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HYDROGEN-BONDING INTERACTION OF UREA WITH DNA BASES: A DENSITY FUNCTIONAL THEORY STUDY

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This work deals with the interaction between urea and DNA bases (adenine, thymine, guanine, and cytosine). The optimized geometries, binding energies, and harmonic vibrational frequencies are calculated using the DFT/B3LYP functional combined with the 6-31+G(*d*,*p*) basis set. Their interactions are studied aiming to understand more about the nature of the intercalation binding forces between urea and DNA. Fourteen stable complexes are found on the potential energy surface. The structures are cyclic; they are stabilized by NH…O/N and CH…O interactions. The binding energies range from –19.9 kJ·mol^{-1} to –74.0 kJ·mol^{-1}. The obtained formation energies indicate that Urea:G and Urea:C are more favorable than Urea:T and Urea:A. In addition, the Atoms in Molecules theory is performed to study the hydrogen bonds in the complexes.

K e y w o r d s: DFT, urea, hydrogen bond, interaction energy.

Hydrogen-bonding interactions (HBs) play a unique role in chemical and biochemical systems, especially between nucleic acids bases [1]. These interactions contribute to the stability and conformational variability of nucleic acids. A proper description of these non-bonded interactions helps to understand the basic principles governing the formation of 3D nucleic acid architectures [2, 3]. Due to the importance, there have been numerous studies, experimental [4] and computational [5], concerned with the association of nucleotide base pairs. The computational studies range from Watson-Crick base pairs [6] to complexes between the bases and other molecules [7, 8].

In living organisms, urea molecules exist around biomolecules and affect their properties as well as the interactions between them [9, 10]. Recently, Y.P. Sun and co-workers have studied the weak HB between urea and the amino acid [11]. They showed the presence of closely linear amide HBs (NH…O and OH…N) to strongly stabilize the amino acid-urea complex with the H…O separation ranging from 1.89 Å to 2.38 Å. Due to the complicated hydrogen bonding and the acid-base properties associated with both the carbonyl group and amino groups in the molecule, urea is a good H-bond donor and an excellent receptor [12—14]. Therefore, it is reasonable to believe the electrostatic interaction or/and hydrogen-bonding interaction to exist in the DNA base-urea complex system.

In the present work, we have performed a theoretical calculation of the interaction of urea with adenine, thymine, guanine, and cytosine. Full geometry optimizations have been performed with the Gaussian 03 package at the B3LYP/6-31+G(*d*,*p*) level. The goal of this study is to analyze constitutionally the interaction between urea and DNA bases.

COMPUTATIONAL DETAILS

Calculations on the isolated molecules and molecular complexes were performed with the GAUSSIAN 03 package [15]. Density functional theory (DFT) was used with the Becke3-Lee-Yang-

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Parr (B3LYP) exchange correlation 6-31+G(*d*,*p*) basis set [16, 17]. According to the recent reports, hybrid functionals can provide better description for the systems with hydrogen bonds [18—20]. All geometries were completely optimized and vibrational frequencies were calculated to verify the nature of the stationary points found on the potential energy surface. The hydrogen bonding energy of the studied complex was corrected with the basis set superposition error (BSSE).

AIM is a very useful tool in analyzing HBs with a large electronic density at the HB critical point and a positive value of $\nabla^2\rho_c$ indicating a strong hydrogen bond [21]. The electron densities ρ_c and Laplacians $\nabla^2\rho_c$ of various H-bond complexes at bond critical points have been calculated at the B3LYP/6-31+G(*d*,*p*) level using Bader′s theory of atoms in molecules (AIM) [22, 23]. All these were obtained using the AIM method as implemented in the GAUSSIAN 03 package.

RESULTS AND DISCUSSION

Calculations at the B3LYP/6-31+G(*d*,*p*) level led to A1—A5, T1—T3, G1—G4, and C1—C2 structures for urea-adenine, urea-thymine, urea-guanine, and urea-cytosine respectively (Fig. 2). These complexes are stabilized by two near-linear hydrogen bonds. Table 2 lists the interaction energies and Table 3 collects the selected structural properties for the hydrogen bonded complexes studied in this work.

Isolated subsystem components. The optimized structures and atom numbering of urea and DNA bases are shown in Fig. 1. The geometrical parameters are presented in Table 1 for urea and DNA bases. A comparison of the geometries with the experimental parameters shows close values of bond lengths and angles.

The structural parameters of DNA bases are collected in Table 1. Experimental data from a statistical survey of the X-ray structures in the Cambridge Structural Database are reported in the same table [24]. As a general feature, we note that bond lengths and bond angles of the bases agree well with the experimental data. The optimized structures of adenine, thymine, guanine, and cytosine are planar with the exception of the cytosine and adenine amino groups that are non-planar (pyramidal). The calculated pyramidality of the cytosine and guanine amino groups (X—C—N—H dihedral angles of –9.9° and 6.1°, and –11.9° and 31.3° respectively). While in the crystal, torsions generally lie within 1 sem of either 0° or 180° [24]. These deviations due to the hydrogen bonds formed between the amino group and the neighboring molecules in the crystal lead to a more planar amino group than for

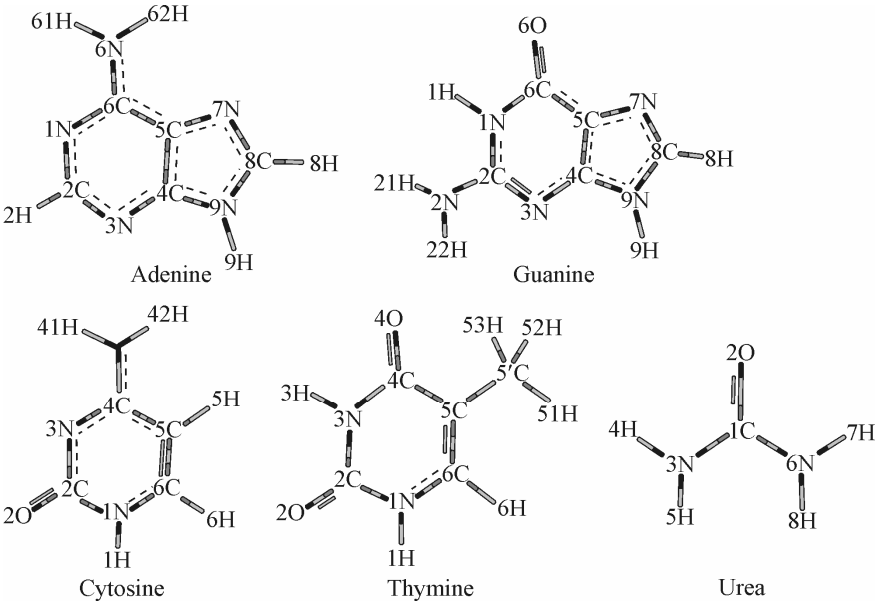

Fig. 1. Optimized conformers (B3LYP/6-31+G**) of the isolated components: urea, adenine, cytosine, guanine, and thymine

Table 1

Geometrical parameters calculated with density functional method (B3LYP/6-31+G**) *for the isolated components*

Parameter	Adenine		Guanine		Parameter	Cytosine		Thymine	
	B3LYP	Exp.	B3LYP	Exp.		B3LYP	Exp.	B3LYP	Exp.
N1—C2	1.344	1.340	1.372	1.371	N1—C2	1.427	1.397	1.387	1.376
C2—N3	1.337	1.332	1.312	1.324	C2—N3	1.370	1.355	1.385	1.373
N3—C4	1.339	1.344	1.358	1.351	N3—C4	1.321	1.335	1.406	1.381
C4—C5	1.399	1.385	1.396	1.378	C4—C5	1.441	1.424	1.468	1.446
C5—C6	1.411	1.406	1.439	1.418	C5—C6	1.360	1.340	1.353	1.339
C6—N1	1.345	1.351	1.437	1.391	C6—N1	1.356	1.365	1.381	1.379
C5—N7	1.385	1.387	1.381	1.388	C2—O2	1.223	1.242	1.221	1.218
N7—C8	1.312	1.311	1.308	1.304	C4—N4(O4)	1.361	1.334	1.224	1.228
C8—N9	1.381	1.372	1.385	1.373	C6—N1—C2	123.2	120.3	123.7	121.2
N9—C4	1.378	1.374	1.370	1.374	N1—C2—N3	116.3	119.1	112.8	114.4
C6—N6(O6)	1.354	1.336	1.221	1.238	C2—N3—C4	120.3	120.0	127.8	127.1
C2—N2			1.376	1.337	N3—C4—C5	123.9	121.9	114.8	115.3
C6—N1—C2	118.6	118.5	126.4	125.1	C4—C5—C6	116.1	117.4	117.9	118.0
N1—C2—N3	128.5	129.2	123.4	123.7	C5—C6—N1	119.9	121.0	122.7	123.6
C2—N3—C4	111.4	110.6	112.7	112.0	N1—C2—O2	118.1	118.9	123.1	123.1
N3—C4—C5	126.7	126.7	129.0	128.7	N3—C2—O2	125.4	121.9	124.0	122.3
C4—C5—C6	115.9	117.0	118.6	118.8	N3—C4—N4(O4)	116.9	120.0	120.1	119.9
C5—C6—N1	118.6	117.6	109.6	111.4	C5—C4—N4(O4)	119.1	120.2	124.9	124.9
C4—C5—N7	111.3	110.6	110.8	110.8	C4—C5—M5			118.1	119.0
C5—N7—C8	104.0	103.9	104.6	104.4	C6—C5—M5			123.9	122.9
N7—C8—N9	113.2	113.8	112.7	113.1		Urea			
C8—N9—C4	106.7	105.8	106.7	106.4		B3LYP	Exp.		
N9—C4—C5	104.5	105.8	104.9	105.4	O2—C1	1.225	1.221		
N3—C4—N9	128.6	127.3	125.9	125.9	C1—N3	1.386	1.378		
C6—C5—N7	132.7	132.5	130.4	130.5	N3—H4	1.010	1.021		
N1—C6—N6(O6)	118.9	118.5	119.0	120.0	N3—H5	1.010	0.998		
C5—C6—N6(O6)	122.4	123.6	131.2	128.7	O2—C1—N3	122.8	122.6		
N3—C2—N2			119.5	119.8	H4—N3—C1	113.6	114.7		
N1—C2—N2			117.0	116.4	H5—N3—C1	118.9	119.1		
					H4—N3—C1—O2	11.8	10.8		
					H5—N3—C1—O2	152.3	156.9		

the free molecule [25]. Florián and Leszczyński [26] have shown that the amino groups of cytosine and guanine bases become more planar when hydrogen bonded in pairs than they are in the isolated molecules.

The optimized geometrical parameters of urea are listed in Table 1, in which the DFT and experimental results [27] were compared. The first gas phase structural study for urea was performed with the microwave spectrum. As reflected in the table, the bond lengths and bond angles are in good agreement with the experimental structure. The structure calculated showed a nonplanar urea moiety, concordant with the possible nonplanar urea structure in the gas phase proposed by Meier [28].

Interaction energy. For each system, several minimum energy structures were found. The interaction energies with the BSSE correction of each of the complexes are reported as ΔE_{CP} in the third column of data in Table 2, under the convention that negative ΔE corresponds to a favorable binding

Table 2

Interaction energies of urea—adenine, urea—thymine, urea—guanine, and urea—cytosine conformers (kJ/mol) *calculated at* B3LYP/6-31+G** *and* MP2/6-31+G** *levels*

Conformer	B3LYP		MP2		Conformer	B3LYP		MP2	
	ΔE	ΔE_{CP}	ΔE^{MP2}	ΔE_{CP}^{MP2}		ΔE	ΔE_{CP}	ΔE^{MP2}	ΔE_{CP}^{MP2}
A1	–21.6	–19.9	–25.9	–17.9	T3	–27.3	–25.7	–33.9	–25.0
A2	–22.1	–20.3	–28.9	–20.6	G1	–77.1	–74.0	–78.7	–65.2
A3	–50.7	–48.1	–54.0	–42.5	G2	–43.4	–41.2	–48.8	–39.5
A4	–47.8	–45.0	–51.2	–39.5	G3	–40.2	–38.4	–46.0	–37.1
A5	–31.8	–29.9	–38.8	–30.3	G4	–47.8	–45.2	–50.1	–38.0
T1	–48.3	–45.6	–53.9	–42.3	C1	–46.8	–43.0	–58.1	–44.8
T2	–50.2	–47.7	–55.2	–43.3	C2	–65.3	–62.5	–68.9	–56.8

energy. Moreover, the BSSE-corrected energy (ΔE_{CP}^{MP2}) calculated using MP2/6-31+G(*d*,*p*) was more improved than the interaction energy at B3LYP/ 6-31+G(*d*,*p*). The ΔE_{CP} and ΔE_{CP}^{MP2} give similar results.

The comparison of the formation energies of the systems shows that the G1 complex, whose formation energy is –74.0 kJ·mol^{-1}, is the most preferred among all the studied complexes. The interaction energy of the structure G1 is somewhat lower than for the pairing energy of the normal Watson-Crick G:C base pair (HB = –104 kJ·mol^{-1}) [29]. It can be deduced that the binding ability of urea is lower than that of C when bound in structure G1. Among the urea:G complexes, G4 is found to have the interaction energy of –45.2 kJ·mol^{-1}, whereas the complex G3 is observed with the smallest interaction energy of –38.4 kJ·mol^{-1}. Notably, the interaction energy order is G1 > G4 > G2 > G3. In the case of urea:C complexes, the stabilization energy of the C2 complex is essentially larger than that of C1. The complex C2 is associated with strong N_{16}…H_6N_1 and $N_{18}H_{19}$…O_5 contacts in nearly the same plane and is by far a more favorable configuration.

As can be seen in Table 2, the interaction energies of the structures A3 and A4 are ~ –45 kJ·mol^{-1}. This is somewhat lower than for the pairing energy of the normal Watson-Crick A:T base pair (HB = = –54 kJ·mol^{-1}) [29]. It can be deduced that the binding ability of urea is near to that of T when bound in the structures A3, A4. However, A1, A2, and A5 are less stable than A3 and A4 owing to the difference between NH…O and CH…O, and the interaction energy order is as follows: A3 > A4 > A5 > A2 > A1. In the case of urea:T, the interaction energy for T2 is found to be high (–47.7 kJ·mol^{-1}) and the next stable complex is T1 with the interaction energy of –45.6 kJ·mol^{-1}. Hence, the stability order is T2 > T1 > T3. Furthermore, the T1 and T2 conformers have similar conformations by O atom hydrogen bonding to NH, and they are more stable than T3 owing to the difference between the NH…O and CH…O contacts.

Geometry of complexes. Urea binds strongly with the DNA bases through the HB interactions. Strong HBs are formed between urea and DNA bases, and the HB lengths are found to be within 2.4 Å. The optimized geometries of all the complexes are almost planar, whereas the geometries of A2, T3, G2, and C1 deviate from planarity. The energetic characteristics of all complexes are given in Table 2. The present results show that the planar structure is energetically favorable over the nonplanar structure. Table 3 lists the equilibrium distances between the proton and the proton acceptor atom, the intrinsically preferred H-bond length. This quality is generally correlated with ΔE, with a stronger H-bond associated with a shorter length.

As the most stable complex, G1 (Fig. 2) shows a configuration with an HB between O_5 and H_9N_{10} with a distance of 1.758 Å and an HB between O_{14} and H_3N_2 with a distance of 1.849 Å, with the HBs in G1 ($N_{10}H_9O_5$ and $O_{14}H_3N_2$ bond angles are 173.5° and 176.2° respectively) being practically linear. It is clear that short strong NH…O HBs contribute to the stability of the complex G1.

Table 3

Optimized geometry parameters of complexes at B3LYP/6-31+G** *level*

Complex	H-bond	Length	Angle	H-bond	Length	Angle
A1	$N_{15}…H_6N_1$	2.074	171.8	$C_{17}H_{20}…O_5$	2.397	145.7
A2	$N_1H_6…N_{19}$	2.072	172.9	$O_5…H_{20}C_{17}$	2.394	147.3
A3	$N_1H_6…N_{19}$	1.996	176.0	$O_5…H_{21}N_{18}$	1.851	178.8
A4	$N_1H_6…N_{13}$	2.008	179.1	$O_5…H_{22}N_{18}$	1.870	166.3
A5	$N_{13}…H_3N_2$	2.085	168.0	$C_{10}H_{12}…O_5$	2.204	143.1
T1	$O_{15}…H_6N_1$	1.910	171.1	$O_5…H_{18}N_{14}$	1.810	172.8
T2	$N_{14}H_{18}…O_5$	1.799	174.5	$O_{22}…H_3N_2$	1.894	171.4
T3	$O_5…H_{20}C_{16}$	2.322	171.6	$N_1H_6…O_{22}$	1.988	173.2
G1	$N_{10}H_9…O_5$	1.758	173.5	$O_{14}…H_3N_2$	1.849	176.2
G2	$N_1H_8…N_{17}$	2.191	175.2	$O_{14}…H_7N_2$	2.069	172.9
G3	$N_1H_6…N_{17}$	2.018	165.9	$O_5…H_{23}C_{21}$	2.248	137.8
G4	$N_1H_6…N_{16}$	2.042	174.5	$N_{15}H_{20}…O_5$	1.822	177.5
C1	$N_{16}…H_8N_1$	2.131	157.7	$N_{18}H_{19}…N_2$	2.080	162.0
C2	$N_{16}…H_6N_1$	1.954	172.2	$N_{18}H_{19}…O_5$	1.813	179.1

In all the observed conformers, the NH…N contacts have a higher occurrence level than the NH…O contacts, with a longer H…N separation ranging between 1.954 Å and 2.191 Å, covering a broader angle range from 157.7° to 179.1°. Although both NH…N and NH…O belong to amino H-bonds, the latter stabilizes the conformer more strongly than the former as the relative bond lengths and bond angles are compared.

A few of CH…O contacts are observed in A1, A2, A5, T3, and G3 conformers. Because of a low occurrence of the CH…O contact involving the O atom of urea and the CH bond of the DNA base, the associated H…O separation markedly lengthens to the range between 2.204 Å and 2.397 Å. Because of the bond length difference, the intermolecular CH…O H-bonds observed in A1, A2, and A5 are less stable and more liable to bend than NH…N ones. Even if individually weak, a small number of such contacts exert an influence upon the configuration of the complex.

As presented in Fig. 2, the HBs are the main factors of the DNA base-urea complexes. Strong HBs form between urea and the DNA bases and the HB lengths are found to be within 2.4 Å. It is also confirmed that the NH…O/N contacts are more stable than the CH…O contact. For the most strongly H-bonded conformers (G1, C2, T2, and A3) the corresponding NH…O and NH…N contacts have preferred H…O/N separations and near-linear H-bond arrangements.

AIM analysis. The atoms in molecules theory (AIM) provides a universally applicable tool for the classification of the bonding interactions that take place in any molecular system, even inside a supermolecule [30]. It is used to analyze the bonding characteristics based on a topological analysis of the electron density (ρ_c) and the Laplacian ($\nabla^2\rho_c$). The ρ_c value is used to describe the bond strength; a stronger bond is associated with a larger ρ_c value. The $\nabla^2\rho_c$ value describes the characteristic of the bond. $\nabla^2\rho_c = \lambda_1 + \lambda_2 + \lambda_3$, where λ_i is eigenvalues of the Hessian matrix of ρ_c. If $\nabla^2\rho_c < 0$, it is named as the covalent bond. If $\nabla^2\rho_c > 0$, it refers to a closed-shell interaction and the characteristic of an ionic bond, hydrogen bond, or Van der Waals interaction. Here we are concerned with the ρ_c and $\nabla^2\rho_c$ values for the O/N…H bonds listed in Table 4. Small and positive values of $\nabla^2\rho_c$ indicate that a small charge concentration takes place along the bond path linking two nuclei. It can be observed that the behavior of $\nabla^2\rho_c$ is parallel to that exhibited by ρ_c.

For all the intermolecular bond critical points (BCPs) we note that the two negative eigenvalues of the Hessian (λ_1, λ_2) have small magnitudes, which reflects the low concentration of the charge density at the BCPs. The computed values of the positive curvature (λ_3) were found to be very small. Ac-

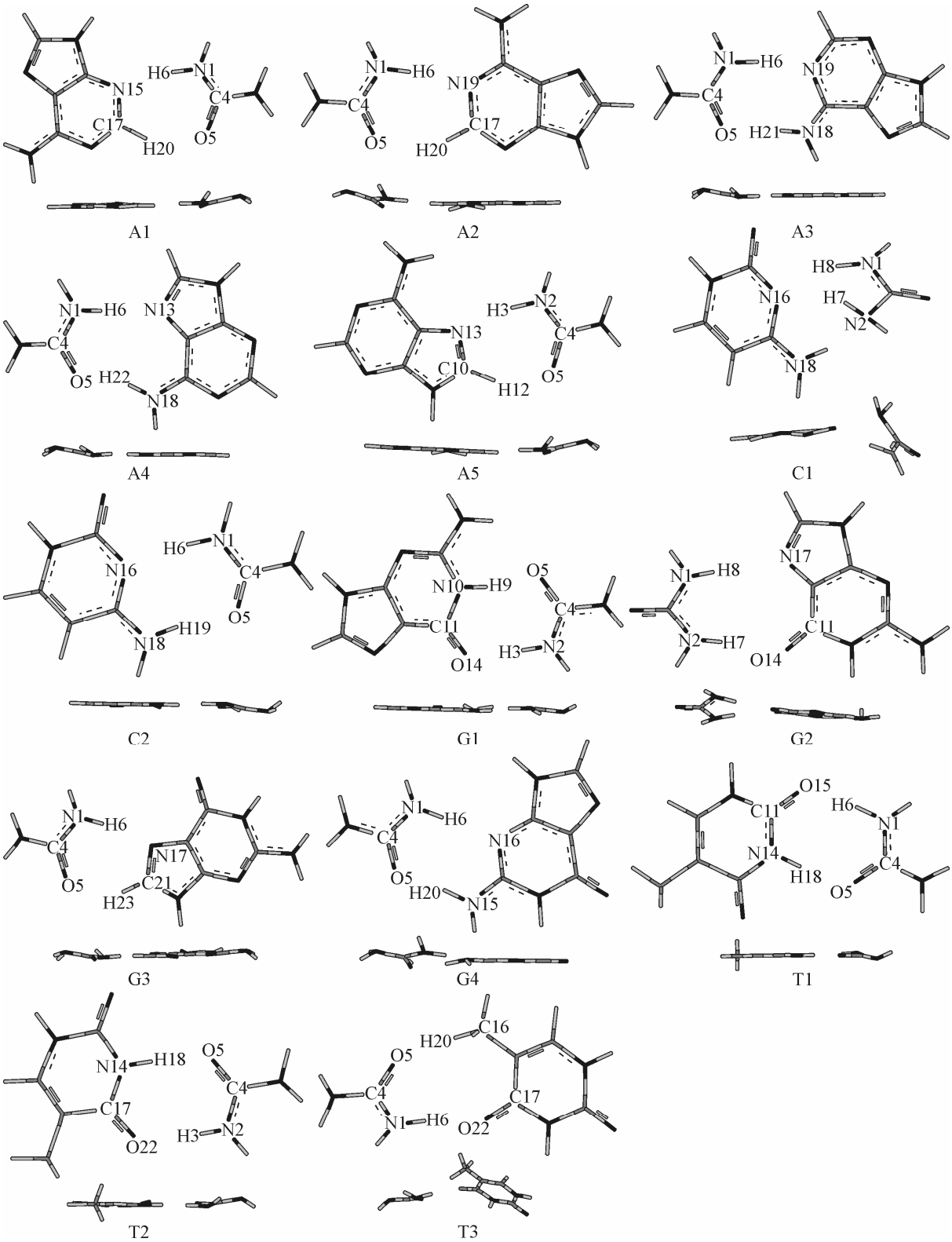

Fig. 2. Optimized conformers (B3LYP/6-31+G**) of the complexes: urea—adenine, urea—thymine, urea—guanine, and urea—cytosine

Table 4

Critical point properties (a.u.) *of the electron density for the complexes*

Conformer	Bond	ρ_c	λ_1	λ_2	λ_3	$\nabla^2\rho_c$
A1	$N_{15}…H_6$	0.0224	–0.0280	–0.0260	0.1115	0.0575
	$O_5…H_{20}$	0.0112	–0.0117	–0.0113	0.0579	0.0349
A2	$N_{19}…H_6$	0.0230	–0.0287	–0.0267	0.1129	0.0574
	$O_5…H_{20}$	0.0113	–0.0118	–0.0114	0.0581	0.0348
A3	$N_{19}…H_6$	0.0276	–0.0365	–0.0341	0.1367	0.0660
	$O_5…H_{21}$	0.0312	–0.0446	–0.0426	0.1777	0.0904
A4	$N_{13}…H_6$	0.0260	–0.0340	–0.0319	0.1314	0.0654
	$O_5…H_{22}$	0.0291	–0.0404	–0.0389	0.1673	0.0880
A5	$N_{13}…H_3$	0.0214	–0.0263	–0.0245	0.1072	0.0563
	$O_5…H_{12}$	0.0163	–0.0182	–0.0178	0.0847	0.0487
T1	$O_{15}…H_6$	0.0269	–0.0366	–0.0350	0.1511	0.0795
	$O_5…H_{18}$	0.0335	–0.0496	–0.0479	0.1962	0.0987
T2	$O_5…H_{18}$	0.0345	–0.0518	–0.0500	0.2032	0.1013
	$O_{22}…H_3$	0.0281	–0.0386	–0.0372	0.1583	0.0825
T3	$O_5…H_{20}$	0.0127	–0.0136	–0.0131	0.0646	0.0378
	$O_{22}…H_6$	0.0211	–0.0269	–0.0254	0.1188	0.0664
G1	$O_5…H_9$	0.0400	–0.0626	–0.0601	0.2375	0.1148
	$O_{14}…H_3$	0.0319	–0.0457	–0.0439	0.1793	0.0896
G2	$N_{17}…H_8$	0.0175	–0.0202	–0.0191	0.0865	0.0471
	$O_{14}…H_7$	0.0187	–0.0228	–0.0221	0.1006	0.0557
G3	$N_{17}…H_6$	0.0247	–0.0321	–0.0300	0.1273	0.0651
	$O_5…H_{23}$	0.0150	–0.0162	–0.0160	0.0783	0.0461
G4	$N_{16}…H_6$	0.0246	–0.0310	–0.0290	0.1206	0.0604
	$O_5…H_{20}$	0.0333	–0.0490	–0.0468	0.1930	0.0972
C1	$N_{16}…H_8$	0.0205	–0.0242	–0.0229	0.1007	0.0535
	$N_2…H_{19}$	0.0234	–0.0286	–0.0280	0.1127	0.0560
C2	$N_{16}…H_6$	0.0295	–0.0404	–0.0377	0.1511	0.0730
	$O_5…H_{19}$	0.0339	–0.0503	–0.0481	0.1971	0.0986

$\nabla^2\rho_c$ is the sum of λ_1, λ_2 and λ_3; λ_i is one of the eigenvalues of the Hessian matrix of the electron density (B3LYP/6-31+G**).

cording to Bader, a small value of this curvature is indicative that it is easy to ″move″ the position of the critical point along the bond path, and therefore the bond and its properties are more affected by the charge in the molecule. Low electron densities ρ_c at the intermolecular BCPs reflect the weak character of these bonds. These values fall in the range from 0.0112 a.u. to 0.0400 a.u. They are less than that of a general single bond (about 0.3 a.u.) calculated by the same method.

Moreover, the values of the charge density at the intermolecular BCPs are found to be parallel to ΔE; the stabilization of the conformer is reflected in increased ρ_c values. As can be seen, for the conformer G1, both ρ_c values of $H_9\cdots O_5$ and H3⋯O14 BCPs are relatively high (0.0400 a.u. and 0.0319 a.u. respectively). But for the conformer A1, the ρ_c values at the $N_{15}\cdots H_6$ and $O_5\cdots H_{20}$ BCPs are relatively low (0.0224 a.u. and 0.0112 a.u. respectively). In agreement with the values of the binding energy at this level of the calculation, the conformer G1 has more stability than the others in this work, while the conformer A1 has the most instability. Further, the correlations have been found be-

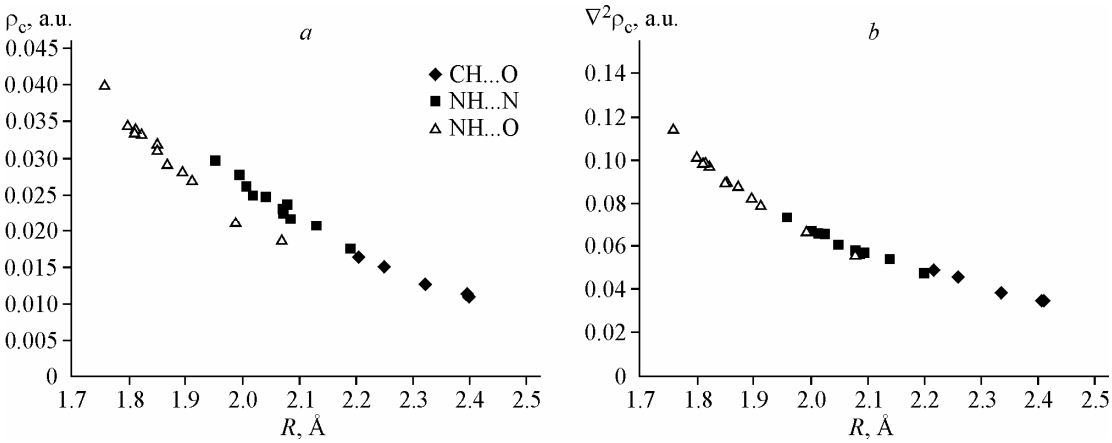

Fig. 3. Correlation between the electron density ρ_c and the hydrogen bond distance, *R* (Å) (*a*), correlation between the Laplacian of the electron density, $\nabla^2\rho_c$ and the hydrogen bond distance, *R* (Å) (*b*) at the BCP calculated at the B3LYP level of theory for the interacting complexes

tween the hydrogen bond distance, electron density and the Laplacian of the electron density of urea complexes; they are shown in Fig. 3. The figures show that the electron density and the Laplacian of the electron density decrease with increasing HB length, and a typically smaller HB length goes together with a stronger HB strength.

CONCLUSIONS

We have investigated the complexes between urea and DNA bases using the DFT method. Five stable conformers were identified on the potential energy surface for the urea:A complex, three for the urea:T complex, four for the urea:G complex, and two for the urea:C complex. It is observed that urea binds strongly with the DNA bases through the hydrogen bond interactions.

Calculations at the B3LYP/6-31+G(*d,p*) level adequately characterize the relative energies of these conformers. The calculated interaction energies for the complexes vary from –19.9 kJ/mol to –74.0 kJ/mol. For each complex series, the most stable conformer contains both NH…O and NH…N contacts above a binding energy of –45 kJ·mol^{-1}. The strong NH…O and NH…N contacts are indicated by a short separation and their near-linear arrangements. A significant values of ρ_c and $\nabla^2\rho_c$ for all the observed H-bonds are positive within the following ranges: 0.0112—0.0400 a.u. for the electron density and 0.0348—0.1148 a.u. for its Laplacian.

In conclusion, we have presented evidence that the DNA base-urea complexes possess different types of intermolecular H-bonds. The stability of all the conformers were in the order urea:G > > urea:C > urea:T ~ urea:A.

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