Study of the Thymine Molecule: Equilibrium Structure from Joint Analysis of Gas-Phase Electron Diffraction and Microwave Data and Assignment of Vibrational Spectra Using Results of Ab initio Calculations

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Thymine is one of the nucleobases which forms the nucleic acid (NA) base pair with adenine in DNA. The study of molecular structure and dynamics of nucleobases can help to understand and explain some processes in biological systems and therefore it is of interest. Because the scattered intensities on the C, N, and O atoms as well as some bond lengths in thymine are close to each other the structural problem cannot been solved by the gas phase electron diffraction (GED) method alone. Therefore the rotational constants from microvawe (MW) studies and differences in the groups of N—C, C═O, N—H, and C—H bond lengths from MP2 (full)/cc-pVQZ calculations were used as supplementary data. The analysis of GED data was based on the C_s molecular symmetry according to results of the structure optimizations at the MP2 (full) level using 6-311G (d,p), cc-pVTZ, and cc-pVQZ basis sets confirmed by vibrational frequency calculations with 6-311G (d,p) and cc-pVTZ basis sets. Mean-square amplitudes as well as harmonic and anharmonic vibrational corrections to the internuclear distances (r_e–r_a) and to the rotational constants ($B_e^{(k)}$–$B_0^{(k)}$, where $k = A, B, C$) were calculated from the quadratic (MP2 (full)/cc-pVTZ) and cubic (MP2 (full)/6-311G (d,p)) force constants (the latter were used only for anharmonic corrections). The harmonic force field was scaled using published IR and Raman spectra of the parent and N_1,N_3-dideuterated species, which were for the first time completely assigned in the present work. The main equilibrium structural parameters of the thymine molecule determined from GED data supplemented by MW rotational constants and results of MP2 calculations are the following (bond lengths in Angstroms and bond angles in degrees with 3σ in parentheses): r_e (C5═C6) = 1.344 (16), r_e (C5—C9) = 1.487 (8), r_e (N1—C6) = 1.372 (3), r_e (N1—C2) = 1.377 (3), r_e (C2—N3) = 1.378 (3), r_e (N3—C4) = 1.395 (3), r_e (C2═O7) = 1.210 (1), r_e (C4═O8) = 1.215 (1), $\angle_e$ (N1—C6═C5) = 123.1 (5), $\angle_e$ (C2—N1—C6) = 123.7 (5), $\angle_e$ (N1—C2—N3) = 112.8 (5), $\angle_e$ (C2—N3—C4) = 128.0 (5), $\angle_e$ (N3—C4—C5) = 114.8 (5), $\angle_e$ (C6═C5—C9) = 124.4 (9). The experimental structural parameters are in good agreement with those from MP2 (full) calculations with use of cc-pVTZ and cc-pVQZ basis sets.

1. Introduction

Thymine, cytosine, adenine, and guanine are the nucleobases which form the nucleic acid (NA) base pairs (thymine with adenine, cytosine with guanine) in DNA. The pairwise compositions of the bases occur due to formation of hydrogen bonds. The building by minor tautomers of NA bases of nonstandard base pairs may lead to changes in the genetic code.[1,2]

The study of molecular structure and dynamics of these molecules can help to understand and explain some processes in biological systems. This knowledge is of great interest due to its importance for developing of pharmacological substances and methods of therapy against cancer, virus infections, malformations, and so forth.

Thymine is the first subject of our systematic studies of these nucleobases by the gas-phase electron diffraction (GED) method. Being the main method for the determinations of the molecular structure of free molecules [3–6] the GED cannot solve the structural problem completely when the scattered intensities on the atoms and the bond lengths in the molecule are close to each other. In this case, the support of GED analysis by data from rotational and vibrational spectroscopy and by results of theoretical calculations is mandatory.

In the microwave study[7] of the parent and two monodeuterated species, the diketo form of thymine was found to be the most abundant tautomer in the gas phase. However, because of the low resolution of the free-jet Stark-modulated experiment,[7] the presence of about 10% of enol forms could not be excluded. Recently the molecular beam Fourier transform microwave spectroscopy method (MB FTMW), which provides the necessary high resolution, has been applied for the study of the parent species and two ^{15}N and five ^{13}C monosubstituted isotopomers of thymine.[8] Since no lines, which could be attributed to the enol tautomers, were obtained in the jet-cooled rotational spectrum of thymine, the diketo form was established unambiguously.

In the ab initio calculations at the MP2/aug-cc-pVDZ[9] and MP2/6-311++G (d,p)[8] levels of theory, the diketo form was predicted to be the lowest energy tautomer well separated from the next lowest energy enol form by more than 9 kcal mol^{-1}. According to results of ab initio Car—Parrinello molecular dynamics simulations of conformational phase space,[10] the thymine has a very flexible ring. The population analysis predicted wide set of different nonplanar ring conformations providing the main contribution to the total population. How-

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ever, the ring structure was found to be planar in the minimum of the potential energy surface.

A partial molecular structure (r_s parameters) of the diketo form has been determined very recently in the extensive laser ablation MB FTMW study[8] using the substitution method of Kraitchman. Such structure is not free from vibrational effects and, especially in the case of nonrigid molecules, it can remarkably deviate from the equilibrium one.

An equilibrium structure can be determined from GED data alone only for the smallest polyatomic molecules (see review paper[11] and references therein). In the cases of large molecules, harmonic and anharmonic vibrational corrections can be calculated using quantum chemical harmonic and anharmonic force constants and data of vibrational spectroscopy. Since thymine was expected to be a nonrigid molecule, an analysis of GED data should be carried out taking into account nonlinear kinematic effects.[12–15]

Thus, the main purpose of this work is the determination of the equilibrium structure of the isolated thymine molecule from GED data supplemented by MW rotational constants from the literature,[7,8] reliable harmonic and anharmonic force fields, and some structural differences from ab initio calculations.

2. GED Experiment

The thymine sample was purchased from Merck Co. (purity >99%) and used without further purification. The GED experiment was carried out in the Moscow State University on the EG-100M apparatus using the new r^3 sector from brass produced with high precision in the workshop of the University of Ulm. In comparison to the old handmade sector, which was used during several years in the Moscow GED laboratory, the new unit, which was milled more exactly, has a significantly better sector function, yielding a smoother background. The experimental conditions were the following: accelerating voltage of ca. 57 kV, electron beam current of 1.7 μA, vacuum of 6×10^{-6} mm Hg. The nozzle temperature was kept as low as possible. The necessary pressure of a few Torr was reached at 219 (5) °C, i.e., less than the melting point of about 300 °C. The diffraction patterns were recorded on photo films (MACO EM-Film EMS) at the long (LD) and short (SD) nozzle-to-film distances of 362.16 and 193.82 mm, respectively. The patterns of CCl_4 were recorded to calibrate the wavelength of the electron beam. The structural parameters of the CCl_4 molecule were taken from ref 16. The stability of the wavelengths of electrons during the experiment was higher than 0.05%. The diffraction patterns were scanned in the University of Ulm using the Epson Perfection V750 Pro commercial scanner in the 16-bit/300dpi scanning mode. The calibration of the scanner was carried out using a gray scale for Kodak ektachrome films. Data of scanning were transformed into intensity curves $I(s)$ using program UNEX which follows the method described in ref 17.

Experimental intensities $I(s)$ (three for each nozzle-to-film distance) with relative low experimental noise factor R_f of ca. 1.9% (LD) and 2.3% (SD) for each curve were averaged in the ranges of $s = 3.0 - 18.5$ Å^{-1} (LD) and $s = 7.0 - 33.75$ Å^{-1} (SD) in steps of 0.125 and 0.25 Å^{-1}, respectively. The averaged $I(s)$ curves are presented in Figure 1 and in Table 1S of Supporting Information.

3. Ab initio Calculations

All quantum-chemical calculations for thymine were carried out at the MP2 (full) level of theory using 6-311G (d,p), cc-pVTZ, and cc-pVQZ basis sets by means of the GAUSSIAN03 program package.[18] In each case, the geometry optimization was started from the molecular configuration without symmetry and converged to the structure of C_s total symmetry with methyl group in the staggered position with respect to the C4—C5 bond as shown in Figure 2. The optimized geometrical parameters are presented in Table 1. As can be seen, the results of the calculations with cc-pVTZ and cc-pVQZ basis sets are very close to each other. Therefore, it can be expected that they are obtained with high accuracy within the MP2 method.

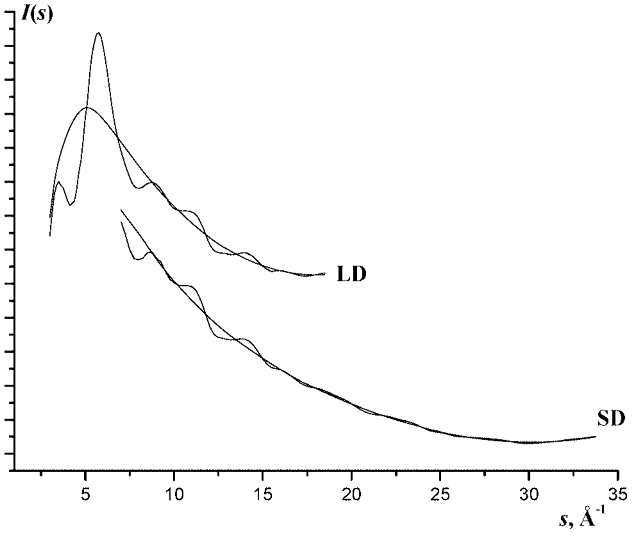

Figure 1. Experimental intensity curves $I(s)$ with the background lines for the long (LD) and short (SD) nozzle-to-film distances.

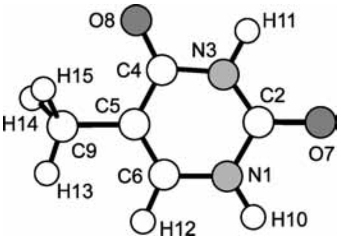

Figure 2. Molecular model of thymine (C_s symmetry) with atom numbering.

The harmonic force constants and fundamental frequencies were calculated using the 6-311G (d,p) and cc-pVTZ basis sets. The absence of imaginary frequencies confirmed that the determined geometrical parameters correspond to the equilibrium conformation. The cubic force constants were calculated using the 6-311G (d,p) basis set. The force field calculations were performed using analytical expressions for the second energy derivatives and by numerical differentiation of analytic second derivatives.

4. Spectroscopic Calculations and Interpretation of Vibrational Spectra

The vibrational spectra of the parent thymine-d_0[9,19–22] and its N1,N3-d_2 isotopomer[21] obtained in the gas phase and/or in an Ar matrix were jointly analyzed in the present work assuming the C_s molecular symmetry predicted by ab initio calculations. The use of mostly gas-phase and matrix isolation spectra makes it possible to exclude medium effects on the solution of the inverse spectral problem.

The normal coordinate analysis was carried out with the use of the scaling of the quantum chemical harmonic force field by fitting the calculated frequencies to the experimental ones

TABLE 1: Equilibrium r_e Parameters of the Thymine Molecule Obtained by the Joint Structural Analysis of the GED and MW Data in Comparison with the Microwave r_s Structure and the Results of MP2 (full) Calculations (For Atom Numbering See Figure 2; Bond Lengths in Angstroms, Angles in Degrees)

	GED+MW	MW[8]	MP2(full), r_e		
parameter	r_e[a]	r_s	6-311G(d,p)	cc-pVTZ	cc-pVQZ
C5=C6	1.344 (16)	1.370 (7)	1.354	1.3441	1.3448
C4−C5	1.466 (9) [b]	1.457 (4)	1.4646	1.4506	1.4524
C5−C9	1.487 (8)	1.501 (2)	1.4964	1.4849	1.4856
N1−C6	1.372 (3) [c]	1.355 (7)	1.3774	1.3689	1.3687
N1−C2	1.377 (3)[c]	1.34 (5)	1.3853	1.3755	1.3738
C2−N3	1.378 (3)[c]	1.42 (2)	1.3858	1.3758	1.3743
N3−C4	1.395 (3)[c]	1.384 (4)	1.4020	1.3922	1.3917
C2=O7	1.210 (1)[d]		1.2136	1.2126	1.2118
C4=O8	1.215 (1)[d]		1.2195	1.2179	1.2168
N1−H10	1.008 (9)[e]	0.998 (2)	1.0084	1.0042	1.0035
N3−H11	1.012 (9)[e]	1.007 (3)	1.0127	1.0087	1.0080
C6−H12	1.094 (11)[f]		1.0853	1.0762	1.0777
C9−H13	1.101 (11)[f]		1.0927	1.0848	1.0844
C9−H14 (15)	1.102 (11)[f]		1.0932	1.0856	1.0853
O8...H14 (15)	2.882 (37)		2.8628	2.8446	2.8499
C4−C5=C6	117.6 (6)[b]	117.3 (4)	118.39	118.26	118.10
N1−C6=C5	123.1 (5)	122.8 (3)	122.47	122.67	122.63
C2−N1−C6	123.7 (5)	124.3 (10)	124.04	123.71	123.80
N1−C2−N3	112.8 (5)	113.7 (8)	112.19	112.50	112.58
C2−N3−C4	128.0 (5)	126 (2)	128.75	128.39	128.30
N3−C4−C5	114.8 (5)	115.5 (3)	114.16	114.47	114.59
C6=C5−C9	124.4 (9)	124.3 (4)	123.87	123.82	123.86
C5=C6−H12	121.97 [h]		122.16	121.91	121.97
C6−N1−H10	121.5 (11)	121.4 (10)	120.90	121.12	121.07
N1−C2=O7	123.1 (9)		123.60	123.48	123.46
C2−N3−H11	114.8 (15)[b]	117 (2)	115.18	115.41	115.49
N3−C4=O8	120.6 (12)		120.98	120.71	120.67
C5−C9−H13	110.0 (15)[g]		111.05	111.03	110.97
C5−C9−H14 (15)	109.5 (15)[g]		110.40	110.51	110.51
C6−C5−C9-H14 (15)	±117.4 (17)		±120.09	±121.04	±120.99
R (GED),%	3.40				

[a] The values in parentheses are three times the estimated standard errors (3σ). [b] Dependent parameter. [c] Refined in one group. Differences between parameters in the group were assumed at the values from MP2 (full)/cc-pVQZ calculations (see text). [d] See footnote *c*. [e] See footnote *c*. [f] See footnote *c*. [g] See footnote *c*. [h] Assumed at the value from MP2 (full)/cc-pVQZ calculations.

according to Pulay.[23,24] The nonredundant set of local symmetry internal coordinates is presented in Table 2. Refinements of 21 scale factors by fitting of theoretical vibrational frequencies to the same set of more than 70 experimental frequencies (Table 3) were carried out for the MP2 (full)/cc-pVTZ as well as MP2 (full)/6-311G (d,p) force fields presented in Supporting Information, Table S2. The assignments of the bands were conformed by the agreement of the quantum-chemical IR and Raman intensities with the experimental ones. The results of the spectral analysis are presented in Table 3. The scale factors obtained for the MP2 (full)/cc-pVTZ force constants are listed in Table 2. The agreement between the theoretical and experimental vibrational frequencies for both isotopomers, which was achieved after the MP2 (full)/cc-pVTZ force field scaling, is characterized by mean deviations of 3.9−4.6 cm^{-1} (0.4−0.5%), whereas the deviations of 5.5−6.0 cm^{-1} (0.8−0.9%) were obtained when the MP2 (full)/6-311G (d,p) force field was used.

The quadratic force constants calculated in the MP2 (full)/6-311G (d,p) and MP2 (full)/cc-pVTZ approximations include a great number of relatively large constants for the internal coordinate interactions, which is characteristic of the molecules with strongly delocalized electron density. Although differences between the scaled constants of both force fields are relatively small (see Supporting Information, Table S2), an unambiguous interpretation of the spectra has proved to be only possible with the use of the MP2 (full)/cc-pVTZ force field.

We have refined the earlier suggested assignment of the spectral bands for the light-d_0 isotopomer, which was based on the detailed comparison of IR and Raman spectra for matrix-isolated thymine,[20] and especially for the N1,N3-d_2 isotopomer[21] (see Table 3). For the parent isotopomer, the reassignment concerns the vibrations with the ν_{10}, ν_{11}, ν_{13}, ν_{14}, ν_{20}, ν_{21}, and ν_{37} frequencies. Experimental frequency ν_{37} (A″) for the methyl group torsional motions estimated in the MW study[8] using the high barrier approximation ($\nu_{tors} = 161\ (1)\ cm^{-1}$, $V_3 = 1.50\ (1)$ kcal mol^{-1}) is also given in Table 3 for comparison.

Spectroscopic calculations were performed using the ANCO/SCAL/PERT[25] and SHRINK-07 (updated 2007 version)[12,26] program packages.

5. Joint Analysis of GED and MW Data Supplemented by Results of ab initio and Spectroscopic Calculations

To carry out the joint analysis of experimental data from the different methods correctly, it is necessary to bring them to the same basis. Thermal-average bond distances $r_{ij,a}$ from GED and rotational constants for the ground vibrational state $B_0^{(k)}$ ($k = A, B, C$) from MW were converted to the parameters of equilibrium structure (as standard (reference) configuration), $r_{ij,e}$ and $B_e^{st\,(k)}$ values, respectively. The transformations were carried out taking into account nonlinear kinematic effects at the level of the first-order perturbation theory.[12,13] The harmonic ($\delta_{ij,h1}$ and $\delta_{h1}^{(k)}$, including also centrifugal distortions due to vibrations[14]) and anharmonic ($\delta_{ij,anh1}$ and $\delta_{anh1}^{(k)13}$) corrections were calculated using scaled quadratic MP2 (full)/cc-pVTZ and cubic MP2 (full)/6-311G (d,p) force fields, respectively. Cor-

TABLE 2: Nonredundant Set of Local Symmetry Internal Coordinates and the Scale Factors for the MP2 (full)/cc-pVTZ Force Field (For Atom Numbering See Figure 2)

coordinate [a]			
no.	notation	definition of coordinate	scale factor
1−4	N−C str	N1−C2 str, N1−C6 str, C2−N3 str, N3−C4 str	0.865
5	$(C-C)_{cyc}$ str	C4−C5 str	0.916
6	$C-C_{Me}$ str	C5−C9 str	0.916
7	C═C str	C5═C6 str	0.947
8−9	N−H str	N1−H10 str, N3−H11 str	0.904
10−11	C═O str	C2═O7 str, C4═O8 str	0.906
12	$C_{cyc}-H$ str	C6−H12 str	0.896
13	Me s.str	(C9H13 str + C9H14 str + C9H15str)/$\sqrt{3}$	0.903
14	Me str A	(2 C9H13 str − C9H14 str − C9H15 str)/$\sqrt{6}$	0.887
15	Me str B	(C9H14 str − C9H15 str)/$\sqrt{2}$	0.887
16	Me s.def	(H14C9H15 bend + H13C9H15 bend +H13C9H14 bend − C5C9H13 bend − C5C9H14 bend − C5C9H15 bend) /$\sqrt{6}$	0.952
17	Me def A	(2 H14C9H15bend − H13C9H15bend − H13C9H14bend)/$\sqrt{6}$	0.930
18	Me def B	(H13C9H15 bend − H13C9H14 bend)/$\sqrt{2}$	0.930
19	Me rock A	(2 C5C9H13 bend − C5C9H14 bend − C5C9H15 bend)/$\sqrt{6}$	1.005
20	Me rock B	(C5C9H14 bend − C5C9H15 bend)/$\sqrt{2}$	1.005
21−22	N−H rock	(C6N1H10 bend − C2N1H10 bend)/$\sqrt{2}$, (C2N3H11 bend −C4N3H11 bend)/$\sqrt{2}$	1.103
23	C2═O rock	(N1C2O7 bend − N3C2O7 bend)/$\sqrt{2}$	0.979
24	C4═O′ rock	(N3C4O8 bend − C5C4O8 bend)/$\sqrt{2}$	0.979
25	$C-C_{Me}$ rock	(C4C5C9 bend − C6C5C9 bend)/$\sqrt{2}$	1.058
26	$C_{cyc}-H$ rock	(C5C6H12 bend − N1C6H12 bend)/$\sqrt{2}$	0.945
27	ring def A	(N1C2N3 bend − C6N1C2 bend − C2N3C4 bend + N3C4C5 bend − C4C5C6 bend + C5C6N1 bend)/$\sqrt{6}$	1.013
28	ring def B	(2 C2N3C4 bend − C6N1C2 bend − N1C2N3 bend − N3C4C5 bend − C4C5C6 bend +2 C5C6N1 bend)/2$\sqrt{3}$	1.013
29	ring def C	(N1C2N3 bend − C6N1C2 bend − N3C4C5 bend + C4C5C6 bend)/ 2	1.013
30−31	N−H wag	N1H10/C2N1C6 out-of-plane, N3H11/C4N3C2 out-of-plane	0.871
32	C2═O wag	C2═O7/N3C2N1 out-of-plane	0.932
33	C4═O′ wag	C4═O8/C5C4N3 out-of-plane	0.932
34	$C-C_{Me}$ wag	C5C9/C6C5C4 out-of-plane	1.014
35	$C_{cyc}-H$ wag	C6H12/N1C6C5 out-of-plane	0.900
36	ring tor A	(C5═C6 tor − C4C5 tor + N3C4 tor − C2N3 tor + N1C2 tor − N1C6 tor)/$\sqrt{6}$	0.945
37	ring tor B	(C5═C6 tor − N3C4 tor + C2N3 tor − N1C6 tor)/2	0.945
38	ring tor C	(2 C4C5 tor + 2 N1C2 tor − N3C4 tor − N3C2 tor − C5═C6 tor − N1C6 tor)/2$\sqrt{3}$	0.945
39	Me tor	C9 [H13, H14, H15] − C5 [C4, C6] tor	1.0 assumed

[a] Notations of vibrations: str, stretching; bend, bending for the bond angle; def, local symmetry deformation vibration for the CH_3 fragment; rock, rocking; wag, wagging; tor, torsional, which is defined as the sum of the motions in the tetra-atomic fragments; s, symmetric vibration. Letters A, B, and C denote quasi-degenerate vibrations, cyc denotes atom in the cycle.

rections for centrifugal distortion effects due to the overall rotation, $\delta_{ij}^{\mathrm{cent,rot}}$ and $\delta^{\mathrm{cent,rot}\,(k)}$ according to ref 27 and corrections due to rotational−vibrational interactions according to refs 28 and 29 were also included. The total corrections ($r_{ij,\mathrm{e}} - r_{ij,\mathrm{a}}$) and ($B_{\mathrm{e}}^{\mathrm{st}\,(k)} - B_0^{(k)}$) calculated by means of SHRINK-07 program are listed in Tables 4 and 5, respectively.

Since GED intensity is not sensible to rotation of the methyl group around the C9−C5 bond, its conformation was assumed to be staggered with respect to the C4−C5 bond according to results of ab initio calculations. The geometrical molecular model of C_s symmetry (see Figure 2) was described by two bond lengths (C5═C6 and C5−C9), four group of internuclear distances ((1) N1−C6, N1−C2, C2−N3, and N3−C4; (2) C2═O7 and C4═O8; (3) N1−H10 and N3−H11; (4) C6−H12, C9−H13, and C9−H14 (15)), ten bond angles listed in Table 1, one group of angles (C5−C9−H13 and C5−C9−H14 (15)) and C6═C5−C9−H14 (15) dihedral angle. Differences between parameters within each of the five groups relative to N1−C6, C2═O7, N1−H10, C6−H12, and C5−C9−H13, respectively, were assumed at the values from the MP2 (full)/cc-pVQZ calculation.

The root-mean-square (rms) vibrational amplitudes $u_{ij,h1}$ were calculated using a scaled quadratic MP2 (full)/cc-pVTZ force field (see section above). The calculated amplitudes were assumed or used as starting values in the analysis, as well as their differences were used in the refinements of experimental amplitudes in groups as shown in Table 4.

The fitting of GED intensities and MW rotational constants was performed by varying simultaneously most of the molecular parameters using the KCED25 program[30] adapted for PC at the Eötvös Budapest University (Hungary) and modified at the Moscow State University. The *R*-factors for the GED and MW components of the total functional were 3.4 and 0.003%, respectively.

The weights of the rotational constants relative to the GED intensities were empirically adjusted so that to obey a balance between sufficiently accurate reproducing both rotational constants and GED intensities. The identity matrices of weight factors were used for the experimental molecular scattering intensities. For the $B_{\mathrm{e}}^{\mathrm{st}\,(k)}$ rotational constants, the relative weights were taken according to errors estimated as standard deviations of the effective $B_0^{(k)}$ constants with addition of

TABLE 3: Band Assignment in the Spectra of Parent Thymine-d$_0$ (IR in the Gas Phase,[19] IR and Raman in an Ar Matrix[20–22]), and Isotopomer N$_1$,N$_3$-d_2 (IR (Ar)[21] Based on the Scaled MP2 (full)/cc-pVTZ Force Field (See Text for More Details)[a]

no., sym. type	calculations							experiment	
	mode[b]	Parent isotopomer -d$_0$					N$_1$,N$_3$-d_2	-d_0 [19, if not noted][c]	N$_1$,N$_3$-d_2[21 c]
		PED %	I (IR)	I (Ra)	D (p)	ν cm^{-1}	ν cm^{-1}	ν cm^{-1}	
1 A′	N1—H str	99	119.1	102.8	0.23	3497.8	2566.0	3494.2 s[9]	2567 (17)
2 A′	N3—H str	99	75.7	76.8	0.26	3448.6	2528.2	3444.5 s[9]	2538 (15)
3 A′	C$_{cyc}$—H str	99	3.8	91.2	0.31	3076.0	3076.0	3076 m	
4 A′	Me str A	100	8.8	65.1	0.73	2994.9	2995.0	2997 (42) Ra[20]	2993 (8)
5 A″	Me str B	100	5.5	75.9	0.75	2978.1	2978.1	2984	2972 (8)
6 A′	Me s.str	99	17.1	166.0	0.02	2941.0	2941.1	2941	2941 (9)
7 A′	C2═O str	60	779.1	14.3	0.34	1774.7	1746.0	1772 vs	1744 (345)
	N1—H rock	9							
8 A′	C4═O′ str	49	423.6	65.6	0.19	1719.8	1708.6	1725 vs	1707 (552)
	C═C str	16							
9 A′	C═C str	46	4.5	21.7	0.20	1674.0	1665.3	1668 s	1670 (52)
	C4═O′ str	24							
10 A′	N1—H rock	53	123.9	23.0	0.43	1507.7	1440.1	1518 m	1436 (83)
	C2═O str	14							
11 A′	Me def A	77	27.8	5.9	0.75	1470.1	1472.7	1472 (115)IR[20]	1461 (43)
12 A″	Me def B	88	7.5	11.0	0.75	1446.5	1446.5	1455 (7) IR[20]	1446 (48)
13 A′	N3—H rock	55	4.8	5.0	0.69	1426.3	1237.3	1431 (11) IR[20]	1238 (3)
	N3—C4═ str	8							
14 A′	(C—C)$_{cyc}$ str	15	52.7	0.4	0.71	1415.8	1318.6	1409 s	1323 (76)
	N3—H rock	13							
	N3—C2═ str	9							
15 A′	Me s.def	91	9.6	8.5	0.67	1390.6	1390.9	1393 s	1389 (9)
16 A′	C$_{cyc}$—H rock	43	8.6	30.3	0.39	1354.8	1351.4	1357 (31) Ra[20]	1353 (19)
	N1—C2═ str	11							
17 A′	C—C$_{Me}$ str	28	4.9	7.6	0.14	1218.8	1210.2	1220 (6) Ra[20]	1207 (11)
	N1—C6═ str	13							
18 A′	N1—C6═ str	23	134.7	0.9	0.68	1178.9	1097.4	1178 s	1093 (9)
	C$_{cyc}$—H rock	18							
19 A′	N3—C4═ str	28	7.1	3.6	0.55	1144.8	1057.3	1139 (7) IR[20]	1045 (1)
	N1—C6═ str	18							
20 A″	Me rock B	77	1.4	0.1	0.75	1078.9	1078.9	1078 m	1085 (12)
21 A′	Me rock A	50	2.0	3.0	0.40	1019.0	947.2	1031 vw	927 (2)
	Ring def A	16							
22 A′	N1—C2═ str	23	11.5	4.7	0.26	946.4	866.2	963 vw	858 (22)
	N3—C2═ str	13							
	Ring def A	11							
23 A″	C$_{cyc}$—H wag	100	14.9	1.7	0.75	887.6	887.6	885 w	890 (17)
24 A′	Ring def A	38	2.8	6.1	0.12	795.8	768.4	804 vw	763 (16)
	C—C$_{Me}$ str	22							
25 A″	C4═O′ wag	75	21.7	0.8	0.75	777.3	775.9	767 w	777 (2)
26 A″	C2═O wag	100	25.9	1.2	0.75	750.7	750.5	755 w	753 (24)
27 A′	(C—C)$_{cyc}$ str	37	4.8	11.6	0.09	721.2	700.7	727 (12) Ra[20]	702 (3)
	Ring def B	12							
28 A″	N3—H wag	97	68.5	1.6	0.75	660.1	504.9	658 w	505 (28)
29 A′	C2═O rock	25	1.3	6.5	0.43	605.9	589.7	601 (7) Ra[20]	
	C4═O′ rock	22							
30 A″	Ring def B	49	57.0	0.6	0.75	539.2	526.7	541 w	528 (5)
	N3—C2═ str	9							
31 A′	N1—H wag	89	6.4	4.7	0.35	539.1	413.4	541 (w)	413 (8)
32 A′	Ring def C	68	17.0	4.4	0.44	459.2	455.7	462 vw	451 (18)
	C—C$_{Me}$ str	10							
33 A″	Ring tor B	62	18.3	1.7	0.75	402.3	368.7	407 (-) Ra[20]	370 (35)
	Ring tor A	10							
34 A′	C4═O′ rock	35	19.8	1.6	0.72	382.1	379.9	391 (2) Ra[20]	378
	C2═O rock	26							
35 A″	C—C$_{Me}$ wag	74	0.4	0.2	0.75	309.5	308.8	307 (0.6) Ra[20]	
36 A′	C—C$_{Me}$ rock	70	2.6	0.2	0.55	281.1	280.8	282 (0.5) Ra[20]	280 (3)
37 A″	Me tor	96	0.1	0.2	0.75	175.3	175.2	(161[9])[d]	
38 A″	Ring tor A	52	1.3	0.1	0.75	156.0	152.3	155 (0.1) Ra[20]	
	Ring tor B	45							
39 A″	Ring tor C	100	0.03	0.2	0.75	112.5	111.9		

[a] PED, potential energy distribution; I (IR), intensity of IR bands calculated in the MP2 (full)/cc-pVTZ approximation (km·mol^{-1}); I (Ra), Raman scattering activity (Å^4·AMU^{-1}); D (p), depolarization ratios for plane incident light calculated in the MP2 (full)/6-311G (d,p) approximation; s, strong; m, medium; w, weak; v, very. [b] Notations of vibrations are given in Table 3. [c] The experimental total relative integrated IR intensities or Raman scattering strengths of the bands[20,21] are given in parentheses. [d] Estimation based on the MW data.

TABLE 4: Vibrational Corrections ($r_e - r_a$) to the Thermal-Average Internuclear Distances r_a and Deviations of the Experimental Mean Amplitudes from Those Calculated Using Scaled MP2 (full)/cc-pVTZ Force Field ($u_{exp} - u_{calc}$) (in Å)[a]

distance	r_a[b]	$r_e - r_a$	u_{calc}	$u_{exp} - u_{calc}$[c]
N1−H10	1.023 (9)	−0.0151	0.0716	assumed
N3−H11	1.028 (9)	−0.0151	0.0721	assumed
C6−H12	1.110 (11)	−0.0156	0.0768	assumed
C9−H13	1.116 (11)	−0.0155	0.0781	assumed
C9−H14 (15)	1.118 (11)	−0.0157	0.0782	assumed
C2═O7	1.213 (1)	−0.0034	0.0387	0.0051 (18)
C4═O8	1.218 (1)	−0.0033	0.0391	0.0051 (18)
C5═C6	1.351 (16)	−0.0069	0.0433	0.0029 (32)
N1−C6	1.384 (3)	−0.0113	0.0473	0.0029 (32)
C2−N3	1.388 (3)	−0.0097	0.0485	0.0029 (32)
N1−C2	1.390 (3)	−0.0119	0.0485	0.0029 (32)
N3−C4	1.407 (3)	−0.0111	0.0507	0.0029 (32)
C4−C5	1.475 (9)	−0.0094	0.0506	0.0019 (56)
C5−C9	1.498 (8)	−0.0112	0.0513	0.0019 (56)
N3...O8	2.276 (12)	−0.0070	0.0597	−0.0021 (23)
N1...O7	2.286 (10)	−0.0097	0.0588	−0.0021 (23)
N3...O7	2.297 (12)	−0.0093	0.0589	−0.0021 (23)
N1...N3	2.313 (8)	−0.0181	0.0580	−0.0021 (23)
C5...O8	2.387 (16)	−0.0112	0.0622	−0.0026 (30)
N1... C5	2.404 (12)	−0.0160	0.0567	−0.0026 (30)
C4...C6	2.413 (11)	−0.0085	0.0587	−0.0026 (30)
N3...C5	2.427 (8)	−0.0159	0.0614	−0.0026 (30)
C2...C6	2.437 (7)	−0.0121	0.0594	−0.0026 (30)
C2...C4	2.501 (5)	−0.0085	0.0615	−0.0026 (30)
C6...C9	2.512 (11)	−0.0079	0.0707	−0.0026 (30)
C4...C9	2.550 (13)	−0.0185	0.0765	−0.0026 (30)
N3...C6	2.689 (7)	−0.0131	0.0683	−0.0026 (30)
N1...C4	2.791 (8)	−0.0145	0.0666	0.0037 (54)
C2...C5	2.885 (7)	−0.0149	0.0655	0.0037 (54)
O8...C9	2.893 (12)	−0.0231	0.1197	0.0037 (54)
C6...O7	3.544 (9)	−0.0114	0.0632	0.0037 (24)
C6...O8	3.545 (7)	−0.0074	0.0625	0.0037 (24)
C2...O8	3.571 (7)	−0.0018	0.0663	0.0037 (24)
C4...O7	3.600 (11)	−0.0062	0.0672	0.0037 (24)
N1...C9	3.792 (9)	−0.0170	0.0709	0.0037 (24)
N3...C9	3.793 (8)	−0.0226	0.0748	0.0037 (24)
N1...O8	3.999 (8)	−0.0103	0.0681	0.0021 (64)
C5...O7	4.093 (7)	−0.0136	0.0669	0.0021 (64)
C2...C9	4.377 (7)	−0.0206	0.0744	0.0058 (109)
O7...O8	4.552 (8)	0.0040	0.0788	0.0058 (109)
O7...C9	5.585 (7)	−0.0195	0.0755	0.0086 (128)

[a] For atom numbering of thymine molecule see Figure 2. The values in parentheses are twice the estimated standard errors (2σ) for mean amplitudes u and three times the estimated standard errors (3σ) for internuclear distances r_a. [b] For description of molecular model, see Table 1 and text. [c] Mean amplitudes with equal uncertainties were refined in one group with retaining the differences equal to those for the calculated values.

uncertainties in $B_e^{st\,(k)} - B_0^{(k)}$ corrections which are arbitrarily estimated to be 5% of their total values. The relative weights of the GED and MW data in the joint analysis were chosen so that standard deviations for the determined B_e (GED + MW) constants (see Table 5) were close to the estimated errors mentioned above.[31] This procedure was successfully used in previous studies.[32,33] As is seen from Table 5, the rotational constants calculated from the joint analysis of GED and MW data are very close to the experimental ones. The geometrical parameters resulting from the joint refinement of the GED and MW data are presented in Table 1 in comparison to those from ab initio calculations. Agreement attained for rotational constants of ten isotopomers is illustrated by Table 5.

Molecular intensity and radial distribution curves with their theoretical analogues corresponding to final molecular model are shown in Figures 3 and 4, respectively.

6. Discussion and Conclusions

MP2 (full)/cc-pVTZ level of calculations with including polarization f-functions seems to be appropriate for analysis of experimental vibrational spectra (see Table 3) which were completely assigned for the first time in the present work. This analysis was more successful than that based on MP2 (full)/6-311G (d,p) calculation.

The success of the vibrational spectra assignment and the GED analysis, based on the assumptions according to results of MW study[7,8] and our theoretical calculations that thymine exists as a ketone form with C_s symmetry, points to correctness of these assumptions.

The equilibrium structure parameters (r_e, $\angle_e$) obtained from GED data supplemented by MW rotational constants are close to those from MP2 (full)/cc-pVTZ and MP2 (full)/cc-pVQZ calculations (see Table 1).

As can be seen from Tables 1 and 4, there are large differences between some structural parameters determined in the MW (r_s)[8] and present GED (r_e/r_a) studies, respectively, even taking into account their different physical meaning. Because of limitations of the MW method not all geometrical parameters could be obtained with high precision. So, the position of the C2 atom lying very close to the main rotational

TABLE 5: Rotational Constants B_e Determined by the Joint GED + MW Analysis in Comparison with the Experimental Rotational Constants B_0[7,8] and Their Corrected Values B_e^{st} Corresponding Equilibrium Standard Configuration, and B_e Values from MP2 (full)/cc-pVTZ Calculations (in MHz)[a]

isotopomer	rotational constant	$B_0^{7,8}$	$(B_e^{st} - B_0)$ calc	B_e^{st} (MW)	δ (B_e^{st})	B_e (GED + MW)	B_e (MP2)
parent-d$_0$	*A*	3201.21289 (16)	22.35883	3223.572	1.12	3223.527 (75)	3246.7073
	B	1404.80085 (15)	9.05107	1413.852	0.45	1413.868 (29)	1417.1210
	C	982.60760 (14)	6.85139	989.459	0.34	989.462 (21)	992.45257
^{14}N1-*d*$_1$	*A*	3125.9867 (20)	21.34268	3147.329	1.07	3147.318 (189)	3169.5687
	B	1392.0601 (36)	8.93689	1400.997	0.45	1400.975 (62)	1404.2071
	C	969.2624 (25)	6.67748	975.940	0.33	975.924 (33)	978.86584
^{14}N3-*d*$_1$	*A*	3124.9244 (19)	21.69187	3146.616	1.08	3146.575 (184)	3168.9823
	B	1401.1681 (37)	8.89581	1410.064	0.44	1410.029 (62)	1413.4769
	C	973.5544 (23)	6.69730	980.252	0.33	980.236 (32)	983.30502
^{15}N1	*A*	3170.73050 (44)	22.27893	3193.009	1.11	3193.010 (137)	3215.8823
	B	1400.0133 (55)	8.99298	1409.006	0.45	1409.072 (43)	1412.2768
	C	977.39036 (45)	6.81584	984.206	0.34	984.231 (25)	987.18866
^{15}N3	*A*	3180.65571 (48)	22.25780	3202.914	1.11	3202.868 (110)	3226.0544
	B	1403.2555 (59)	9.01456	1412.270	0.45	1412.285 (33)	1415.5698
	C	979.91204 (49)	6.81938	986.731	0.34	986.735 (23)	989.75610
^{13}C5	*A*	3194.93550 (33)	22.11673	3217.052	1.11	3217.009 (123)	3240.1585
	B	1399.3768 (49)	8.99244	1408.369	0.45	1408.326 (39)	1411.6533
	C	979.36044 (40)	6.79619	986.157	0.34	986.134 (22)	989.15829
^{13}C6	*A*	3154.81555 (74)	21.96222	3176.778	1.10	3177.084 (143)	3199.5389
	B	1404.631 (12)	9.01249	1413.644	0.45	1413.642 (29)	1416.9082
	C	978.10021 (91)	6.79731	984.898	0.34	984.933 (23)	987.89677
^{13}C2	*A*	3201.26311 (33)	22.26707	3223.530	1.11	3223.487 (75)	3246.6623
	B	1394.7246 (48)	8.94392	1403.669	0.45	1403.656 (31)	1406.8829
	C	977.67164 (40)	6.78515	984.457	0.34	984.446 (22)	987.41608
^{13}C4	*A*	3187.46326 (53)	22.10557	3209.569	1.11	3209.461 (120)	3232.7362
	B	1402.6625 (80)	8.97748	1411.640	0.45	1411.655 (35)	1414.8722
	C	980.26562 (64)	6.79120	987.057	0.34	987.052 (22)	990.04259
^{13}C9	*A*	3187.47755 (78)	22.08771	3209.565	1.10	3209.622 (134)	3232.4118
	B	1377.781 (11)	8.87991	1386.661	0.44	1386.676 (47)	1390.0878
	C	968.04871 (94)	6.73653	974.785	0.34	974.789 (28)	977.81341

[a] The error estimates are given as the following: for B_0 as standard deviations upon the MW data analysis (in parentheses), δ (B_e^{st}) for B_e^{st} values as the same standard deviations with addition of the uncertainties in the calculated corrections (which are arbitrarily taken to be 5% of their total values), and for B_e (GED + MW) as standard deviations upon the joint structural analysis (in parentheses).

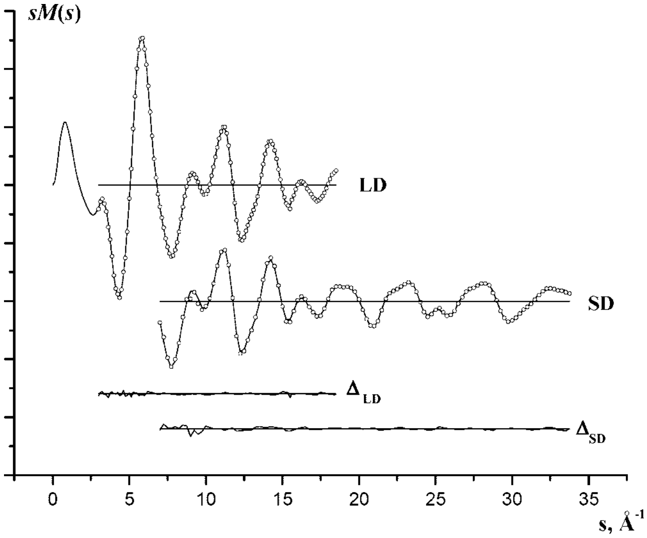

Figure 3. Experimental (open circles) and theoretical (solid line) molecular intensity curves *sM*(*s*) and their differences (Δ) for the long (LD) and short (SD) nozzle-to-film distances.

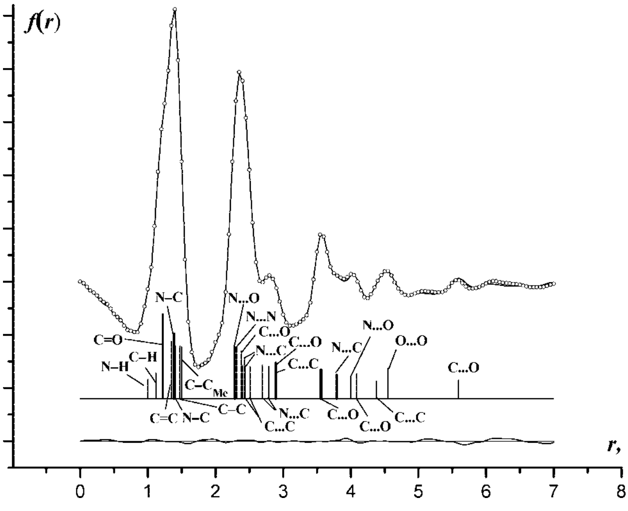

Figure 4. Experimental (open circles) and theoretical (solid line) radial distribution curves *f*(*r*) and difference curve (damping factor of exp ($-0.00202s^2$)).

axis could not be determined precisely. Therefore, the bond lengths and angles including this atom (N1—C2, C2—N3, C2—N1—C6, C2—N3—C4, and so forth) have large uncertainties. Moreover, some structural r_s parameters (C2═O7, C4═O8, N1—C2═O7, N3—C4═O8, and so forth) could not be determined in ref 8 at all.

The thermal average bond lengths (r_g) for thymine are in agreement with those for uracil[35] (r_g (thymine)/r_g (uracil) in Å: 1.217 (1)/1.212 (3) for (C═O)mean; 1.352 (16)/1.343 (24) for C5═C6; 1.394 (3)/1.399 (6) for (N—C)mean; 1.476 (9)/1.462 (8) for C4—C5). Relative small vibrational corrections ($r_a - r_\alpha$) and amplitudes pointed to relative rigidity of the uracil molecule.[34] Vibrational corrections ($r_a - r_e$) and amplitudes for thymine, calculated in the more appropriate approximation, are

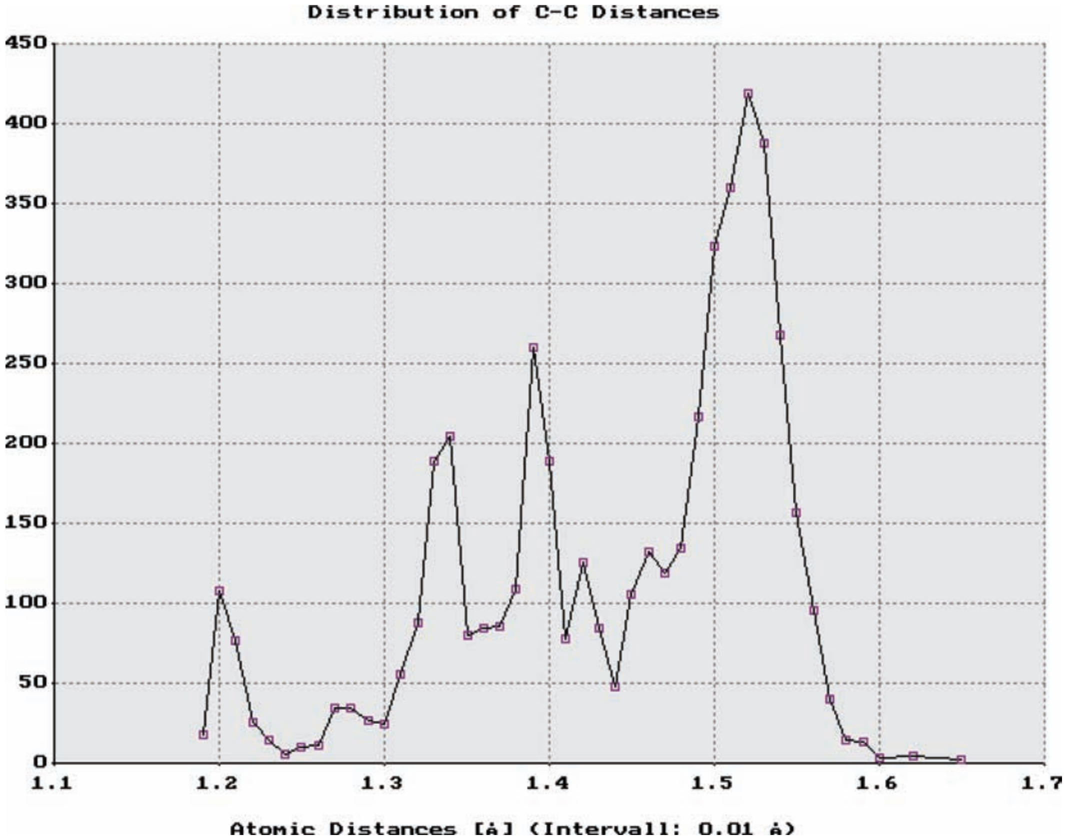

Figure 5. Distribution of the C—C bond lengths of organic gas-phase compounds in the MOGADOC database[35] (number of molecules is indicated on the vertical axis).

even smaller than for uracil. This result excludes high flexibility of the thymine ring, being in contradictory with conclusions of molecular dynamic simulations.[10] The methyl group is also not very flexible. Its position is slightly stabilized due to two weak hydrogen bonds of 2.88 (4) Å (see Table 1). The barrier to internal rotation of this group estimated in the MP2 (full)/cc-pVTZ approximation is 1.52 kcal mol^{-1}, being characteristic of the hindered rotation. This value is close to that (1.502 (9) kcal mol^{-1}) obtained from the experimental data.[8]

Out-of-plane motions of the ring could be adequately considered in the present study on the basis of quadratic force field taking into account nonlinear kinematic effects, i.e., without the quartic force field or potential energy surface for these vibrations. The low factor R_f of 3.4%, which characterized the goodness of fit, confirms that the theoretical model,[12–15] applied in the GED analysis, is appropriate for the molecular dynamics description of thymine. At such high level of agreement between experimental data and theoretical model, the extension of the model in order to better describe the nonplanar ring deformations as well as the methyl group torsion seems to be not necessary because of obvious small sensibility of experimental intensities to additional parameters.

On the other side, as can be seen from Table 4, the determined equilibrium bond lengths (r_e) are systematically shorter than the thermal-average distances (r_a). The differences between the r_e and r_a values being for the most of parameters between 0.003 and 0.012 Å exceed the experimental errors of a few thousands of Å. In the cases of N—H and C—H bond lengths, these differences are even larger (ca. 0.015 Å). Therefore, for the correct determination of the molecular geometry by GED, the precise harmonic and anharmonic (cubic) vibrational corrections have to be taken into account.

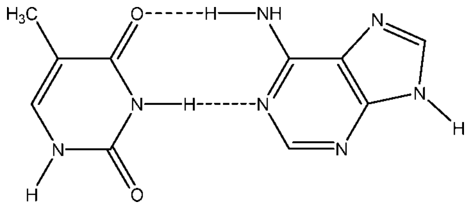

Figure 6. Thymine—adenine NA base pair.

It is remarkable that the experimental C4—C5 internuclear distance (r_e = 1.466 (9) Å and r_a = 1.475 (9) Å in Tables 1 and 4, respectively) is shorter than the typical single C—C bond of ca. 1.52 (2) Å (see distribution of the C—C bond lengths of organic gas-phase compounds in the MOGADOC database,[35] Figure 5). It points to a slightly "aromatic" nature of thymine. Additionally, the aromaticity index, NICS (abbreviation from nucleus-independent chemical shift; for definition see[36] and references therein), of 1.35 ppm, calculated in the MP2/cc-pVTZ approximation, confirms the weak "aromaticity" of the molecule.

It should be noted that the determined C4═O8 and N3—H11 bond lengths are longer than the C2═O7 and N1—H10 distances, respectively. It can explain why just the O8 and H11 atoms participate in the hydrogen bonding with adenine (see Figure 6).

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Supporting Information Available: Experimental intensity curves with final backgrounds (Table 1S), MP2 (full)/cc-pVTZ and MP2 (full)/6-311D (d,p) quadratic force constants after scaling in internal coordinates (Table 2S). This material is available free of charge via the Internet at http://pubs.acs.org.

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