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Dedicated to the Memory of Prof. Herman Geise, University of Antwerp (UIA)

Molecular Structure of 6-Methyluracil in the Gas Phase and Characteristics of the 6-Methyluracil–Water System

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Abstract—Geometric parameters of the 6-methyluracil molecule were determined by gas-phase electron diffraction: interatomic distances (r_a, Å) N^1–C^2 1.390(3), C^2–N^3 1.384(3), N^3–C^4 1.407(3), C^4–C^5 1.455(10), C^5–C^6 1.336(20), C^1–C^6 1.395(3), C–Me 1.519(5); bond angles (deg) $N^1C^2N^3$ 114.1(), $C^2N^3C^4$ 126.3(7), $N^3C^4C^5$ 114.3(5), $C^4C^5C^6$ 121.6(5), $C^5C^6C^1$ 119.7(5), $C^7C^6C^5$ 11C^5.4(8), $O^8C^2N^1$ 123.5(1.5), $O^9C^4N^3$ 123.3(10). The heterocycle is planar. One of the C–H bonds of the methyl group and the C^5=C^6 bond are coplanar. The nearest surrounding of the heterocycle by water molecules (four and five molecules) was examined by AM1 and B3LYP/6-31G** calculations, and the energies of the hydrogen bonds in the heterocycle–water system were estimated.

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The energies of dimerization of 5- and 6-methyluracils were estimated in [1] by the HF/6-31**, B3LYP/6-31G**, and AM1 (MOPAC) methods. Experimental data on the geometry of these molecules in the gas phase are lacking. 6-Methyluracil (6-MeU) along with other pyrimidine bases is a component of many drugs and is widely used in pharmaceutics [2, 3]. As a rule, the biological activity of drugs is manifested in a liquid medium, and the gas phase is more similar to the liquid than the crystalline phase. Therefore, it was appropriate to examine the structure of 6-methyluracil by electron diffraction. Furthermore, 6-MeU molecules in solutions can form dimers and solvates with water. It was important to determine the structure of these solvates and to estimate the energies of 6-MeU–water hydrogen bonds. This was the subject of the present study.

Electron diffraction study. The results of quantum-chemical calculations of 6-MeU are given in Table 1. It can be seen that the main internuclear distances vary within narrow limits (1.35–1.50 and 2.3–2.9 Å) (Fig. 1). This fact complicates their correct determination becase of their inevitable correlations with each other and with other structural parameters. In such cases, it is appropriate to use the so-called MOCED method [4], i.e., to combine in structural analysis the experimental electron diffraction data and quantum-

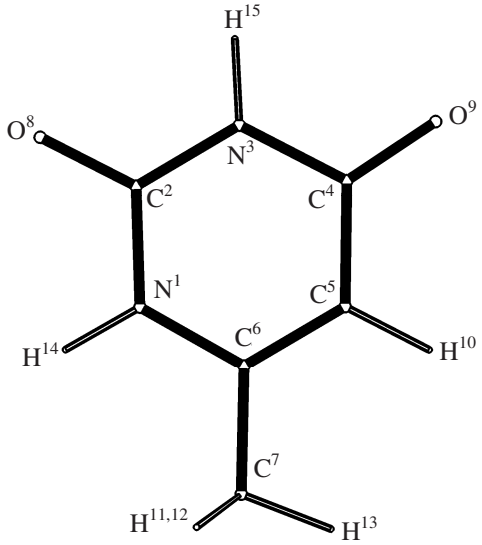

Fig. 1. Atomic numbering in 6-methyluracil.

† Deceased.

Table 1. Geometric parameters of 6-methyluracil

Parameter	HF/6-31G**	B3LYP/6-31G**	Experiment, gas, r_a, Å	Experiment, crystal[a]	
				I	**II**
N^1–C^2	1.373	1.393	1.390 (3)	1.369 (9)	1.361(6)
C^2–N^3	1.367	1.383	1.384 (3)	1.361 (5)	1.397(8)
N^3–C^4	1.390	1.412	1.407 (3)	1.422(8)	1.392 (5)
C^4–C^5	1.460	1.457	1.455 (10)	1.415 (10)	1.406 (7)
C^5–C^6	1.334	1.355	1.336 (20)	1.358 (9)	1.338 (6)
N^1–C^6	1.378	1.383	1.395 (3)	1.411 (8)	1.388 (5)
C–Me	1.499	1.500	1.519 (5)	1.515 (10)	1.487 (7)
N–C_{av}	1.377	1.393	1.394	1.391	1.385
C=O_{av}	1.195	1.220	1.225 (5)	1.212 (8)	1.232 (5)
C–H^{10}	1.071	1.081	1.081		
N^1–H^{14}	0.994	1.010	0.995		
N^3–H^{15}	0.997	1.013	0.997		
NH_{av}	0.995	1.012	0.996		
C–H_{Me}	1.085	1.094	1.084 (6)		
$C^6N^1C^2$	124.3	124.8	124.0 (4)	112.5 (9)	122.8 (3)
$N^1C^2N^3$	113.8	112.9	114.1(5)	113.8 (9)	116.2 (3)
$C^2N^3C^4$	127.2	127.8	126.3 (7)	128.2 (9)	124.6 (4)
$N^3C^4C^5$	114.1	113.6	114.3 (5)	112.5 (9)	115.5 (4)
$C^4C^5C^6$	120.3	121.1	121.6(5)	123.4 (6)	121.8 (4)
$C^5C^6N^1$	120.3	119.8	119.7 (5)	118.5 (9)	119.0 (4)
$C^7C^6C^5$	124.5	124.5	125.0 (6)	114.1 (6)	118.5 (9)
$C^7C^6C^1$	115.2	115.7	115.4 (8)	126.2 (8)	116.5 (4)
$O^8C^2N^1$	122.5	122.6	123.5 (1.5)	121.8 (7)	121.8 (4)
$O^8C^2N^3$	123.7	124.5	122.4 (1.5)		
$O^9C^4N^3$	120.3	120.3	123.3 (10)	125.2 (10)	119.0(4)
$O^9C^4N^5$	125.5	126.1	122.4 (10)		
R factor, %			5.02_{av}		

[a] (**I, II**) Polymorphic forms.

chemical calculations. The commonly used data calculated quantum-chemically are theoretical corrections to the correlated parameters.

The geometric parameters were refined by the least-squares method (program written by M.B. Zuev and modified by M.A. Tafipol'skii) using two curves $sM(s)$ taken in the range from 3.6 to 24.2 s $Å^{-1}$ with a step of 0.10 s (Fig. 2). The program we used allows inclusion or exclusion of certain geometric parameters in the course of calculation and correction of the background without exit from the program.

As independent parameters we chose the C=C, N^1–C^6, C^6–C^7, C=O, and C–H distances. The other internuclear distances were determined by the group procedure with the corrections taken from an ab initio HF/6-31G** calculation (Table 1). The endocyclic

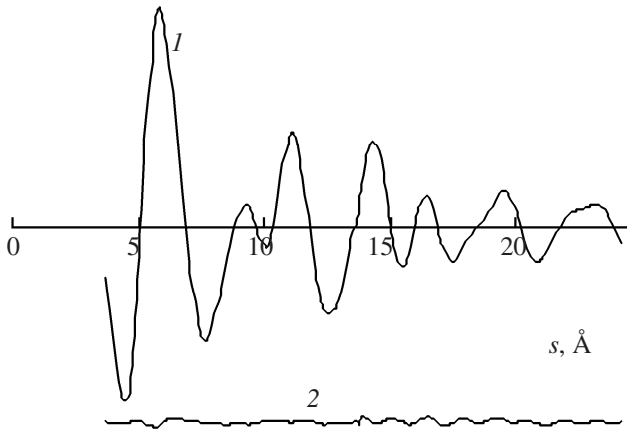

Fig. 2. (*1*) Joined experimental function $sM(s)$ and (*2*) differential curve $2\Delta(s)$, $\Delta = sM(s)_{exp} - ksM(s)_{theor}$.

Table 2. Root-mean-square amplitudes u_{ij} in 6-methyluracil molecule

Parameter	r_{ij}, Å	Theory, Å	Experiment, Å
C=O	1.22		0.046 (3)
N^1–C^2	1.39	0.048	0.054
C^2–N^3	1.38	0.049	0.055 (6)[a]
N^3–C^4	1.41	0.050	0.056
C^4–C^5	1.45	0.052	0.058
C^5–C^6	1.35	0.044	0.050
C^6–N^1	1.40	0.049	0.054
C^1···N^3	2.4	0.064	0.066
C^2···C^4	2.4	0.061	0.063 (2)[b]
N^3···C^5	2.4	0.059	0.061
C^4···C^6	2.4	0.050	0.056
C^5···N^1	2.4	0.059	0.061
C^6···C^2	2.5	0.062	0.064
C^7···N^1	2.4	0.078	0.080
C^7···C^5	2.5	0.074	0.076
O^8···N^1	2.3	0.060	0.062
O^8···N^3	2.3	0.060	0.062
O^9···N^3	2.3	0.061	0.063
O^9···C^5	2.4	0.065	0.067
N^1···C^4	2.8	0.070	0.085 (3)[c]
C^2···C^5	2.8	0.069	0.084
N^3···C^6	2.8	0.070	0.085
C^4···O^8	3.6	0.069	0.070 (2)[d]
C^6···O^8	3.6	0.067	0.068
C^2···O^9	3.6	0.068	0.069
C^6···O^9	3.6	0.066	0.067
C^7···C^8	4.7	0.098	
C^7···C^9	4.9	0.090	
C^7···N^3	4.2	0.082	
O···O	4.6	0.083	

[a, b, c, d] Grouping scheme of amplitudes.

bond angles and $C^5C^6C^7$ angle in the pyrimidine ring were refined independently. Weak parameters (N–H) were not refined. The results of the structural analysis are given in Table 1.

As for the root-mean-square amplitudes u_{ij}, in the course of refinement they were subdivided into groups (Table 2) and refined together with the geometric parameters. The initial amplitudes were the theoretical values calculated by the NCA program (written by Tafipol'skii). This is a convenient program requiring only the output file of ab initio calculations. The experimental and theoretical joined curve $sM(s)$ and radial distribution curve $rf(r)$ are shown in Figs. 2 and 3. All the information on the internuclear bond dis-tances is contained in the first peak; the second peak is related to bond angles in the molecules. The atomic scattering amplitudes required for calculating the *sM* curves were taken from [5].

6-Methyluracil–water systems. In [1] we studied the conformations of dimeric 5- and 6-methyluracils and estimated the dimerization energy by the Hartree–Fock and semiempirical AM1 methods. In this respect, this study is a continuation of [1]. Uracil unsubstituted in positions N^1 and N^3 is a convenient model for studying such important properties as intermolecular hydrogen bonds (H bonds). The problem of hydration of uracil and other biologically important compounds such as thymine, cytosine, adenine, and guanine was studied comprehensively by experimental (IR spectroscopy) [6–8] and theoretical (atom–atom potentials, Monte Carlo simulation, quantum-chemical calculations of various theoretical levels) methods. In this study, preliminary calculations were performed by the AM1 semiempirical method. We analyzed systems containing the maximal number of water molecules per 6-methyluracil molecule in its nearest surrounding. We considered the possibility of hydrogen bonding of protons of water molecules $O^{16}H_2$ and $O^{19}H_2$ (Fig. 4, structure *1*) with the carbonyl groups, i.e., of polyfurcate H bonding. In [9], this problem was discussed for the crystalline phase. Calculation showed that protons of water molecules $O^{16}H_2$ and $O^{19}H_2$ do not form H bonds with carbonyl oxygen atoms. Similar pattern was observed with the $O^{25}H_2$ molecule, in contrast to the system of H bonds $C^5H\cdots O^{22}H_2$ (Fig. 4, structure *1*). It should be noted that in calculations in this step we assumed symmetrical arrangement of protons of water molecules $O^{16}H_2$ and $O^{19}H_2$ relative to the ring plane (torsion angles $H–O\cdots H^{15}–N^3$ are close to ±50°– 60°, and $O\cdots H–N^{15}$ angle, to 130°). As a result, the angles in the hydrogen systems appeared to be close to 90°, and the PLAATON program [10] did not identify the $O^{16}H$ and $O^{19}H$ distances as intramolecular hydrogen bonds.

A more detailed study of complex **1** (Fig. 4) by the B3LYP/6-31G** method showed that bifurcate hydrogen bonds $N^3–H^{15}\cdots O$ were not realized. An ab initio calculation of the system 6-MeU + $4H_2O$ showed that the bond angles O–H···O=C and $H_2O\cdots HN$ in this system (model **1a**) are close to 180°. This pattern suggested that one more water molecule should be added to the system. Finally, the model including five

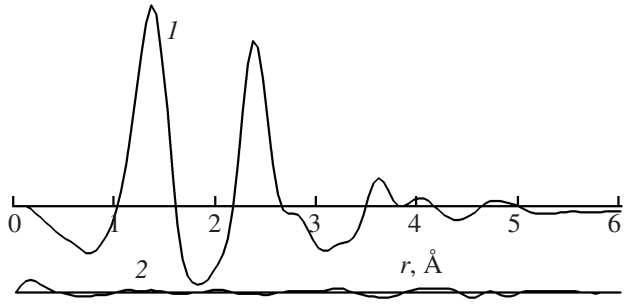

Fig. 3. (*1*) Experimental radial distribution function $f(r)$ and (*2*) differential curve $2\Delta(r)$, $\Delta = f(r)_{exp} - kf(r)_{theor}$.

water molecules (Fig. 4, model **2**) appeared to be the most probable model of the complex. For this complex, using the B3LYP/6-31G** method, we refined the molecular geometry and calculated the theoretical force field and vibration frequencies. This is important for analyzing the effect exerted by the nearest water surrounding on the 6-MeU molecule, primarily on the atomic charges and geometric parameters of the base. The parameters and energies of the H bonds are given in Table 3. It can be seen that this model is well consistent with conclusions made in the classical Pullman's paper [11] about the nearest surrounding of unsubstituted uracil. It is also promising for simulation of the secondary shell of the 6-MeU–5H_2O system because of the presence of four free hydroxy groups. In this connection we should note a paper [12] where the authors using the B3LYP/6-31G** method suggested a model of a complex of uracil with 11 water molecules and a similar model for thymine including the hydrophobic moiety of the base.

Although the optimal model of the 6-MeU + H_2O system was principally constructred, we continued the analysis of the system with four water molecules. Taking into account the results of ab initio study of the system 6-MeU + 5H_2O, we returned to the model with four water molecules. We constructred such a model with a primary water shell (Fig. 4, model **3**) in which all the exocyclic groups of 6-MeU were involved in hydration, as in the system with five water molecules. The parameters and energies of the hydrogen bonds are given in Table 3. It should be noted that the sum of the energies of the hydrogen bonds in the complex with four H_2O molecules is larger than that in the complex 6-MeU + 5H_2O.

The influence of the number of water molecules on the geometric parameters of the methyluracil ring is illustrated by Table 4. As a rule, with an increase in

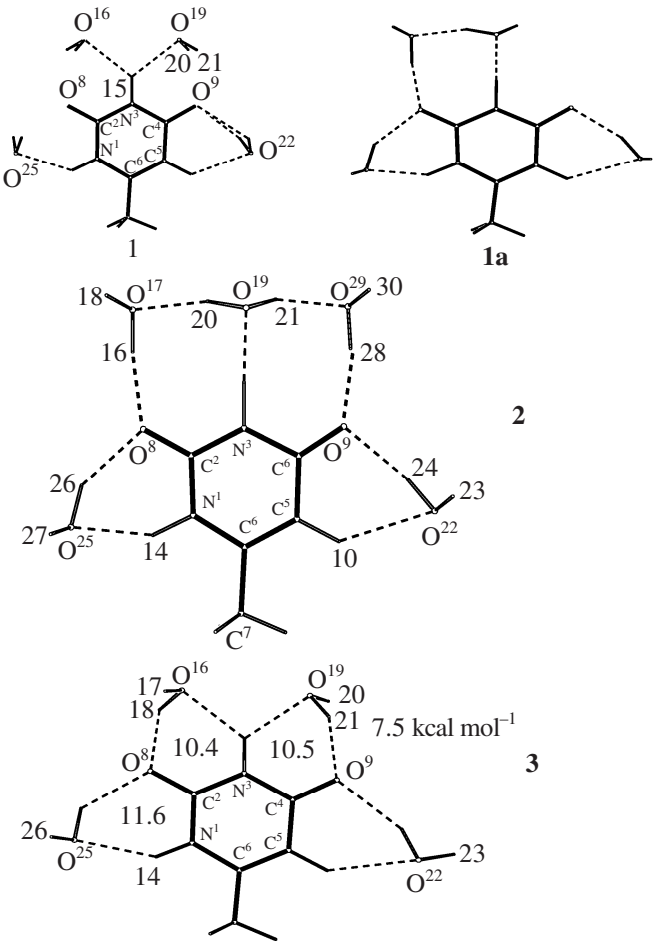

Fig. 4. Models of complexes 6-MeU–H_2O.

the number of water molecules the endocyclic bonds become shorter compared to the free (nonhydrated) ring. The lengths of the exocyclic bonds C=O and NH increase by ~0.025 and ~0.09 Å, respectively. To estimate the stretching energy, the energies of these bonds should be taken into account. For example, stretching of the C–C bond in ethane by 0.1 Å requires 3.5 kcal mol^{-1} [13]. The stretching energy of the C=O bond is certainly higher, because the energy of the C=O bond in ketones, according to Syrkin [14], is 155–157 kcal mol^{-1}, whereas the energy of the C–C bond in ethane is considerably lower (~63 kcal mol^{-1}). As a result, under the influence of the system of H bonds the endocyclic bond lengths in 6-MeU become shorter than those in the free molecule. The H bonds make longer the N–H bonds and, to a considerably lesser extent, the C–H bonds (Table 4). Note that all the calculations were performed by the same method, B3LYP/6-31G**.

Table 3. Parameters of hydrogen bonds in the 6-MeU–H_2O system (B3LYP/6-31G**)

A–B···C	A–B, Å	B···C, Å	A···C, Å	A–B···C, deg	*E*, kcal mol^{-1}
6-MeU + $5H_2O$[a]					
$N^1H^{14}\cdots O^{25}$	1.003	2.109	2.898	134.1	7.7
$O^{25}H^{26}\cdots O^8$	0.979	1.932	2.800	145.8	
$N^3H^{15}\cdots O^{19}$	1.007	2.015	3.012	170.3	8.8
$O^{19}H^{20}\cdots O^{17}$	0.963	2.067	2.761	127.6	
$O^{17}H^{16}\cdots O^8$	0.964	2.127	3.083	170.6	3.3
$O^{22}H^{24}\cdots O^9$	0.963	2.259	2.640	102.4	6.0
$C^5H^{10}\cdots O^{22}$	1.083	2.347	3.20	134.3	
$O^{29}H^{28}\cdots O^9$	0.964	2.177	3.132	170.6	6.9
$O^{19}H^{21}\cdots O^{29}$	1.103	2.293	3.107	129.0	
6-MeU + $4H_2O$[b]					
$N^1H^{14}\cdots O^{25}$	1.020	2.068	2.952	143.7	10.2
$O^{25}H^{26}\ldots O^8$	0.971	2.142	2.819	127.5	
$N^3H^{15}\cdots O^{16}$	1.035	2.228	2.974	126.6	9.2
$O^{16}H^{18}\cdots O^8$	0.965	2.210	2.624	104.6	
$N^3H^{15}\cdots O^{19}$	1.035	2.205	2.951	127.5	9.3
$O^{19}H^{21}\cdots O^9$	0.965	2.231	2.620	102.8	
$C^5H^{10}\cdots O^{22}$	1.082	2.298	3.205	140.2	6.6
$O^{22}H^{24}\cdots O^9$	0.971	2.108	3.013	154.4	

[a] Model **2**, Fig. 4. [b] Model **3**, Fig. 4.

Table 4. Influence of water on geometric parameters of 6-methyluracil

Bond, angle	6-MeU	6-MeU + $4H_2O$	6-MeU + $5H_2O$
Bond lengths, Å			
N^1–C^2	1.393	1.383	1.378
C^2–N^3	1.383	1.381	1.367
N^3–C^4	1.412	1.402	1.391
C^4–C^5	1.457	1.446	1.445
C^5–C^6	1.355	1.354	1.358
C^6–N^1	1.383	1.379	1.378
C=O^8	1.218	1.235	1.244
C=O^9	1.221	1.239	1.246
C–C_{Me}	1.500	1.499	1.499
C^5– H^{10}	1.081	1.082	1.083
N^3–H^{15}	0.997	1.035	1.070
N^1–H^{14}	0.994	1.082	1.083
Bond angles, deg			
$C^2N^1C^6$	124.8	123.7	123.5
$N^1C^2N^3$	112.9	115.8	116.0
$C^2N^3C^4$	127.8	124.2	124.6
$N^3C^4C^5$	113.6	116.2	116.2
$C^4C^5C^6$	121.1	120.3	119.9
$C^5C^6N^1$	119.8	119.7	119.7

What are the causes of these trends? The atomic charges in the free 6-MeU molecule and its complexes with water are given in Table 5. Under the influence of hydrating water molecules, the charges on atoms of the pyrimidine ring change significantly, leading to shortening of the endocyclic bond lengths in the complex and to extension of the exocyclic bonds C=O, N–H, and C–H.

Interesting results were obtained by Leonidov et al. [15] who revealed the polymorphism of 6-MeU in the crystal lattice. In the first modification whose structure was determined for a pharmacopeia-grade sample of **I** (Table 1), infinite ribbons in which the monomers are linked by a pair of $N^3H\cdots O{=}C$ bonds are formed in the crystal [16]. In a recrystallized sample (modification **II**), such dimers are also present. Leonidov et al. attribute some differences in the structural parameters of **I** and **II** to the error of X-ray diffraction analysis (powder method). Forms **I** and **II** differ essentially in the crystal packing. Leonidov et al. believe [15] that in aqueous solutions the compound can form both dimeric associates and solvates. Leonidov et al. reported [17, 18] that the two forms of 6-MeU differ in the structure and in physicochemical and biological characteristics. These differences may be due to the effect of water.

The results of the normal-coordinate analysis of H bonds in 6-methyluracil hydrated with five water molecules are given in Table 6. In the calculations we used a common scaling factor (0.95). Let us note some characteristics of the hydrogen bonds. The force constants of the hydrogen bonds, including the O···H bonds between water molecules, vary within 0.229–0.541 mdyne Å^{-1}. The low frequencies are assigned to the torsion vibrations around O···H hydrogen bonds; high frequencies, to vibrations of free O–H bonds; and somewhat (by ~200 cm^{-1}) lower frequencies, to O–H bonds involved in hydrogen bonding. The heteroring vibration modes in Table 6 are omitted. Full normal-coordinate analysis of free 6-MeU is performed in [1, 19].

Table 5. Charges (au) on atoms in free 6-MeU and its complexes with water molecules

Atom	6-MeU	6-MeU + 4 H_2O	6-MeU + 5 H_2O
N^1	–0.609	–0.622	–0.620
C^2	0.741	0.790	0.781
N^3	–0.602	–0.621	–0.626
C^4	0.608	0.614	0.636
C^5	–0.221	–0.234	–0.230
C^6	0.367	0.360	0.364
O^8	–0.500	–0.602	–0.587
O^9	–0.509	–0.539	–0.585
H^{14}	0.202	0.300	0.302
H^{15}	0.289	0.327	0.339
H^{10}	0.111	0.135	0.136

Thus, the effect of H_2O molecules in the complex is primarily manifested in the geometric parameters of the heterocycle. The atomic charges and, as a consequence, the vibration frequencies of the exocyclic groups C=O, N–H, and C–H change: The $\nu(C^2O)$ frequency is 1735 cm^{-1} in the complex 6-MeU + C^5H_2O and 1795 cm^{-1} in 6-MeU; $\nu(C^4{=}O)$ 1694 and 1757, $\nu(N^1H)$ 3231 and 3552, $\nu(N^3H)$ 2582 and 3530, and $\nu(C^5H)$ 3148 and 3173 cm^{-1} in the complex and in 6-MeU, respectively. As can be seen, all the frequencies in the complex decrease, in accordance with shortening of the endocyclic bonds, with the most pronounced effect for N^3H.

EXPERIMENTAL

The experiment was performed on an EMR-100/APDM-1 apparatus complex allowing simultaneous recording of the electron diffraction patterns and mass spectra of the vapor. The electron diffraction patterns were taken at an accelerating voltage of 81 kV with two distances between the effusion orifice and photographic film, equal to 338 and 598 mm. Recording of each electron diffraction pattern was accompanied by recording of the electron impact mass spectrum at an ionizing voltage of 50 V. The electron wavelength was determined with a polycrystalline ZnO sample before and after recording the electron diffraction patterns.

The electron diffraction patterns were subjected to photometry on an MD-100 automated microdensitometer (Carl Zeiss, Jena). The intensity functions of electron scattering $sM(s)$ were obtained in the ranges s = 3.6–13.9 and 3.6–24.2 (Δs 0.10) for the long and short distances between the orifice and photographic plate,

Table 6. Results of normal-coordinate analysis of the system

ν, cm^{-1}	PED, %[a]
26	$24\tau(O^9\cdots H^{28}) + 15\tau(N^3\cdots O^{19}) + 13\tau(C^4O^9)$
36	$12\tau(N^1H) + 11\tau(H^{14}\cdots O^{25}) + 13\gamma C^9$
45	$15\tau(O^{19}–H^{21}) + 12\tau(O^{29}\cdots H^{21})$
62	$23\tau(O^{19}–H^{21}) + 18\tau(O^{29}\cdots H^{21}) + 15\tau(O^{19}–H^{20}) + 10\tau(O^{17}\cdots H^{20})$
64	$12\tau(O^{25}\cdots H^{14}) + 15\gamma(O^8) + \tau 12(N^1–H^{14})$
75	$12\alpha(H^{16}–O^8\cdots H^{26}) + 13\alpha(H^{24}\cdots O^9\cdots H^{28})$
93	$17\alpha(H^{16}–O^8\cdots H^{26}) + 12\nu(O^8\cdots H^{26})$
128	$23\nu(O^8\cdots H^{26}) + 15\nu(O^{25}\cdots H^{14})$
146	$26\nu(O^8\cdots H^{16}) + 21\nu(O^9\cdots H^{24})$
152	$28\nu(O^9\cdots H^{28}) + 12\nu(O^8\cdots H^{16})$
165	$27\nu(O^{25}\cdots H^{14}) + 19\nu(O^9\cdots H^{28}) + 12\nu(H^{24}\cdots O^9)$
177	$21\nu(O^8\cdots H^{16})$
186	$12\nu(O^9\cdots H^{28})$
194	$29\nu(O^8\cdots H^{26}) + 26\nu(O^{25}\cdots H^{14})$
197	$16\nu(O^{19}\cdots H^{15}) + 16\nu(O^8\cdots H^{26}) + 16\nu(O^{17}\cdots H^{20}) + 13\nu(O^{29}\cdots H^{21})$
211	$16\tau(O^{22}H^{24})$
239	$10\nu(O^{19}\cdots H^{15}) + 53\tau(O^{22}H^{24})$
266	$21\tau(O^{19}\cdots H^{21}) + 19\tau(O^{29}\cdots H^{21})$
268	$17\tau(O^{19}\cdots H^{21}) + 13\tau(O^{17}H^{16}) + 11\tau(O^{19}\cdots H^{20}) + 10\alpha(H^{30}O^{29}\cdots H^{21})$
289	$49\tau(O^{17}\cdots H^{16}) + 29\tau(O^8–H^{16})$
295	$34\tau(O^{17}H^{16}) + 15\tau(O^8\cdots H^{16})$
313	$49\tau(O^9\cdots H^{24}) + 31\tau(O^{22}H^{24})$
317	$45\tau(O^9\cdots H^{24}) + 27\tau(O^{22}H^{24})$
341	$42\tau(O^{17}H^{16}) + 37\tau(O^8\cdots H^{16})$
358	$30\tau(O^8\cdots H^{26}) + 11\tau(O^{17}H^{16}) + 17\alpha(H^{27}O^{15}\cdots H^{14})$
374	$18\tau(O^{17}H^{16}) + 17\tau(O^8\cdots H^{16})$
432	$12\tau(O^8\cdots H^{26})$
590	$10\alpha(O^{17}H^{16}\cdots O^8) + 10\alpha(O^{19}–H^{21}\cdots O^{29})$
682	$21\alpha(O^{22}H^{24}\cdots O^9) + 14\tau(O^{19}H^{20}) + 11\tau(O^{19}H^{21})$
722	$25\alpha(O^{25}H^{26}\cdots O^8) + 18\alpha(H^{26}O^{25}\cdots H^{14}) + 10\tau(O^{19}H^{21})$
866	$32\tau(O^{25}\cdots H^{14}) + 30\tau(N^1H^{14})$
900	$15\alpha(O^{19}H^{21}\cdots O^{29}) + 12\alpha(H^{28}O^{29}\cdots H^{21}) + 16\tau(O^{19}H^{21})$
1099	$16\alpha(H^{21}O^{19}\cdots H^{15})$
3148	$99\nu(C^4H^{10})$
3231	$98\nu(N^1H^{14})$
3415	$66\nu(O^{19}H^{21}) + 18\nu(O^{19}H^{20})$
3462	$54\nu(O^{19}H^{20}) + 23\nu(O^{17}H^{16})$
3508	$52\nu(O^{29}H^{28}) + 21\nu(O^{19}H^{21})$
3526	$78\nu(O^{25}H^{26})$
3545	$67\nu(O^{17}H^{16})$
3566	$90\nu(O^{22}H^{24})$
3766	**$70\nu(O^{22}H^{23}) + 22\nu(O^{29}H^{30})$**[b]
3767	**$73\nu(O^{29}H^{30}) + 23\nu(O^{22}H^{23})$**
3768	**$70\nu(O^{22}H^{23}) + 22\nu(O^{29}H^{30})$**
3771	**$94\nu(O^{17}H^{18})$**

[a] (ν, α, γ, τ) Stretching, scissor, out-of-plane bending, and torsional vibrations, respectively. [b] The vibration frequencies of free OH groups are printed bold.

respectively. All the ab initio calculations were performed using program package [20].

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