Ab initio and DFT Study of Thymine and Water Complexes

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ABSTRACT

The optimized geometries of thymine and all the three isomers of thymine-water complex, isomer-I, isomer-II and isomer-III have been obtained using Ab initio method MP2 and DFT methods B3LYP, X3LYP and B3PW91 with 6-311++G (d,p) basis set. Structural parameters of the optimized geometries, total energies and the APT charges of thymine and all the three isomers of the thymine-water complex have been computed. Frequency calculations are carried out on each optimized structure using DFT methods and their IR and Raman spectra have been discussed. The calculated frequencies of the thymine are found to be in good agreement with the experimental values in most of the cases. We show that addition of water molecules in thymine, the strength of the binding energy decreases i.e. stability increases.

Keywords: Thymine, MP2, DFT, B3LYP, Optimized geometry

INTRODUCTION

Adenine, cytosine, guanine and thymine are the nucleobase that form the Nucleic Acid (NA) base pairs (guanine with cytosine, adenine with thymine) in DNA. Thymine is one of the pyrimidine bases, along with cytosine that makes hydrogen bonds with adenine (6-amino purine) in normal Waston-Crick base pairing. The pair wise creation of the bases occurs due to the formation of hydrogen bonds. The building by minor tautomers of NA bases of non-standard base pairs may lead to changes in the genetic code [1,2]. The perusal of the dynamics of these molecules and molecular structure can help to understand and explain some processes in biological systems. Recently, there has been an increasing interest in studying DNA damage, which may cause various diseases such as cancer [3-7]. This intellect is of great interest due to its importance for developing pharmacological substances and developing therapies against viral infections, cancer, mol formations and so on. In a recent work, the proton affinity of the two oxygen atoms and the deprotonation enthalpies of the two NH bonds of thymine have been computed using the DFT methods employing B3LYP, X3LYP and B3PW91 functional in conjunction with 6-311++G (d,p) basis set. It has been suggested that the energies of the three stable thymine-water complexes depend not only on the proton accepting ability of the oxygen atom but also on the ability of NH groups to donate proton [8]. To establish more general correlations between the acidity and basicity of an amphoteric molecule and its hydrogen bonding ability, the energy of the thymine-water complexes are computed in this work using the DFT (B3LYP) and a 6-311++G (d,p) basis set. Use of an suitable DFT functional combined with an appropriate basis set reproduces the energy of the complex very well; in fact, the energy

and the intermolecular distance obtained for the thymine-water interaction are comparable with thymine calculated at the DFT (B3LYP) and a 6-311++G (d,p) basis set. For proper use of the vibrational spectra of nucleic acid bases in biophysical research, authentic knowledge of the normal mode of each vibration for each relevant IR or Raman band is essential. Three stable structures for the thymine-water complex have been studied in this work. The three thymine water isomers obtained here have been reported earlier by Chandra, et al. [9]. Optimized geometries of all the three isomers of thymine-water complex have been obtained at MP2/6-311++G (d,p), B3LYP/6-311++G (d,p), X3LYP/6-11++G (d,P) and B3PW91/6-11++G (d,p) levels of theory. Structural parameters of the optimized geometries, total energies and the APT charges of the thymine-water complex have been computed. The optimized bond length and bond angles are in agreement with the corresponding experimental results. In this work a study of change in structures and spectra of possible hydrogen bonded thymine-water complexes have been done and these have been compared with that of free thymine. We show that addition of water molecules in thymine, the strength of the binding energy decreases *i.e.* stability increases.

MATERIALS AND METHODS

The vibrational spectra and ground state geometries for free thymine and its hydrogen bonded complexes with molecules of water have been optimized using the *Ab initio* method: (i) MP2 and hybrid Density Functional Theory (DFT) methods (ii) B3LYP which uses parameter Becke's functional three with nonlocal correlation provided by Lee-Young-Parr expression with 6-311++G (d,p) basis set [10-14]. The total energies, structural parameters of the optimized geometries and the APT charges of isomers have been computed using DFT methods only. For all computational calculations, we have used Gaussian 09 package of programs [15]. Initially, *Ab initio* calculations were done at MP2/6-311++G (d,p) level. The optimized geometry at the MP2/6-311++G (d,p) level was taken as the input structure for the DFT calculation using B3LYP/6-311++G (d,p) level. Similarly, the optimized geometry at the B3LYP/6-311++G (d,p) level was used as the input structure for the calculation at the X3LYP/6-11++G (d,p) and B3PW91/6-11++G (d,p) level. The geometries were optimized by minimizing the energies without imposing any constraint on the geometry. It is widely accepted that this level of theory is sufficient to reliably predict molecular geometries of the hydrogen bonded systems. The optimized structures of free thymine and three isomers at B3LYP/6-311++G (d,p) along with atomic numbering have been shown in Figures 1 and 2a-c respectively.
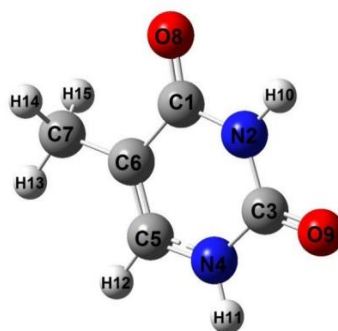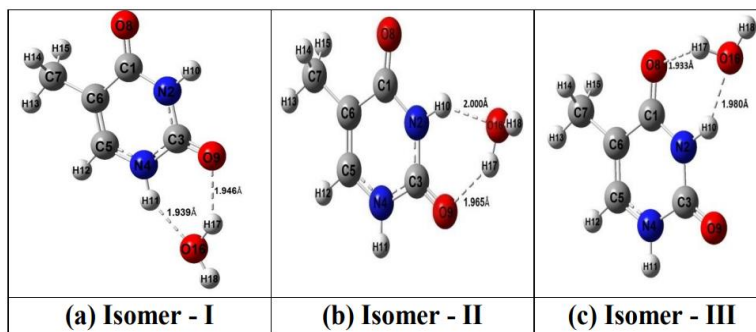

Figure 1: Optimized structure of free thymine at B3LYP/6-311++G (d,p).

Figures 2a-c: Optimized structures of three stable isomers of thymine-water complexes obtained at B3LYP/6-311++G (d,p) level. (Red: Oxygen; Blue: Nitrogen; Grey: Carbon; White: Hydrogen).

RESULTS AND DISCUSSION

Optimized Geometry of Thymine

The geometry optimization and charge distribution of thymine have been calculated in their ground state, at various levels of theory using the Gaussian 09 computer code. The total energy of thymine at MP2/6-311++G (d,p), B3LYP/6-311++G (d,p), X3LYP/6-311++G (d,p) and B3PW91/6-311++G (d,p) levels are found to be -453.05193380 a.u., -454.27574640 a.u., -454.08723750 a.u. and -454.09637532 a.u. respectively as listed in Table 1.

Molecular Geometry

The calculated optimized molecular energies, dipole moments, zero point vibrational energies and thermodynamic function using *Ab initio* method MP2 and DFT methods B3LYP, X3LYP and B3PW91 method with 6-311++G (d,p) basis set for thymine and all the three isomers of thymine-water, *viz.* isomer-I, isomer-II and isomer-III are shown in Table 1. The isomer-I is most stable having least optimized energy while isomer-II and isomer-III are found to have higher energies in all cases. The dipole moment of isomer-I is least and that of isomer-III is largest therefore isomer-III is more polar than the other two isomers.

Table 1: Calculated energies, dipole moment, zero point vibrational energy and thermodynamic functions obtained at different levels.

S. No.	Species	Total energies E (hartree)	Zero point vibrational energy (J/mol)	Dipole moment (Debye)	Volume molar heat capacity (C,) (cal/mol K)	Entropy S (cal/mol K)
MP2/6-311++G (d,p)						
1	Thymine	-453.05193380	297752.5	4.3179	28.762	87.289
Thymine-water						
1	Isomer-I	-529.34490302	-	4.2550		
2	Isomer -II	-529.34196051	-	5,1000	-	-
3	Isomer-III	-529.34231448	-	4.7639	-	-
B3LYP/6-311++G (d,p)						
1	Thymine	-454.27574640	299866.2	4.5316	29,465	87,205
Thymine-water						
1	Isomer-I	-530.75078380	364093.0	3.7693	37.143	99.359
2	Isomer -II	-530.74788215	364685.1	4.8116	39.195	102.130
3	Isomer-III	-530.74849881	364839.0	4.5653	39.053	101.965
X3LYP/6-311++G (d,p)						
1	Thymine	-454.08723750	300512.5	4.5392	29.398	87.140
Thymine-water						
1	Isomer-I	-530.53364363	364902.4	3.7786	37.048	99.182
2	Isomer -II	-530.53070011	365495.0	4.8088	39.103	101.945
3	Isomer-III	-530.53131129	365634.9	4.5609	38.965	101.803
B3PW91/6-311++G (d,p)						
1	Thymine	-454.09637532	301184.1	4.4971	29.388	87,239

	Thymine-water					
1	Isomer-I	-530.53995348	365616.3	3.7575	37,047	99,321
2	Isomer -II	-530.53714789	366327.8	4.8611	39,058	101,941
3	Isomer-III	-530.53782868	366607.7	4.6350	38,868	101,567

Structural Parameters

The optimized geometrical parameters namely bond length (Å) and bond angles (in degree) of the thymine and all the three isomers of thymine-water, isomer-I, isomer-II and isomer-III computed using *Ab initio* method MP2 and DFT method B3LYP, X3LYP and B3PW91 functional with 6-311++G (d,p) basis set are reported along with corresponding experimental value in Tables 2-5. We see that the calculated bond lengths are very close to experimental values while calculated using B3PW91/6-311++G (d,p) and bond angles are very close to experimental values while calculated using B3LYP/6-311++G (d,p).

Table 2: Optimized bond lengths (Å) and bond angles (in degree) of free thymine and thymine-water complexes at MP2/6-311++G (d,p) level.

Parameters	Experimental	Free thymine	Isomer 1	Isomer 2	Isomer 3
Bond length					
C1-N2	1.413	1.404	1.407	1.405	1.396
N2-C3	1.345	1.387	1.382	1.378	1.387
C3-N4	1.314	1.386	1.377	1.382	1.389
N4-C5	1.408	1.380	1.379	1.382	1.378
C5-C6	1.369	1.357	1.358	1.356	1.357
C6-C7	1.522	1.499	1.499	1.498	1.499
C1-O8	1.193	1.223	1.223	1.222	1.232
C3-O9	1.246	1.218	1.228	1.227	1.217
N2-H10	-	1.015	1.015	1.024	1.024
N4-H11	-	1.010	1.020	1.010	1.011
C5-H12	-	1.086	1.086	1.086	1.086
C7-H13	-	1.093	1.093	1.093	1.093
C7-H14	-	1.094	1.094	1.093	1.093
C7-H15	-	1.094	1.094	1.093	1.093
O16-H17	-	-	0.97	0.968	0.959
O16-H18	-	-	0.959	0.959	0.969
H11-O16	-	-	1.937	-	-
O9-H17	-	-	1.983	2.003	-
O16-H10	-	-	-	1.982	1.97
O8-H17	-	-	-	-	1.974
Bond angles					
O9-C3-N4	122	123	124	122	123
O9-C3-N2	121	124	123	124	124
N4-C3-N2	118	112	113	113	113

C3-N4-C5	123	123	123	123	124
N4-C5-C6	120	122	123	122	122
C5-C6-C7	112	123	124	124	124
C5-C6-C1	119	118	118	118	118
C7-C6-C1	119	118	118	118	118
C6-C1-N2	114	114	114	115	115
C6-C1-O8	125	124	125	124	123
O8-C1-N2	121	120	120	121	121
C1-N2-C3	126	128	128	127	127
H17-O16-H18	-	-	105	105	105
N4-H11-O16	-	-	145	-	-
H11-O16-H17	-	-	86	-	-
O16-H17-O9	-	-	141	140	-
H17-O9-C3	-	-	108	109	-
N2-H10-O16	-	-	-	144	144
H10-O16-H17	-	-	-	87	138
O16-H17-O8	-	-	-	-	142
C1-O8-H17	-	-	-	-	111

Table 3 : Optimized bond lengths (Å) and bond angles (in degree) of free thymine and thymine-water complexes at B3LYP/6-311++G (d,p) level.

Parameters	Experimental	Free thymine	Isomer 1	Isomer 2	Isomer 3
Bond length					
C1-N2	1.413	1.407	1.409	1.407	1.396
N2-C3	1.345	1.384	1.379	1.375	1.384
C3-N4	1.314	1.387	1.378	1.382	1.391
N4-C5	1.408	1.380	1.377	1.381	1.376
C5-C6	1.369	1.349	1.351	1.348	1.350
C6-C7	1.522	1.500	1.499	1.499	1.500
C1-O8	1.193	1.217	1.217	1.216	1.229
C3-O9	1.246	1.213	1.225	1.225	1.212
N2-H10	-	1.013	1.012	1.023	1.024
N4-H11	-	1.009	1.019	1.009	1.009
C5-H12	-	1.083	1.083	1.083	1.083
C7-H13	-	1.091	1.092	1.092	1.092
C7-H14	-	1.093	1.093	1.093	1.093
C7-H15	-	1.093	1.093	1.093	1.093
O16-H17	-	-	0.974	0.973	0.975
O16-H18	-	-	0.96	0.961	0.961
H11-O16	-	-	1.939	-	-

O9-H17	-	-	1.946	1.965	-
O16-H10	-	-	-	2	1.98
O8-H17	-	-	-	-	1.933
Bond angles					
O9-C3-N4	122	123	123	122	123
O9-C3-N2	121	124	123	124	124
N4-C3-N2	118	112	113	114	113
C3-N4-C5	123	123	123	123	124
N4-C5-C6	120	122	123	122	122
C5-C6-C7	112	123	124	124	124
C5-C6-C1	119	118	118	118	118
C7-C6-C1	119	118	118	118	118
C6-C1-N2	114	114	114	115	116
C6-C1-O8	125	125	125	125	124
O8-C1-N2	121	120	120	120	120
C1-N2-C3	126	128	128	127	127
H17-O16-H18	-	-	108	107	107
N4-H11-O16	-	-	143	-	-
H11-O16-H17	-	-	88	-	-
O16-H17-O9	-	-	140	142	-
H17-O9-C3	-	-	110	110	-
N2-H10-O16	-	-	-	142	143
H10-O16-H17	-	-	-	86	84
O16-H17-O8	-	-	-		143
C1-O8-H17	-	-	-		112

Table 4: Optimized Bond lengths (Å) and Bond angles (in Degree) of free thymineand thymine-water complexes at X3LYP/6-311++G (d,p) level.

Parameters	Experimental	Free thymine	Isomer 1	Isomer 2	Isomer 3
Bond length					
C1-N2	1.413	1.406	1.407	1.405	1.395
N2-C3	1.345	1.383	1.378	1.374	1.383
C3-N4	1.314	1.386	1.377	1.380	1.389
N4-C5	1.408	1.379	1.376	1.381	1.375
C5-C6	1.369	1.348	1.350	1.347	1.349
C6-C7	1.522	1.499	1.499	1.498	1.499
C1-O8	1.193	1.216	1.216	1.215	1.228
C3-O9	1.246	1.212	1.224	1.224	1.212

N2-H10	-	1.012	1.012	1.023	1.024
N4-H11	-	1.008	1.019	1.008	1.009
C5-H12	-	1.083	1.083	1.083	1.083
C7-H13	-	1.092	1.091	1.092	1.092
C7-H14	-	1.093	1.093	1.093	1.093
C7-H15	-	1.093	1.093	1.093	1.093
O16-H17	-	-	0.974	0.973	0.974
O16-H18	-	-	0.959	0.960	0.960
H11-O16	-	-	1.930	-	-
O9-H17	-	-	1.938	1.955	-
O16-H10	-	-	-	1.990	1.970
O8-H17	-	-	-	-	1.924
Bond angles					
O9-C3-N4	122	123	123	122	123
O9-C3-N2	121	124	123	124	124
N4-C3-N2	118	112	113	114	113
C3-N4-C5	123	123	123	123	124
N4-C5-C6	120	122	123	122	122
C5-C6-C7	112	123	124	124	124
C5-C6-C1	119	118	118	118	118
C7-C6-C1	119	118	118	118	118
C6-C1-N2	114	114	114	115	116
C6-C1-O8	125	125	125	124	124
O8-C1-N2	121	120	120	120	121
C1-N2-C3	126	128	128	127	127
H17-O16-H18	-	-	108	107	107
N4-H11-O16	-	-	143	-	-
H11-O16-H17	-	-	88	-	-
O16-H17-O9	-	-	140	142	-
H17-O9-C3	-	-	110	110	-
N2-H10-O16	-	-	-	142	143
H10-O16-H17	-	-	-	86	84
O16-H17-O8	-	-	-	-	143
C1-O8-H17	-	-	-	-	112

Table 5: Optimized Bond lengths (Å) and Bond angles (in Degree) of free Thymine and Thymine-Water complexes at B3PW91/6-311++G (d,p) level.

Parameters	Experimental	Free thymine	Isomer 1	Isomer 2	Isomer 3
Bond length					
C1-N2	1.413	1.402	1.404	1.402	1.391
N2-C3	1.345	1.380	1.374	1.371	1.380
C3-N4	1.314	1.383	1.374	1.377	1.387
N4-C5	1.408	1.375	1.372	1.376	1.371
C5-C6	1.369	1.349	1.350	1.347	1.350
C6-C7	1.522	1.494	1.494	1.494	1.495
C1-O8	1.193	1.215	1.215	1.214	1.227
C3-O9	1.246	1.211	1.223	1.22	1.211
N2-H10	-	1.012	1.012	1.024	1.025
N4-H11	-	1.008	1.020	1.008	1.008
C5-H12	-	1.084	1.084	1.084	1.084
C7-H13	-	1.092	1.092	1.092	1.092
C7-H14	-	1.094	1.094	1.094	1.094
C7-H15	-	1.094	1.094	1.094	1.094
O16-H17	-	-	0.973	0.972	0.974
O16-H18	-	-	0.958	0.959	0.959
H11-O16	-	-	1.914	-	-
O9-H17	-	-	1.933	1.951	-
O16-H10	-	-	-	1.976	1.954
O8-H17	-	-	-	-	1.916
Bond angles					
O9-C3-N4	122	123	123	122	123
O9-C3-N2	121	124	123	124	124
N4-C3-N2	118	112	113	114	113
C3-N4-C5	123	123	123	123	124
N4-C5-C6	120	122	123	122	122
C5-C6-C7	112	123	124	124	124
C5-C6-C1	119	117	118	118	118
C7-C6-C1	119	118	118	118	118
C6-C1-N2	114	114	114	115	116
C6-C1-O8	125	125	125	124	124
O8-C1-N2	121	120	120	120	121
C1-N2-C3	126	128	128	127	127
H17-O16-H18	-	-	108	107	107
N4-H11-O16	-	-	143	-	-
H11-O16-H17	-	-	88	-	-

O16-H17-O9	-	-	141	143	-
H17-O9-C3	-	-	110	109	-
N2-H10-O16	-	-	-	143	143
H10-O16-H17	-	-	-	85	84
O16-H17-O8	-	-	-	-	143
C1-O8-H17	-	-	-	-	112

Atomic Polar Tensor (APT) charges

The Atomic Polar Tensor (APT) charges for the thymine and thymine-water complexes computed at using DFT method B3LYP, X3LYP and B3PW91 method with 6-311++G (d,p) basis sets are collected in Tables 6-8 for atomic numbering scheme, see Figure 1 and Figure 2a-c respectively. In terms of the charge of electron $1e = 1.602188 \times 10^{-19}$ C from Tables 6-8, we see that due to high negativity of the respective atoms compared to the other atoms result enhancement of the bond length. In free thymine, we see that the bond length of magnitudes of the bond lengths between the pair (C1-O8) and (C3-O9) are found to be differed due to O9 is more negative than the O8. Thus O9 attracts more to C atoms than O8 which gives difference in their bond lengths. Hence the bond length of (C3=O9) is shorter than the bond length of (C1=O8) similarly, with the help of APT (Atomic Polar Tensor) charges we can explain the difference in the bond length of others pairs e.g. C1-N2 and N2-C3; C3-N4 and N4-C5; C5-C6 and C6-C7.

Table 6: APT charges at various atomic sites of free thymine molecule and thymine-water complexes at B3LYP/6-311++G (d,p) level.

Atoms	Free thymine	Isomer I	Isomer II	Isomer III
C1	1.134	1.135	1.139	1.153
N2	-0.727	-0.727	-0.789	-0.786
C3	1.335	1.337	1.351	1.339
N4	-0.737	-0.791	-0.747	-0.733
C5	0.459	0.488	0.439	0.459
C6	-0.296	-0.305	-0.279	-0.32
C7	0.086	0.086	0.083	0.0893
O8	-0.837	-0.85	-0.827	-0.927
O9	-0.922	-1.01	-1.005	-0.912
H10	0.219	0.221	0.346	0.348
H11	0.244	0.38	0.245	0.244
H12	0.053	0.055	0.052	0.053
H13	-0.008	-0.008	-0.01	-0.009
H14	-0.001	-0.003	-0.001	-0.002
H15	-0.001	-0.003	0.001	-0.001
O16	-	-0.723	-0.669	-0.682
H17	-	0.288	0.399	0.272
H18	-	0.43	0.273	0.416

Table 7: APT charges at various atomic sites of free thymine molecule and thymine-water complexes at X3LYP/6-311++G (d,p) level.

Atoms	Free thymine	Isomer I	Isomer II	Isomer III
C1	1.140	1.140	1.145	1.160
N2	-0.731	-0.731	-0.794	-0.791
C3	1.341	1.343	1.357	1.345
N4	-0.742	-0.796	-0.752	-0.738
C5	0.462	0.492	0.442	0.462
C6	-0.299	-0.308	-0.282	-0.323
C7	0.085	0.085	0.082	0.088
O8	-0.841	-0.853	-0.831	-0.932
O9	-0.926	-1.015	-1.009	-0.916
H10	0.221	0.222	0.349	0.351
H11	0.245	0.383	0.246	0.245
H12	0.054	0.0558	0.053	0.054
H13	-0.008	-0.007	-0.01	-0.008
H14	-0.001	-0.002	0.001	-0.001
H15	-0.001	-0.002	0.001	-0.001
O16	-	-0.728	-0.674	-0.687
H17	-	0.290	0.401	0.274
H18	-	0.432	0.275	0.418

Table 8: APT Charges at various atomic sites of free thymine molecule and thymine-water complexes at B3PW91/6-311++G (d,p) level.

Atoms	Free thymine	Isomer I	Isomer II	Isomer III
C1	1.128	1.128	1.132	1.146
N2	-0.725	-0.724	-0.793	-0.790
C3	1.329	1.331	1.344	1.333
N4	-0.737	-0.793	-0.745	-0.732
C5	0.454	0.483	0.433	0.454
C6	-0.294	-0.303	-0.276	-0.318
C7	0.069	0.069	0.065	0.071
O8	-0.833	-0.845	-0.822	-0.927
O9	-0.919	-1.010	-1.004	-0.908
H10	0.222	0.223	0.357	0.360
H11	0.247	0.390	0.248	0.247
H12	0.247	0.057	0.054	0.056
H13	-0.004	-0.003	-0.005	-0.004
H14	0.004	0.001	0.005	0.002
H15	0.004	0.001	0.005	0.004
O16	-	-0.731	-0.675	-0.689

H17	-	0.291	0.402	0.274
H18	-	0.434	0.274	0.421

Thermodynamic Properties

Few calculated thermo dynamical parameters such as the Zero Point Vibration Energies (ZPVE) the molar capacity at constant volume, the entropy and dipole moment are listed in table in the previous section. The variations in the ZPVES (Zero Point Vibration Energies) seem to be insignificant. Changes in the total entropy and the molar capacity at constant volume of thymine and thymine-water at DFT method B3LYP, X3LYP and B3PW91 method with 6-311++g (d,p) basis set are also marginal only.

CONCLUSION

The optimized geometries of thymine and three isomers of thymine-water complexes have been calculated employing *Ab initio* method MP2 and DFT method B3LYP, X3LYP and B3PW91 method with 6-311++G (d,p) basis set using Gaussian 09 program. Most of the geometrical parameters for thymine-water complexes remain the same as thymine except for the geometry of the site of the water bonded atom. Structural parameters of the optimized geometries, total energies and the APT charges of the thymine-water complex have been discussed in detail. From this analysis, it is noted that the theoretically calculated optimized bond lengths are comparatively larger than the experimental values because the theoretical calculations refer to isolated molecules in the gas phase while it is in the solid state for experimental results. We show that addition of water molecules in thymine, the strength of the binding energy decreases *i.e.* stability increases. The optimized bond length and bond angles are in agreement with the corresponding experimental results.

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