285*	—	365		492*
$\nu_{as}X(Y)_n$			3025	3028	3375	3381							1544	1543		
$\nu_s X(Y)_n$			2964	2953	3275	3327							1327	1332		
δ scissors $X(Y)_n$				1461	1588	1582							658	672		
δ pendulum $X(Y)_n$			1447	1440	1100	1112							454	469		

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* Here and subsequently, the frequencies of the normal vibrations to which the vibrations of C–X bonds contribute are designated by an asterisk.

TABLE 4. Observed and Calculated Frequencies of In-Plane Normal Vibrations of 1,3-Dideutero-5-substituted Uracils (cm^{-1})

Type of vibration	5-ND2-Uracil		Uracil		5-F-Uracil		5-Cl-Uracil		5-Br-Uracil	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
$\nu N_{(1)}-D$	2270	2366	2265	2324	2300	2323	2410	2324	2290	2324
$\nu N_{(3)}-D$	2190	2237	2135	2186	2140	2323	2187	2150	2142	2187
$\nu C_{(6)}-H$	3090	3103	3065	3088	3064	3098	3055	3098	3040	3098
$\nu C_{(5)}-R_\nu$ ring	1295	1304	3065	3110	1244	1229*	—	708*		688*
$\nu C_{(2)}=O$	1730	1744	1712	1714	1730	1729	1695	1692	1692	1690
$\nu C_{(4)}=O$, $\nu C=C$, $\delta C_{(6)}-H$	1675	1689	1680	1663	1670	1674	1667	1675	1665	1665
$\nu C_{(4)}=O$, $\nu C=C$, $\delta C_{(6)}-H$	1630	1639	1590	1609	1617	1619	1628	1630	1630	1621
ν ring, $[C_{(2)}-N_{(1)}$, $C_{(2)}-N_{(3)}]$	1428	1419	1460	1437	—	1418	1436	1452	1438	1431
ν ring, $[C_{(4)}-N_{(3)}$, $C_{(4)}-C_{(5)}]$	1488	1492	1400	1393	—	1404	1430	1420	1387	1393
ν ring, $[C_{(2)}-N_{(3)}$, $C_{(4)}-N_{(3)}]$	1240	1218	1238	1239	1186	1195	1255	1250	1235	1237
ν ring	970	962	988	923	958	964	930	959	945	948
ν ring, $\delta N_{(1)}D$	868	842	820	818	820	821	770	769	727	748
ν ring	1012	1022	1000	979	1244	1229	1055	1087	1028	1016
ν ring $\delta N_{(3)}D$	1125	1144	1140	1149	1124	1120	1148	1162	1145	1153
$\delta C_{(5)}R$	—	303	1200	1189	—	334	—	224	—	172
$\delta C_{(6)}H$, ν ring	1380	1382	1400	1417	1330	1322	1322	1333	1328	1327
$\delta C=O$	571	591	560	559	—	571	625	581	580	576
$\delta C_{(2)}=O$, $\delta C_{(4)}=O$	430	400	430	406	—	380	438	431	410	411
δ ring, $\delta N_{(1)}D$	780	795	770	743	730	738	—	825	780	815
δ ring	655	642	620	659	670	679	660	682	647	681
δ ring,	540	546	740	680	—	560*	370	369*	—	284*
$\nu_{as}ND_{(2)}$	2530	2536								
$\nu_s ND_{(2)}$	2390	2447								
δ scissors $ND_{(2)}$	1100	1108*								
δ pendulum, $ND_{(2)}$	810	842								

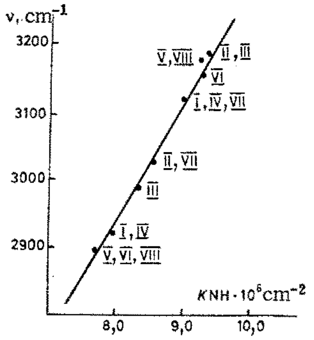

Fig. 2. Dependence of the frequencies of the stretching vibrations of the NH groups of substituted uracils (I-VIII) on the force constants of these bonds (the numbers beside the points correspond to the numbers of the compounds).

the positions of the frequencies under discussion in the spectrum of 5-fluorouracil depend not only on the kinematic factors but also on the peculiarities of the electronic properties of the fluorine atom; this shows up in a decrease in the force constant of the C = C bond as compared with uracil and its 5-chloro and 5-bromo derivatives (Table 2). The $\Delta\nu$ value for 5-fluorouracil is the same as for other halo derivatives. Thus the decrease in the $\Delta\nu$ value in the spectrum of 5-fluorouracil with respect to uracil is due to a change in the electron density on the C = C bond caused by the maximum capacity of the fluorine atom for conjugation.

When the substituents differ markedly from one another with respect to their geometrical and electronic structures (amino, methyl, or nitro groups), it is impossible to clearly separate the kinematic and electronic effects, inasmuch as a change in the electronic properties of the substituent has an effect not only directly on the force constant of the $C_{(5)}=C_{(6)}$ bond and the adjacent bonds and angles but also on other remote (from the substituents) ring bonds and constants of interactions of these bonds.

In addition to the frequencies corresponding to the vibrations of multiple bonds, three frequencies related to the stretching vibrations of the ring are also characteristic in form. In all cases the highest of these frequencies corresponds to a ring vibration with predominant participation of the ring C−N bonds between which the $C_{(2)}=O$ group is included, whereas the second corresponds to a ring vibration with participation of the $C_{(4)}-N_{(3)}$ and C−C ring bonds. The third frequency corresponds to a ring stretching vibration in which primarily the C−N bonds included between the carbonyl group participate. It should be noted that, as in the case of uracil, the in-plane deformation vibrations of the N−H bonds make a certain contribution to the last two ring vibrations.

From the calculated forms of the vibrations it can be shown that the vibrations of exocyclic $C_{(5)}-Hal$, $C_{(5)}-N$, and $C_{(5)}-C$ bonds make a contribution to several frequencies of the normal vibrations rather than just to one. The assignment of only one frequency to $\nu C_{(5)}-R$ presented in Tables 3 and 4 is therefore arbitrary.

An analysis of the forms of the normal vibrations shows that the stretching symmetrical and asymmetrical vibrations of the CH_3 groups in thymine and NH_2 in 5-aminouracil are characteristic in form and frequency. The magnitudes of their frequencies are determined by the magnitudes of the force constants of the CH and NH bonds and the force constants of interaction between these bonds, whereas ν_{as} NO_2 and ν_s NO_2 are strongly related to the ring vibrations and are characteristic only with respect to their frequencies. The vibrations of the ring bonds also contribute to the in-plane deformation vibrations of CH_3, NH_2, and NO_2 groups.

Thus our calculations of the in-plane normal vibrations of 5-substituted uracils make it possible to reveal a number of general features characteristic for the IR spectra of these compounds: 1) the stretching vibrations of the NH and CH bonds are characteristic in frequency and form, and the magnitude of their frequencies is determined only by the force constant of the bond; 2) the three frequencies in the multiple bond absorption region are characteristic in form for definite fragments of the uracil molecule [~1700 cm^{-1} $O-C_{(2)}-N_{(1)}-H$, ~1670 and 1600 cm^{-1} $O=C_{(4)}-C_{(5)}=C_{(6)}$] but not for each bond taken individually; 3) the stretching vibrations of the pyrimidine rings of the investigated compounds are also characteristic in form.

EXPERIMENTAL

The calculation of the matrices of the kinematic coefficients, the reduction of the matrices with respect to symmetry, allowance for supplementary relationships, 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 [1, 6]. The IR spectra of suspensions of the compounds in mineral and perfluorinated mineral oils on KBr plates were recorded with a Perkin–Elmer 457 spectrometer.

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