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REGULAR ARTICLE

# Influence of π-stacking on the N7 and O6 proton affinity of guanine

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**Abstract** The influence of π-stacking interactions between guanine (G) and the side chain of tyrosine (Tyr) on the N7 and O6 proton affinities of guanine and on the capability of these sites to act as hydrogen bond acceptors is analyzed at the B3LYP-D, M05-2X and MP2 levels of theory. With all methods, results from full geometry optimizations indicate that stacking interactions increase the N7 and O6 proton affinities by about 5–6 kcal $mol^{-1}$, the increase being slightly larger for N7. Consistently with these results, hydrogen bond distances between guanine and one water molecule decrease in the stacked system. Moreover, interaction energy between $H_2O$ and (G-Tyr) is found to be 2–3 kcal $mol^{-1}$ larger than in G···$H_2O$. This strengthening arises from the additional Tyr–$H_2O$ stabilizing interactions and from a cooperative interplay between stacking and hydrogen bond forces.

## 1 Introduction

Noncovalent interactions play a fundamental role in many fields of science. In biology, they are responsible for the structure and stability of biological macromolecules such as DNA, RNA or proteins [1]. Moreover, they are involved in many molecular-recognition processes as well as in enzymatic reactions. For instance, the removal of damaged nucleobases from DNA by base excision repair (BER) glycosilases, first, by recognition and base flipping and second, by bond cleavage (hydrolysis) of the *N*-glycosydic bond, involves π–π stacking interactions between the nucleobase and nearby aromatic amino acids [2, 3]. In particular, and related to the mechanism of *N*-glycosidic bond hydrolysis, it has been suggested that π-stacking interactions increase the N7 proton affinity of guanine (G) so that it becomes more readily activated by protonation making guanine a better leaving group, thereby improving the catalysis. In order to understand how these interactions influence the mechanism of this reaction, which has been found to proceed either through a highly dissociated $S_N2$ reaction or through a stepwise $S_N1$ mechanism [2, 3], it is important to analyze the variations of N7 proton affinity by the presence of an aromatic molecule such as tyrosine (Tyr) in gas phase.

In the last decade, many theoretical studies have been devoted to analyze stacking interactions between DNA nucleobases [1, 4–8], with the aim of understanding their role in DNA stabilization. Other studies have considered the interaction of nucleobases and alkylated nucleobases with aromatic amino acids [9–12], since protein–DNA stacking interactions are responsible for substrate recognition of damaged methylated bases in the BER mechanism. In this context, computational studies of Rutledge et al. [11, 12] have determined that stacking interactions between nucleobases and aromatic amino acids are significant and increase upon alkylation of the base. Few studies, however, have analyzed the influence of π-stacking interactions on the hydrogen bonding features of nucleobases [13–16]. The study of Mignon et al. has shown that the hydrogen bonding capacity of cytosine increases when considering intrastrand stacked nucleobases [13]. Moreover, some of us have analyzed the mutual

Dedicated to Professor Santiago Olivella for his 65th birthday.

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relationship between stacking and hydrogen bonding in adenine–uracil and adenine–thymine base pairs [17], results showing that these noncovalent interactions are deeply connected and that the presence of the methyl group in thymine nucleobase plays an important role enhancing dispersive interactions. Despite that, to the best of our knowledge, no studies have been performed on the influence of $\pi$-stacking on the hydrogen bonding ability of guanine or more specifically, on its N7 proton affinity which, as mentioned, has been suggested to enhance the hydrolysis of the *N*-glycosidic bond. Thus, in the present paper the $\pi$–$\pi$ stacking interactions between neutral and protonated guanine, both in the N7 and O6 sites, with the side chain of tyrosine, a residue that has been suggested to participate in face-to-face aromatic contacts in AAG alkyl purine glycosylases, are investigated [2, 3].

## 2 Computational details

A proper description of stacking interactions, mainly governed by dispersion forces, requires levels of theory that include electron correlation and large basis sets, to avoid artificial stabilization produced by basis set superposition error (BSSE). At present, the wave function based coupled-cluster method, with single, double and triple excitations estimated perturbatively, CCSD(T), is the most accurate one for calculating dispersion interactions [1]. However, because CCSD(T) in combination with large basis sets is an extremely computationally demanding approach, an efficient strategy to compute stacking interactions is to combine the energy obtained at the lower level MP2 in the complete basis set limit (CBS), $E^{MP2}_{CBS}$ with a $(E^{CCSD(T)}_{medium} - E^{MP2}_{medium})$ correction computed with a medium basis [1]. Nevertheless, this approach is still not feasible for large systems and, because of that, other more cost effective methods need to be applied. One possibility is to use methods based on density functional theory (DFT) but classical functionals such as the popular B3LYP have been shown not to be appropriate to describe systems where dispersion forces are crucial. A simple solution is to add to the calculated DFT energy an empirical force-field like $C_6/R^6$ correction, damped by a distance dependent damping function to compensate for overlap effects [18–20]. A different approach consists in building up new functionals that account for dispersion interactions such as the meta-hybrid ones recently developed by Truhlar et al. [21–23].

In the present work geometry optimizations and energy calculations were carried out using three different approaches. First, we used the post-Hartree Fock MP2 level of theory. Secondly, we performed calculations with the empirically corrected DFT-D method proposed by Grimme [18], which has been proved to be very effective for a number of cases where dispersive interactions are relevant [24]. The DFT approach used in these calculations is the B3LYP one [25, 26]. Finally, the recent meta-hybrid M05-2X functional [23], with a good performance for noncovalent interactions, particularly, the $\pi$-stacking ones, was also considered.

Geometry optimizations and frequency calculations were performed using the 6-31++G(d,p) basis set. Interaction energies were also obtained from single point energy calculations with the larger 6-311++G(3df,2pd) basis set and, in all cases, were corrected for BSSE, using the counterpoise correction method [27]. Net atomic charges have been obtained using the natural population analysis of Weinhold et al. [28]. Thermodynamic corrections have been obtained assuming an ideal gas, unscaled harmonic vibrational frequencies, and the rigid rotor approximation by standard statistical methods [29]. All calculations were carried out with the Gaussian03 program package [30]. Grimme's dispersion term and gradients have been programmed in an external driver.

## 3 Results and discussion

Face-to-face interactions of nucleobases with nearby aromatic amino acids have been invoked to increase N7 proton affinity of purines. Therefore, the stability of different stacked structures formed between N7 protonated guanine ($H^+_{N7}G$) and the side chain of tyrosine have been explored from full geometry B3LYP-D optimizations [18]. Results show that the preferred configuration has the OH of Tyr lying below the five-member ring of guanine, close to the N7 protonated site. For consistency, this configuration is the one that we have considered as the starting point in the optimization of the remaining G-Tyr and O6 protonated $H^+_{O6}$G-Tyr systems. For G-Tyr this configuration is expected to provide also optimal (most negative) stacking interactions since dipole moment vectors of the monomers are aligned in opposite directions [12].

Since all the considered methods (B3LYP-D, M05-2X, MP2) provide minima energy structures with similar orientations, Fig. 1 shows only the fully optimized structures of G-Tyr, $H^+_{N7}$G-Tyr, $H^+_{O6}$G-Tyr stacked dimers at the B3LYP-D level of theory. Side view images show that the planarity of guanine, except for the exocyclic amino group, is maintained in the stacked dimers, the larger distortions being observed for the protonated systems. On the other hand, a displacement of the Tyr moiety towards the five-member ring of guanine is observed upon protonation of the N7 site. This is accompanied by an out-of-plane rotation of the C–OH bond of Tyr so that the hydroxylic hydrogen moves far apart from the nucleobase. Due to the positive charge of the five-member ring of guanine and the

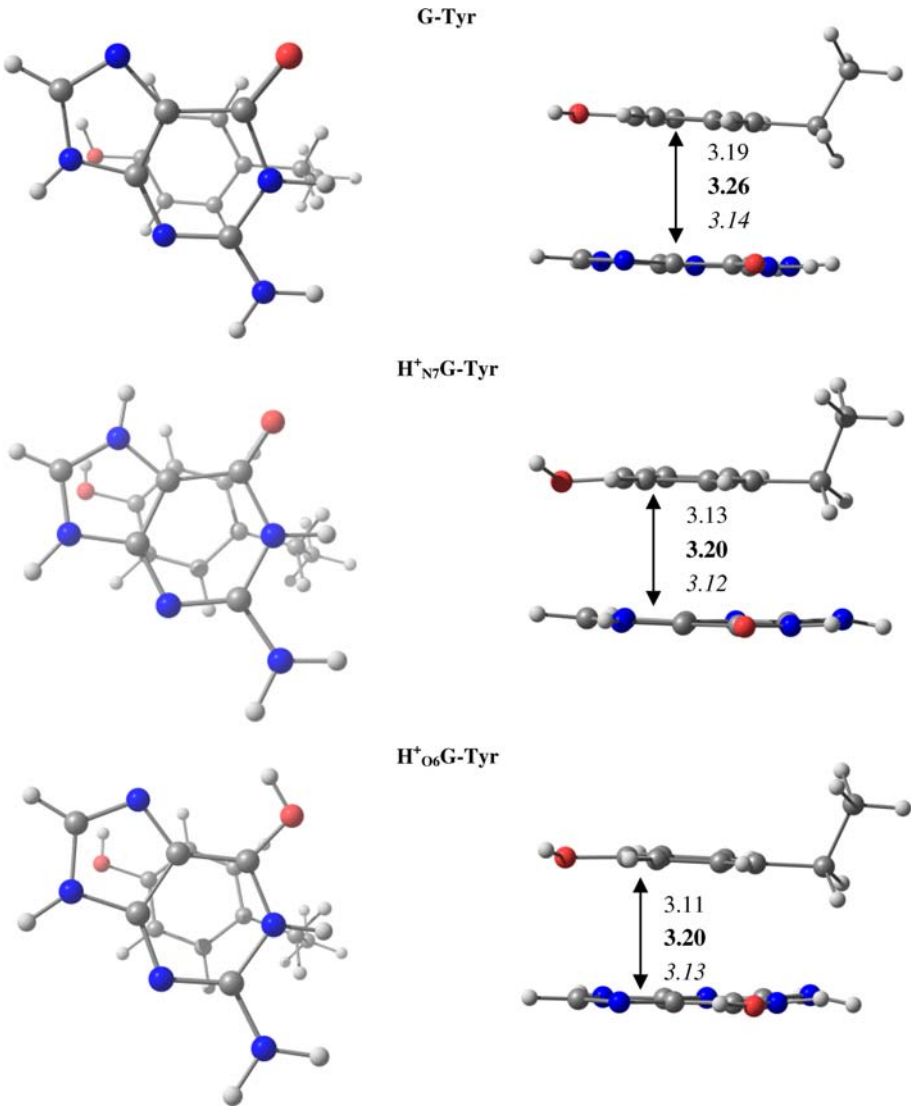



**Fig. 1** Optimized geometries of stacked dimers. Chosen orientation corresponds to the preferred one for $H^+_{N7}$G-Tyr dimer. See text for details. Interplane distances (in Å) at the B3LYP-D, **M05-2X** and *MP2* levels of theory

polarity of the OH bond, this distortion is probably driven by electrostatic forces. Figure 1 also shows the distance ($R$) between the two aromatic moieties computed at the three levels of theory: B3LYP-D, M05-2X and MP2. Once defined, the plane of guanine as xy by three atoms of the six-membered ring, namely, C4, C5 and C6 of guanine, $R$ value corresponds to the average z components of the six carbons atoms of the phenyl group of tyrosine. It can be observed that for the neutral system MP2 is the method that provides a smaller $R$ interplane distance, whereas M05-2X provides the largest values. This would be in agreement with trends already observed in previous studies [1], which indicate that MP2 overestimates dispersion forces, whereas M05-2X appears to slightly underestimate them [21]. Thus, MP2 and M05-2X could be considered an upper and a lower limit, the B3LYP-D value lying just in between. Nevertheless, differences between the considered methods are not too large, the computed values ranging from 3.14 to 3.26 Å for the neutral complexes and from 3.11 to 3.20 Å for the protonated ones. Moreover, all methods provide the same trends, that is, the computed $R$ value decreases upon protonation of the nucleobase.

Table 1 summarizes the interaction energies, $\Delta E$, computed at different levels of theory, as well as the corresponding values after correcting for BSSE with the counterpoise method, $\Delta E^{CP}$. In agreement with the optimized structures, uncorrected interaction energies obtained with the different methods follow the order M05-2X < B3LYP-D < MP2. That is, as found previously MP2 overestimates stacking interactions [1], whereas M05-2X appears to slightly underestimate them [21]. On the other hand, whereas for DFT-based methods the computed counterpoise correction is around 1–2 kcal $mol^{-1}$, for MP2 the correction for BSSE is huge, especially for the smallest 6-31++G(d,p) basis set for which it reaches values of 9–10 kcal $mol^{-1}$. As a result, the MP2 counterpoise

**Table 1** Interaction energies with and without counterpoise correction ($\Delta E^{CP}$, $\Delta E$) for neutral and N7, O6 protonated guanine stacked with the side chain of Tyr (in kcal mol$^{-1}$)

| | G-Tyr | | $G\text{-}H^{+}{}_{N7}G\text{-}Tyr$ | | $G\text{-}H^{+}{}_{O6}G\text{-}Tyr$ | |
|---|---|---|---|---|---|---|
| | $\Delta E$ | $\Delta E^{CP}$ | $\Delta E$ | $\Delta E^{CP}$ | $\Delta E$ | $\Delta E^{CP}$ |
| B3LYP-D/6-31++G(d,p) | −11.0 | −9.2 | −16.9 | −15.1 | −16.4 | −14.2 |
| B3LYP-D/6-311++G(3df,2pd) | −9.7 | −8.5 | −15.7 | −14.3 | −15.4 | −13.7 |
| M05-2X/6-31++G(d,p) | −8.2 | −6.6 | −14.4 | −12.8 | −13.7 | −11.9 |
| M05-2X/6-311++G(3df,2pd) | −7.8 | −6.2 | −14.0 | −12.3 | −13.3 | −11.7 |
| MP2/6-31++G(d,p) | −17.5 | −7.8 | −23.1 | −13.6 | −22.9 | −13.3 |
| MP2/6-311++G(3df,2pd) | −17.1 | −12.1 | −22.5 | −17.6 | −22.4 | −17.5 |

corrected interaction energies with the smallest double zeta basis set are 1–2 kcal mol$^{-1}$ smaller than the corrected B3LYP-D ones. However, with the largest basis set, BSSE is $\approx$5 kcal mol$^{-1}$ and thus, the corrected MP2 values become around 3 kcal mol$^{-1}$ larger than the B3LYP-D ones, in agreement with the already known tendency of MP2 to overestimate stacking interactions [1]. Overall, these results show that interaction energies are very sensitive to the basis sets and methods used. Interestingly, results obtained from spin component scaled MP2 (SCS-MP2), a modification of MP2 in which the total MP2 correlation energy is partitioned into parallel and antiparallel-spin components that are separately scaled [31], with the largest basis set are −12.4, −18.0 and −17.8 kcal mol$^{-1}$, for G-Tyr, $H^{+}{}_{N7}G\text{-}Tyr$ and $H^{+}{}_{O6}G\text{-}Tyr$, respectively, very similar to the corrected MP2 ones. The fact that counterpoise corrected MP2 interaction energies closely resemble the uncorrected SCS-MP2 has been found previously and indicates that the BSSE and the effect of the scaling procedure almost exactly cancel [31].

Nevertheless, all methods provide that face-to-face stabilizing interactions between guanine and tyrosine increase upon protonation (either at N7 or O6) of the nucleobase, this increase being slightly larger when protonation occurs at the N7 site. In this case, the interaction energy increases (becomes more negative) by 5.5–6.2 kcal mol$^{-1}$, depending on the method used. In the case of O6 protonation, the increase lies between 5.2 and 5.7 kcal mol$^{-1}$. These results are in agreement with those found in previous studies for aromatic amino acids interacting with adenine and methylated adenine, which show that stacking interactions are significantly enhanced in the methylated (cationic) system [12]. This is due to the larger electrostatic interaction and charge transfer between the two aromatic moieties in the cationic systems. In these cases, charge transfer occurs from tyrosine to guanine, the computed values being 0.009 and 0.012 au for $H^{+}{}_{N7}G\text{-}Tyr$ and $H^{+}{}_{O6}G\text{-}Tyr$, respectively. The charge transfer is somewhat larger for the O6 protonated system because the LUMO orbital lies lower in energy. For the neutral G-Tyr system, however, the charge transfer is smaller (0.005 au) and occurs in the opposite direction; that is, from guanine to tyrosine.

**Table 2** N7 and O6 proton affinities ($\Delta H_{298\ K}$) in isolated and stacked guanine (in kcal mol$^{-1}$)

| | G | | G-Tyr | |
|---|---|---|---|---|
| | N7 | O6 | N7 | O6 |
| B3LYP-D/6-31++G(d,p) | 230.6 | 224.8 | 236.5 | 230.2 |
| B3LYP-D/6-311++(3df,2pd) | 231.4 | 225.7 | 237.3 | 231.0 |
| M05-2X/6-31++G(d,p) | 227.8 | 223.5 | 234.0 | 228.7 |
| M05-2X/6-311++(3df,2pd) | 227.9 | 223.7 | 234.0 | 228.8 |
| MP2/6-31++G(d,p) | 226.2 | 220.2 | 231.7 | 225.4 |
| MP2/6-311++G(3df,2pd) | 225.3 | 220.4 | 230.7 | 225.7 |

Table 2 shows the proton affinities of the N7 and O6 sites of guanine, either for isolated and stacked guanine. These data show that in both cases, isolated and stacked, N7 is the preferred site for protonation of guanine, the proton affinity at this site being 4–6 kcal mol$^{-1}$ larger than at O6. Stacking interactions increase the proton affinity at both sites since, as shown, they are more stabilizing in the protonated systems (see Table 1). However, because this increase is similar in both sites, stacking effects only slightly enhance the preference for N7 protonation.

Once determined that Tyr stacking interactions increase the proton affinity of N7 and O6 sites, it is important to analyze how this manifests itself in the hydrogen bonding ability of guanine when acting as proton acceptor at these sites, since this is the first step towards protonation. For that, we have compared hydrogen bonded structures of isolated and stacked guanine interacting with one water molecule. Calculations have been carried out at the M05-2X level of theory since this approach has been shown to perform reasonably well both for hydrogen bonding and stacking [21]. Optimized structures are shown in Fig. 2, where it can be observed that for isolated guanine interacting with $H_2O$, the hydrogen bond distance with the *N*-site (2.187 Å) is larger than with the O6 one (2.146 Å).

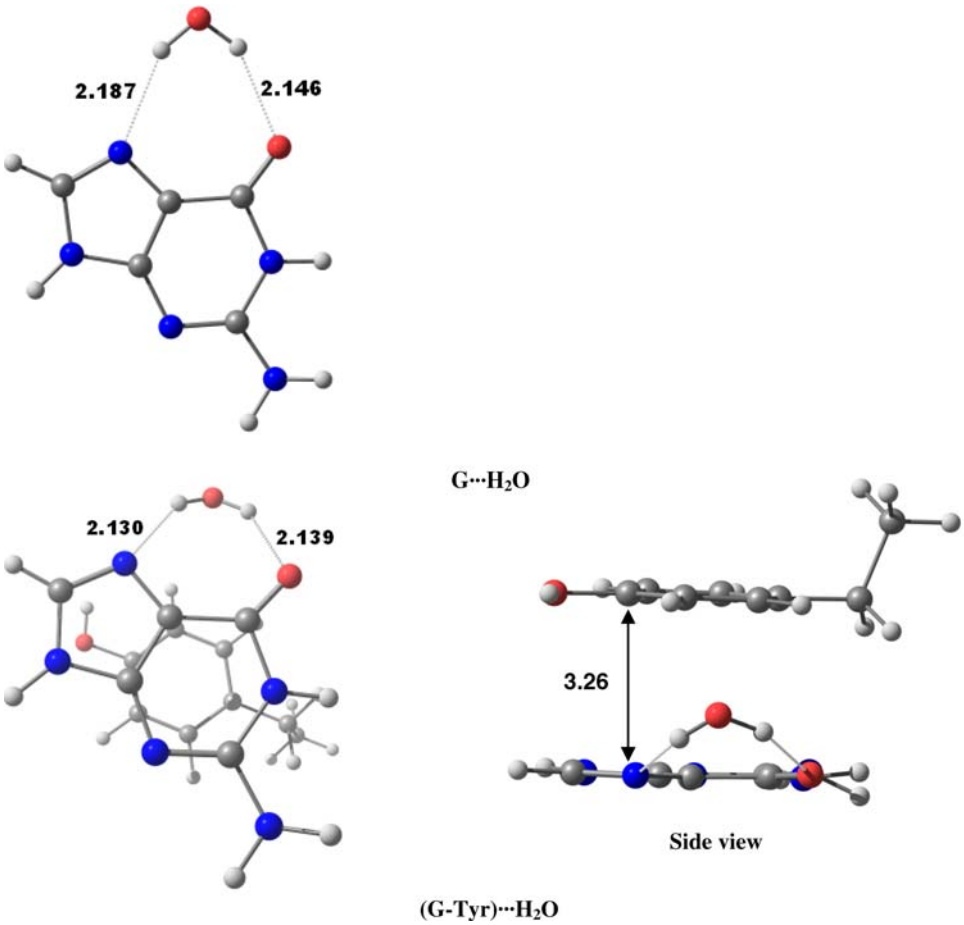
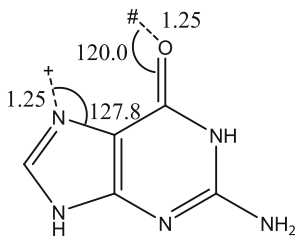



**Fig. 2** Optimized structures for G···$H_2O$ and (G-Tyr)···$H_2O$ at the M05-2X level of theory




| | $N_7(+)$ | $O_6(\#)$ |
|---|---|---|
| Guanine | -0.106081 | -0.106718 |
| Guanine-Tyrosine | -0.106158 | -0.106973 |

**Fig. 3** Molecular electrostatic potential values (in au) in the pointed positions

This was unexpected considering that the proton affinity at the N7 site is larger than that at the O6 one. However, the molecular electrostatic potential (MEP), a reliable descriptor of the hydrogen bond strength [32, 33], computed at 1.25 Å of each basic site [13] (see Fig. 3), is more negative nearby O6 than N7. Thus, present results are consistent with the fact that the more negative the electrostatic potential is, the larger the electrostatic interaction with water molecules, or with hydrogen bond donors in general, is. Nevertheless, it should be mentioned that the optimized G–$H_2O$ structure also results from the best compromise of establishing a simultaneous hydrogen bond interactions with the two sites.

The presence of Tyr decreases the hydrogen bond distances with guanine and moves $H_2O$ water out of the nucleobase's plane. The decrease in H-bond distances is more pronounced for the N7 site than for O6, and is coherent with both the increase of N7 and O6 proton affinities upon interaction with Tyr and with the changes induced on the MEP, which becomes more negative (see Fig. 3). The fact that $H_2O$ moves out of the guanine's plane towards Tyr could be understood considering first, that the vibrational frequency corresponding to the out-of-plane movement of water is very low (25 $cm^{-1}$) and to the appearance of stabilizing electrostatic and dispersive interactions between $H_2O$ and Tyr.

The interaction energies of guanine and Tyr stacked guanine with $H_2O$ are given in Table 3. As expected, considering the already mentioned changes in hydrogen bond distances, the presence of Tyr strengthens the interaction with $H_2O$ by about 2–3 kcal $mol^{-1}$, which represents approximately a 28% increase. This is a significant increase that results both from an additional Tyr–$H_2O$ stabilizing

**Table 3** Interaction energy of $H_2O$ with guanine and with stacked guanine (in kcal $mol^{-1}$) at the M05-2X level of theory

| | 6-31++G(d,p) | | 6-311++G(3df,2pd) | |
|---|---|---|---|---|
| | $\Delta E$ | $\Delta E^{CP}$ [a] | $\Delta E$ | $\Delta E^{CP}$ [a] |
| G···$H_2O$ | −9.9 | −9.2 | −8.9 | −8.7 |
| (G-Tyr)···$H_2O$ | −12.6 | −11.5 | −11.3 | −10.8 |

[a] Counterpoise corrected value

interaction and from a cooperative interplay between stacking and hydrogen bond interactions. Indeed, the stabilizing energy of the trimer ($\Delta E_{G-Tyr-H_2O} = E_{G-Tyr-H_2O} - E_G - E_{Tyr} - E_{H_2O}$), considering the monomers at the geometry of the complex, is −21.5 kcal $mol^{-1}$, more negative than the sum of the pairwise interactions, $\Delta E_{G\text{-}Tyr}$ = −8.5 kcal $mol^{-1}$, $\Delta E_{G-H_2O}$ = −10.0 kcal $mol^{-1}$ and $\Delta E_{Tyr-H_2O}$ = −2.1 kcal $mol^{-1}$, which is −20.6 kcal $mol^{-1}$. Therefore, the three-body term, which accounts for −0.9 kcal $mol^{-1}$, indicates that there is a stabilizing cooperative interaction. These results are in agreement with previous results [13–15] and show the importance of the mutual relationship between stacking and hydrogen bond interactions. Obviously, these gas phase results could be modified by environmental effects such as those of other solvent molecules not taken into account here and that could overwhelm weak stacking interactions.

## 4 Conclusions

The present work analyzes the π-stacking interactions between the side chain of tyrosine and neutral and protonated guanine, since they have been suggested to play an important role in the removal of damaged nucleobases from DNA by BER glycosilases. Particularly, the work analyzes the influence of stacking on the N7 and O6 proton affinities of guanine and on the capacity of these sites to act as hydrogen bond acceptors. The analysis has been carried out by performing full geometry optimizations with three different approaches: (1) B3LYP-D, in which the B3LYP energy is corrected with a damped pairwise dispersion $-C_6/R^6$ term, (2) the hybrid-meta M05-2X functional, and (3) the MP2 post Hartree-Fock method.

All methods provide that stacking interactions increase the N7 and O6 proton affinities by about 5–6 kcal $mol^{-1}$, the increase being slightly larger for N7. Consistently with these results, hydrogen bond distances between guanine and one water molecule are found to decrease in the stacked system. Moreover, interaction energy between $H_2O$ and G-Tyr is found to be 2–3 $kcal^{-1}$ larger than in G···$H_2O$. This strengthening, which amounts to 28%, arises from the additional Tyr–$H_2O$ stabilizing interactions and from a cooperative interplay between stacking and hydrogen bond forces.

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