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Molecular modeling of the selectivity in artificial DNA base pairs

Modelització computacional de la selectivitat en parells de bases d'ADN artificials

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REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

In the context of the Sustainable Development Goals (SDG) included in the 2030 Agenda proposed by the UN, the developed project directly contributes to one of the five major areas (5P) in which the 17 SDG are grouped: People. Specifically, it addresses SDG 3 ("Good Health and Well-being"). The study conducted represent a first approach towards the understanding of the factors that influence the selectivity in the DNA replication process. For such, the study is focused on the stability of different artificial DNA base pairs and compared to Watson-Crick ones. The obtained results can be useful for optimizing the design of new artificial DNA base pairs that can be used as aptamers, acting as molecular sensors or therapeutic agents with significant applications in early disease detection and the creation of new treatments. Moreover, this study provides useful information for the design of new base pairs that could be used in the creation of semi-synthetic organisms capable to produce novel proteins with important diagnostic or therapeutic functions. This initial research could be expanded and complemented with future studies, and its final projection could have a significant impact on society, improving people's health and well-being.

CONTENTS

1. SUMMARY

DNA is the code of life. The idea of being able to modify this essential molecule for life has aroused the interest of many researchers in recent years due to the wide range of possibilities that can be considered. This work can be defined as a first approximation to one of the great challenges we face in addressing this issue, the selectivity in DNA replication, which is directly influenced by the stability of the base pairs incorporated in the double helix of DNA. This work includes a bibliographic review of the different strategies used in the design of artificial DNA base pairs, focusing mainly on their structures and their evolution until reaching selectivity values close to those of natural base pairs. In addition, this work includes a computational study on the predominant non-covalent interactions in these systems (hydrogen bonding and π-π stacking interactions) of a total set of 10 base pairs, including the two Watson-Crick base pairs and eight artificial DNA base pairs, four hydrogen-bonded and four non-hydrogen-bonded. From this study, the level of importance of both interactions in the total stability, as well as the different factors contributing to them, has been demonstrated. On the one hand, it has been demonstrated that hydrogen bonding interactions are predominant in the case of hydrogen-bonded artificial DNA base pairs. In this type of interaction, a significant covalent component has been identified. Additionally, the correlation between charge accumulation in monomers and the strength of hydrogen bonds has been demonstrated. Moreover, it has been demonstrated that for the case of non-hydrogen-bonded artificial DNA base pairs, π-π stacking interactions are predominant, and they are determinant towards the incorporation of such unnatural base pairs in DNA helix. Despite the absence of hydrogen bonds, non-null interactions between bases have also been identified in these base pairs. Furthermore, it has been demonstrated how cross interactions play a significant role in π-π stacking interactions, sometimes becoming more important than stacking between bases in certain systems. Finally, within π-π stacking interactions, an additional interaction, cooperativity, has been identified.

Keywords: DNA base pairs, DNA selectivity, hydrogen bonds, non-covalent interactions, supramolecular chemistry.

2. RESUM

L'ADN és el codi de la vida. La idea de poder modificar aquesta molècula essencial per a la vida ha despertat l'interès de molts investigadors en els darrers anys degut a l'ampli ventall de possibilitats que es poden arribar a plantejar. Aquest treball es pot definir com una primera aproximació a un dels grans reptes als quals ens enfrontem en abordar aquesta qüestió, la selectivitat en la replicació de l'ADN, la qual està directament influenciada per l'estabilitat dels parells de bases incorporats en la doble hèlix de l'ADN. Aquest treball inclou una revisió bibliogràfica de les diferents estratègies utilitzades en el disseny de parells de bases artificials d'ADN, centrant-se sobretot en les seves estructures i la seva evolució fins a arribar a valors de selectivitat propers als dels parells de bases naturals. A més, aquest treball inclou un estudi computacional sobre les interaccions no covalents predominants en aquests sistemes (enllaços per pont d'hidrogen i interaccions d'apilament π-π) d'un conjunt de 10 parells de bases, incloent els dos parells de bases Watson-Crick i vuit parells de bases artificials d'ADN, quatre enllaçats per ponts d'hidrogen i quatre de no enllaçats per ponts d'hidrogen. A partir d'aquest estudi s'ha pogut demostrar el nivell d'importància d'ambdues interaccions per a l'estabilitat total, així com els diferents factors que contribueixen a aquestes. Per una banda, s'ha demostrat que les interaccions per pont d'hidrogen són les predominants en el cas dels parells de bases d'ADN artificial enllaçats per ponts d'hidrogen. En aquest tipus d'interaccions, s'ha identificat una component covalent significativa. A més, s'ha demostrat la correlació entre l'acumulació de càrrega en els monòmers i la força dels enllaços per pont d'hidrogen. D'altra banda, s'ha demostrat com per al cas dels parells de bases artificials d'ADN no enllaçats per ponts d'hidrogen, les interaccions d'apilament π-π són les predominants, i són determinants envers la incorporació d'aquest tipus de parells de bases artificials en l'hèlix d'ADN. Malgrat l'absència d'enllaços per pont d'hidrogen, s'han identificat interaccions no nul·les entre les bases en aquests parells de bases. A més, s'ha demostrat com les interaccions creuades juguen un paper important en les interaccions d'apilament π-π sent de vegades més importants que les d'apilament entre bases en certs sistemes. Finalment, dins les interaccions d'apilament π-π, s'ha identificat una interacció addicional, la cooperativitat.

Paraules clau: parells de bases d'ADN, selectivitat de l'ADN, enllaços d'hidrogen, interaccions no covalents, química supramolecular.

3. INTRODUCTION

3.1. STRUCTURE AND FUNCTION OF DNA

3.1.1. DNA double helix

DNA is formed by two polynucleotide chains composed by four different nucleotide subunits. These nucleotide are formed by the union between a deoxyribose, a single phosphate group and a base that can be either Adenine (A), Thymine (T), Guanine (G) or Cytosine (C). The backbone of the DNA is formed by the union between the sugars and phosphates through covalent phosphodiester bonds. On the other hand, hydrogen bonds between the nitrogenous bases connect the two chains, resulting in all bases being on the inside of the double helix. Generally, a purine is paired with a pyrimidine: A pairs with T through two hydrogen bonds, and G with C through three hydrogen bonds. However, it is important to note that on some occasions wrong pairings can also occur, referred as mismatched base pairs. The two natural base pairs, also known as Watson-Crick base pairs, can be seen in Figure 1. To optimize base-pair packing efficiency, the two strands twist around each other forming the characteristic double helix, making a complete rotation every ten base pairs. The double helix has an antiparallel configuration, where one strand's 5' end (5'phosphate) pairs with the 3' end (3'hydroxyl) of its complementary.[1]

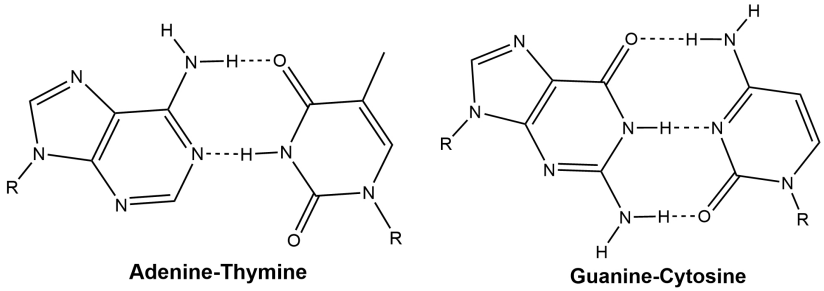


Figure 1: Watson-Crick base pairs A-T and G-C.

3.1.2. Base sequence and genetic code

The sequence of the nucleotides into the DNA stores the genetic information. The four different bases (A, T, G, and C) form the genetic alphabet, which is related to the twenty-letter amino acid alphabet of proteins through codons. Codons are composed of three DNA or RNA nucleotides, and every codon corresponds to an amino acid or termination signal during protein synthesis. Considering that the genetic alphabet is made up of four letters, the full set of codons, known as the genetic code, includes 64 combinations of which 61 corresponds to amino acids, and 3 to termination signals[2] as can be seen in Figure 2.

First base in codon	Second base in codon: T		C		A		G		Third base in codon
T	TTT	Phe	TCT	Ser	TAT	Tyr	TGT	Cys	T
	TTC	Phe	TCC	Ser	TAC	Tyr	TGC	Cys	C
	TTA	Leu	TCA	Ser	TAA	Stop	TGA	Stop	A
	TTG	Leu	TCG	Ser	TAG	Stop	TGG	Trp	G
C	CTT	Leu	CCT	Pro	CAT	His	CGT	Arg	T
	CTC	Leu	CCC	Pro	CAC	Gis	CGC	Arg	C
	CTA	Leu	CCA	Pro	CAA	Gln	CGA	Arg	A
	CTG	Leu	CCG	Pro	CAG	Gln	CGG	Arg	G
A	ATT	Ile	ACT	Thr	AAT	Asn	AGT	Ser	T
	ATC	Ile	ACC	Thr	AAC	Asn	AGC	Ser	C
	ATA	Ile	ACA	Thr	AAA	Lys	AGA	Arg	A
	ATG	Met	ACG	Thr	AAG	Lys	AGG	Arg	G
G	GTT	Val	GCT	Ala	GAT	Asp	GGT	Gly	T
	GTC	Val	GCC	Ala	GAC	Asp	GGC	Gly	A
	GTA	Val	GCA	Ala	GAA	Glu	GGA	Gly	C
	GTG	Val	GCG	Ala	GAG	Glu	GGG	Gly	G

Figure 2: Table with the 64 combinations of three bases in the coding strand of DNA.

3.2. ARTIFICIAL DNA BASE PAIRS

3.2.1. Potential of artificial DNA base pairs

In recent years, numerous artificial DNA base pairs have been developed to expand the genetic alphabet, functioning as an additional base pair in replication, transcription and translation as can be seen in Figure 3. These artificial base pairs are also known as unnatural base pairs (UBPs).[3][4] The potential presented by these UBPs is significant because they increase the structural variety in the DNA and RNA strands that can be synthesized leading to numerous applications.

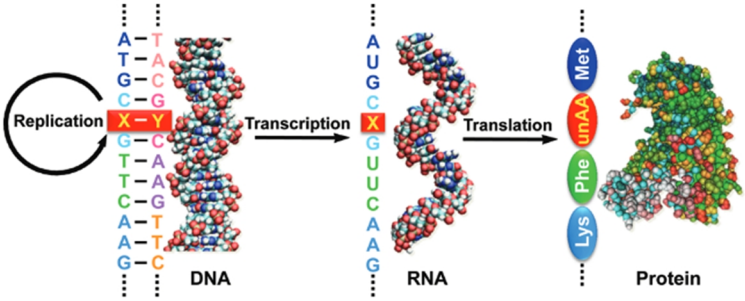


Figure 3: Expansion of the genetic alphabet by an UBP (X-Y). (Extracted from Ref. [3]).

One potential application involves aptamers, which are short strands of DNA or RNA capable of selectively binding to certain targets like proteins or cells, functioning as molecular sensors or as therapeutic agents. Another potential application of UBPs involves the incorporation of non-proteinogenic amino acids into proteins, which can be useful to expand the functional capabilities of proteins. Furthermore, the artificial DNA base pairs have been studied in order to generate semi-synthetic organisms capable of producing novel proteins with potential therapeutic or diagnostic applications.[5] Apart from the possible applications mentioned, it is important to note that researchers are still discovering new uses for the unnatural base pairs in DNA, given that this area of study is relatively recent.

3.2.2. Requirements of artificial DNA base pairs

The UBPs have to be orthogonal to the natural ones and recognized by DNA polymerases, pairing with each other with a fidelity of at least 10^{-3} (one error after 1000 incorporation reactions). In other words, the required selectivity of the unnatural base pairing is 99.9% per replication step. A 99.9% of selectivity means that after 100 cycles of PCR, DNA would retain 90.5% of the unnatural base pairs ($0.999^{100}=0.905$).[5][6]

To take into perspective, the natural bases exhibit a fidelity of 10^{-5}-10^{-6} during natural DNA replication.[6]

4. OBJECTIVES

The present work has two main objectives. The first is to conduct a bibliographic research of various artificial DNA base pairs designed using different strategies with the aim to know the state of the art of this topic. These strategies include altering the hydrogen bonding pattern, increasing the number of hydrogen bonds, or eliminating hydrogen bonding capability altogether. The second objective is to analyze the stability of a set of artificial DNA base pairs using the above strategies with the aim to understand the selectivity of these artificial DNA base pairs compared to Watson-Crick ones. Based on the fact that the selectivity of a DNA base is heavily influenced by its hydrogen bonding patterns, as well as other factors such as stacking forces and solvent effects[7], a computational study will be conducted to characterize the involved noncovalent interactions, focusing on hydrogen bonding and π-π stacking interactions. Solvent effects will be left for further investigation.

5. METHODS

5.1. Bibliographic research

The bibliographic research started with the review articles from 2012 and 2020 by Ichiro Hirao, corresponding to the references 3 and 4 in this work. From these articles, the main strategies used in the synthesis of artificial DNA base pairs, as well as the principal research groups involved, were identified. Additional strategies were identified using the Web of Science database. Once the different strategies were identified, a structural study of the representative base pairs for each strategy was conducted by reviewing articles published by the previously identified research groups. Finally, a selection of 8 artificial DNA base pairs (4 hydrogen-bonded and 4 non-hydrogen-bonded) was made, choosing those with the highest selectivity for the computational study of non-covalent interactions.

5.2. Theoretical methods and computational details

All quantum chemical geometry optimizations and single-point energy calculations reported in the present work were carried out using the Amsterdam Density Functional (ADF) program using dispersion-corrected density functional theory (DFT) at the BLYP-D3(BJ)/TZ2P level of theory with the complete electron model for all atoms (no frozen core) in gas phase. The chosen functional is BLYP-D3(BJ) due to its ability to accurately reproduce structures and hydrogen-bonding energies between the bases, as well as structures and π-π stacking energies between base pairs according to other studies.[8]

The strengths of the hydrogen bonds were determined by calculating the energy difference between the fully optimized monomers and the optimized dimer formed by these monomers,

$$\Delta E = E_{dimer[XY]} - E_{monomer[X]} - E_{monomer[Y]} \qquad \text{Eq.1}$$

Similarly, the stacking energies were determined by calculating the energy difference between the optimized dimers and the stacked system,

$$\Delta E = E_{stacked[XY//XY]} - 2E_{dimer[XY]} \qquad \text{Eq.2}$$

The stacked systems were prepared by separating the base pairs 3.4 Å, which is the average separation in DNA, and rotating them to a twist angle of 36º, which corresponds to the average twist in B-DNA[9] as can be seen in Figure 4. In all the systems studied, the backbone was removed and hydrogen atoms have been inserted in its position, and a Cs symmetry was imposed to mimic the nearly planar arrangement observed in B-DNA.

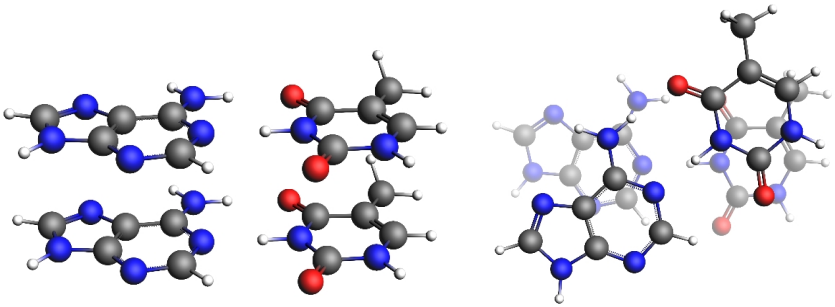


Figure 4: Representation of stacked system preparation by separating the base pairs 3.4 Å (left) followed by a 36º rotation (right).

To gain a deeper understanding of the significance of the ΔE values obtained, an Energy Decomposition Analysis (EDA) was performed for the ΔE associated with the hydrogen bonds, as well as for the interactions due to π-stacking and the parameters contributing to this interaction (base-base stacking and cross interactions). In all cases, the overall bond energy ΔE is composed of two principal components,

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \qquad \text{Eq.3}$$

In the context of hydrogen bond studies, the preparation energy ΔE_{prep} corresponds to the energy needed to modify the individual bases from their equilibrium shape to the configuration they adopt when forming the base pair. When studying the π-stacking interactions and the parameters contributing to this interaction, this term is equal to 0, as the equilibrium geometry of the dimers is used for the preparation of the systems. The interaction energy ΔE_{int} is the actual energy change when the prepared bases or dimers are combined forming the base pair or the stacked system. This interaction energy is divided into four components,

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} + \Delta E_{disp} \qquad \text{Eq.4}$$

The ΔV_{elstat} refers to the classical electrostatic interaction. The Pauli repulsion ΔE_{Pauli} refers to the destabilizing interaction between occupied orbitals that causes the steric repulsion. The orbital interaction ΔE_{oi} includes charge transfer (donor-acceptor interactions between occupied and unoccupied orbitals; in the hydrogen bond context this interaction is between σ-lone pair orbital of the hydrogen bond acceptor with the σ* empty orbital of the hydrogen bond donor as seen in Figure 5) and polarization (redistribution of electron density in one fragment caused by the presence of the other fragment). It must be said that hydrogen bonds are not exclusively electrostatic, but they also exhibit a relevant degree of covalent character. The orbital interaction is divided in two components in planar systems,

$$\Delta E_{oi} = \Delta E_{\sigma} + \Delta E_{\pi} \qquad \text{Eq.5}$$

In the context of hydrogen bond studies the σ component contributes the most, as the sigma orbitals are the ones more involved in charge transfer, i.e., donor-acceptor interaction. Meanwhile, the π component accounts for the polarization in the π system. Finally, the ΔE_{disp} is included to consider the corrections for dispersion (attractive interaction between temporary dipoles).[10][11][12][13]

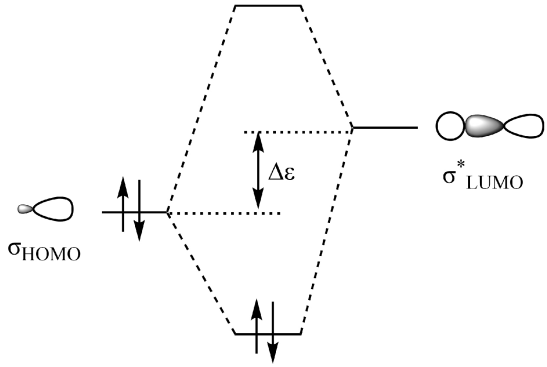


Figure 5: Donor-acceptor interaction between σ-lone pair orbital (HOMO) of the hydrogen bond acceptor with the σ* empty orbital (LUMO) of the hydrogen bond donor. Δε represents the HOMO-LUMO energy gap. (Adapted from ref. [11]).

6. RESULTS AND DISCUSSION

6.1. Compilation of artificial DNA base pairs

6.1.1. Hydrogen-bonded artificial DNA base pairs

The first unnatural base pair (UBP) was proposed in 1962 by Alexander Rich. This corresponds to the constitutional isomers of the natural bases G and C, isoG-isoC, and presents a different hydrogen bond pattern from those of the natural base pairs[14] as can be seen in Figure 6. After a few years, the research group led by Steve Benner reported for the first time in history how a DNA and a RNA polymerase incorporated an UBP, the isoG-isoC base pair, into a growing oligonucleotide.[15] However, this UBP had some problems. On the one hand, despite being the keto isomer the most usual for the isoG base, the enol form also exist in appreciable concentration (10:1 in favor of keto form) and can pair with T as can be seen in Figure 6. The enol form is present in an appreciable concentration because it reinstates the formal aromaticity of the imidazole ring.[16] On the other hand, the incorporation efficiency of isoC is lower than for the natural base pairs, due to the absence of the keto group at position 2 which is crucial for interactions with DNA and RNA polymerases during the replication process. Furthermore, the isoC base is susceptible to decompose under neutral and basic conditions.[4]

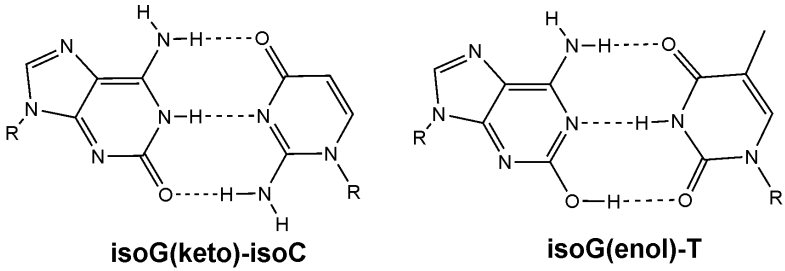


Figure 6: Chemical structures of isoG(keto)-isoC UBP (left) and isoG(enol)-T mispairing (right).

To solve this problems, Benner's group developed a new UBP, the P-Z pair, which is the most important UBP designed by this research group and can be seen in Figure 7. On the one hand, they designed the base P by removing the hydrogen at position 1 of isoG to avoid keto-enol tautomerism, and swapping the keto and amino groups to positions 6 and 2, respectively. Also, N7 shifted to position 5. On the other hand, they designed the base Z from the isoC base in order

to pair with P. This base presents a keto group at position 2 to interact with the DNA polymerase during the replication process and a nitro group at position 5 increasing the stability of the base against oxidation.[17] In order to interact through three hydrogen bonds with P, the keto and amino groups swapped to positions 2 and 4, respectively, and a hydrogen was introduced to N3. Also, N1 was removed. With this optimized UBP, the research group achieved a selectivity for the P-Z pair of 99.8% in PCR under specific conditions.[18] Following the same strategy, they also designed the X-K UBP that can be seen in Figure 7. Analyzing the structure, the difference between this base pair and the mentioned above is that the purine incorporates the two keto groups at positions 6 and 2 while the pyrimidine incorporates the two amino groups at positions 2 and 4.

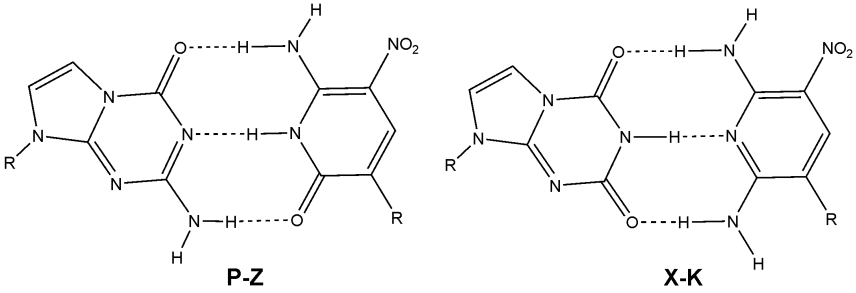


Figure 7: Chemical structures of P-Z (left) and X-K (right) UBPs.

Another research team led by Akira Matsuda developed other hydrogen-bonded UBPs but with four hydrogen bonds. Following this strategy, they designed the first two UBPs with four hydrogen bonds able to be recognized by DNA polymerase: ImN^{O}-NaO^{N} and ImO^{N}-NaN^{O}[19] that can be seen in Figure 8. Analyzing the structures of these base pairs, two notable differences can be observed in comparison to the base pairs mentioned above. Firstly, these UBPs present an expanded hydrogen-bonding pattern. Secondly, they present an expanded aromatic surface. The main problem presented by this kind of UBPs is the low incorporation efficiencies. After some optimizations, the most important UBP designed by Matsuda's team is the ImN^{N}-NaO^{O} base pair that can be seen in Figure 8. This UBP achieved a selectivity of 99.5% per cycle in PCR, which remains low compared to other UBPs designed using different strategies.[20]

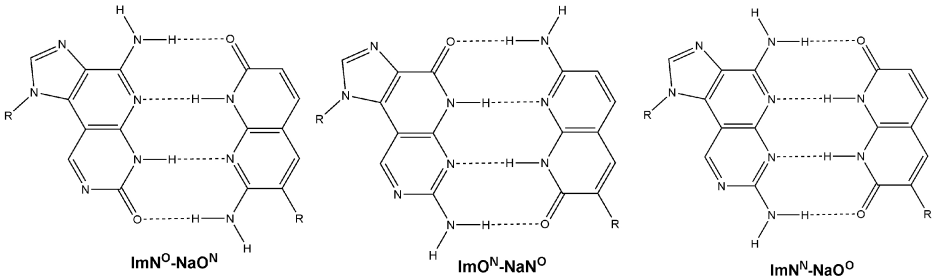


Figure 8: Chemical structures of ImN^{O}-NaO^{N} (left), ImO^{N}-NaN^{O} (center) and ImN^{N}-NaO^{O} (right) UBPs.

The main difference between ImN^{N}-NaO^{O} over the other two base pairs, is the hydrogen bond pattern. While the other two have an alternating H-bond pattern, this one has a [DAAD:ADDA] pattern (D and A refer to donor and acceptor, repectively) avoiding mispairings with natural bases and also increasing the stability of DNA duplex. The increased stability will be discussed in deep detail in a later section, but it can be partially explained by the secondary interactions. The first two bases have six repulsive secondary interactions while ImN^{N}-NaO^{O} has four repulsive and two attractive secondary interactions[21] as can be seen in Figure 9.

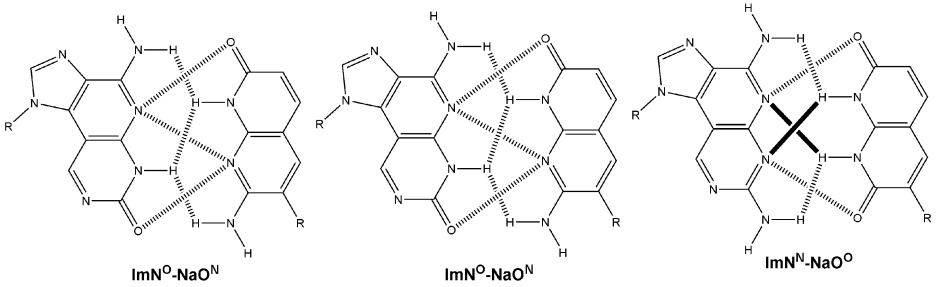
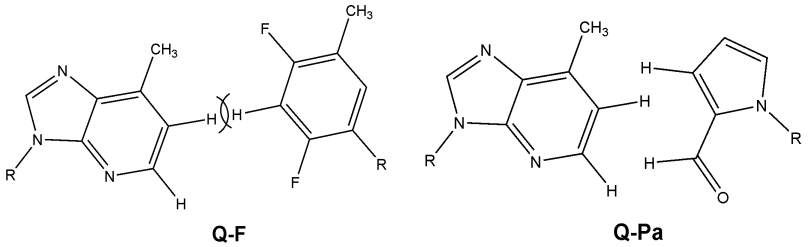


Figure 9: Representation of the secondary interactions present in ImN^{O}-NaO^{N} (left), ImO^{N}-NaN^{O} (center) and ImN^{N}-NaO^{O} (right) UBPs. The dotted lines correspond to repulsive secondary interactions and the bold lines represent the attractive secondary interactions. (Adapted from Ref. [21]).

6.1.2. Non-hydrogen-bonded artificial DNA base pairs

Aside from hydrogen bond interactions, other research teams such as the one led by Ichiro Hirao and the one led by Floyd Romesberg have focused on creating UBPs that pair through hydrophobic and packing forces.

The first non-hydrogen-bonded UBP that drove the development of these types of UBPs was proposed by Eric Kool and his research team, the Q-F pair that can be seen in Figure 10. This base pair, however, has two mainly drawbacks. On the one hand, it has a very low selectivity because it is an isostere of the natural base pair A-T causing mispairings, especially between A and F, and also due to the proton clash between Q-F.[22] It is important to note that the mispairing of Q-T is not very favored due to the H3 protons clash. On the other hand, the F base is not recognized by DNA polymerases due to the lack of a keto group at position 2. To avoid these problems, Hirao's team designed the base Pa in order to pair with Q that can be seen in Figure 10. This base is formed by a five membered ring avoiding the unwanted clash with Q and reducing the mispairing with A. It also incorporates an aldehyde group to interact with DNA polymerases.[22]



Q-F **Q-Pa**

Figure 10: Chemical structures of Q-F (left) and Q-Pa (right) UBPs.

They find out that Pa can be paired with s, which is another base designed by the same team. The resulting UBP can be seen in Figure 11. Despite having a greater steric hindrance due to the thienyl group at position 6, the base s continues to be susceptible to mispair with natural bases. In order to reduce the possible mispairings, they designed the Ds base by replacing the methyl group of the Q base with a thienyl group or, from another point of view, removing the hydrogen-bond residues from the s base. The resulting UBP that can be seen in Figure 11 has one problem left, the Ds-Ds mispairing.[3]

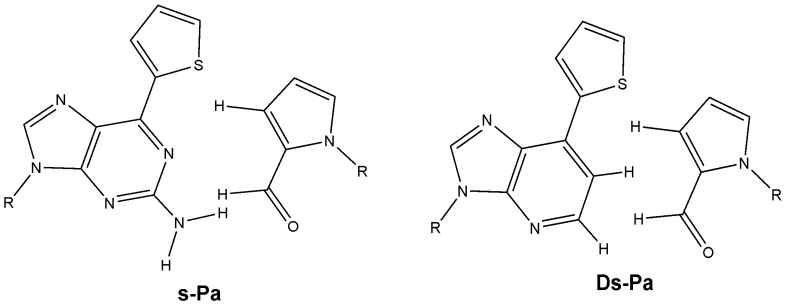


Figure 11: Chemical structures of s-Pa (left) and Ds-Pa (right) UBPs.

Finally, the team designed the Px base in order to pair with Ds. The resultant base pair is the most important UBP designed by Hirao's team and can be seen in Figure 12. Under specific conditions, this UBP achieved a selectivity of 99.9% per cycle in PCR. An interesting feature of this UBP is that the Px base can incorporate different functional groups, and some can reduce the misincorporation rates. Studies have proved how the best combination is Ds with diol-Px achieving a mispairing error close to the natural bases.[23] Analyzing the structure of the Ds base, positions 1 and 2 are occupied by hydrogens to improve the shape complementarity with Px. The position 3 is occupied by a nitrogen in order to interact with the DNA polymerase during the replication process. The position 6 is occupied by a highly planar thienyl group that provides the steric hindrance necessary to avoid mispairing with natural bases, but allow the pairing with five-membered ring bases. It is worth mentioning that in addition to this steric hindrance, the sulfur atom of the thienyl group electrostatically clashes with the 4-keto group of T avoiding especially the Ds-T mispairing. Analyzing now the structure of Px, one of the most notable differences from the bases previously studied is that it has a ring of five members (pyrrole) with the aim to improve the shape complementarity and avoid proton clashing with Ds base. The position 2 is occupied by a nitro group, one of the oxygens interacts with the DNA polymerase, and the other one electrostatically clashes with the 1-nitrogen of A avoiding the A-Px mispairing. On the other hand, the position 3 is occupied by a propynyl group that increases the hydrophobicity and improves the interaction with polymerases and the stacking with neighboring bases, thus improving the incorporation efficiency and avoiding the Ds-Ds mispairing.[3][24]

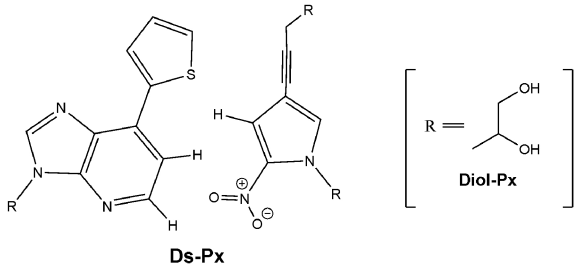


Figure 12: Chemical structure of Ds-Px UBP The functional group enclosed in square brackets represents the functional group that can be attached to the R position in the Px base, reducing misincorporations more effectively.

Romesberg's team studied many pairs of artificial bases focusing at first on self-pairing. Of their first generation of UBPs, the PICS-PICS pair that can be seen in Figure 13, stands out. It presents a high surface area that facilitates its incorporation, but the main problem is that it does not pair edge to edge, which hinders its extension. At this point, the team decided to look for smaller analogs that would not be prone to intercalate, improving the incorporation and extension process, and one of the most promising second generation base pairs they found was MMO2-5SICS that can be seen in Figure 13, althought it still presents low efficiency in replication and transcription.[25]

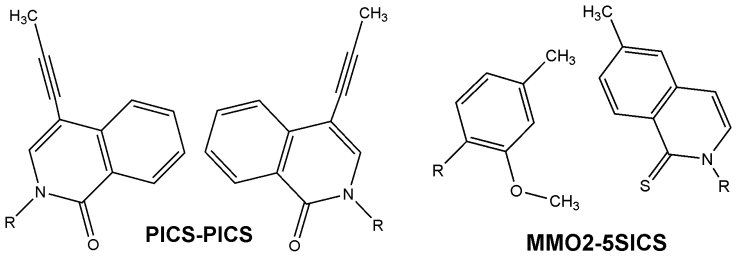


Figure 13: Chemical structure of PICS-PICS (left) and MMO2-5SICS (right) UBPs.

After studying a large number of UBPs and following numerous structural modifications, the most important UBPs in vitro designed by Romesberg team are the NaM-5SICS and NaM-TPT3 pairs that can be seen in Figure 14. It is important to clarify that the two bases mentioned are the two with greater selectivity in vitro, since for studies carried out in vivo other base pairs present

higher retention.[26] Knowing that, under standard conditions the UBP NaM-5SICS achieved a selectivity of 99.9% per cycle in PCR demonstrating that this pair is functionally equivalent to a natural base pair.[27] On the other hand, also under standard PCR conditions, the UBP NaM-TPT3 achieved a selectivity of 99.98% per cycle.[28] Analyzing the structures of the two UBPs, an interesting aspect are the substituents at the position ortho to the glycosidic linkage. In the case of the NaM base, the ortho position to the glycosidic linkage is occupied by a methoxy group that is formed by a hydrophobic methyl group and an oxygen that can interact with polymerases as a hydrogen-bond acceptor. In the case of 5SICS and TPT3 bases, the position is occupied by a sulfur atom which is softer and more polarizable than an oxygen atom, making it more hydrophobic but capable of accepting a hydrogen bond. These specific properties of the ortho substituents are key to an efficient replication. Instead, meta and para positions to the glycosidic linkage are suitable for derivatizations in order to improve replication. Analyzing again the structure of NaM, the meta and para positions are used to form a ring fusion increasing the aromatic surface and favoring local electrostatic and dispersive interactions. Analyzing the structure of 5SICS, the meta and para positions are also forming a ring fusion for the same reason and in addition, a methyl group is added in order to prevent the 5SICS-5SICS mispairing. Finally, analyzing the structure of TPT3, instead of a toluene ring as in 5SICS, the meta and para positions are occupied forming a thienyl ring increasing replication selectivity.[28][29][30]

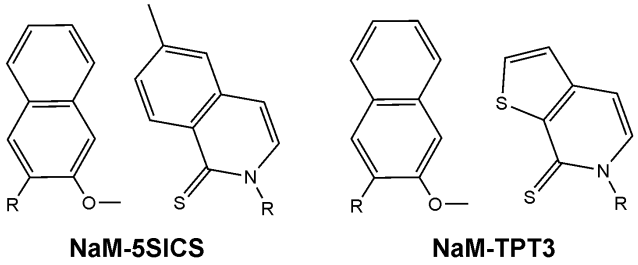


Figure 14: Chemical structure of NaM-5SICS (left) and NaM-TPT3 (right) UBPs.

6.1.3. Metal-mediated artificial DNA base pairs

Another interesting strategy used for the development of UBPs is the substitution of the hydrogen bonds by coordinative bonds. This strategy has been used to develop metal-mediated base pairs with the natural and artificial bases. The main advantage of these base pairs is the wide variety of metal ions with different chemical and physical properties that can be incorporated.

Another important advantage over the other UBPs mentioned above, is the increased stability of DNA because the metal coordination energies are usually two or three times higher than those of hydrogen bonding.[31][32] To ensure compatibility between the bases it is essential that they are arranged in a coplanar manner, and this can be achieved with a linear or square-planar coordination geometry with respect to the metal ion. To date, only 3 base pairs with a linear coordination geometry with respect to the metal ion able to incorporate into DNA have been reported: ^{3}Py-^{3}Py, Imi-Ag-Imi and Tri-Ag-Tri[31] that can be seen in Figure 15.

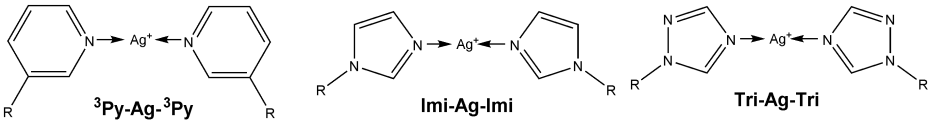


Figure 15: Chemical structure of ^{3}Py-Ag-^{3}Py (left), Imi-Ag-Imi (center) and Tri-Ag-Tri (right) UBPs.

On the other hand, many more base pairs with a square-planar coordination geometry able to incorporate into DNA have been designed. Three that cause a significant increase in DNA melting temperatures (Tm) and therefore cause a greater stabilization of DNA are: ^{5Me}Bpy-Cu-^{5Me}Bpy, H-Cu-H and S-Cu(en)-S that can be seen in Figure 16. Of these three, S-Cu(en)-S is the one with the highest increase of Tm attributed to the formation of a covalent bridge facilitated by ethylenediamine. In addition, it is completely orthogonal to the natural base pairs and can be replicated and amplified by PCR.[31]

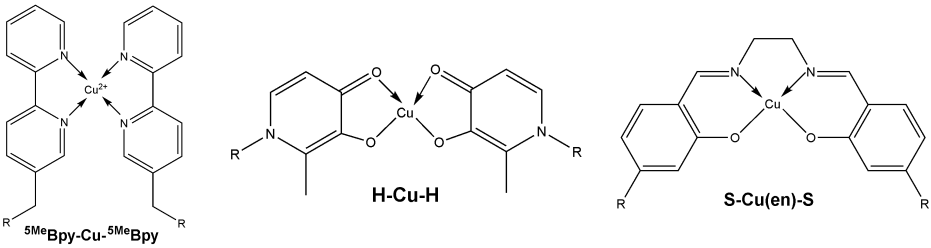
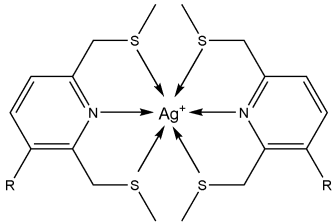


Figure 16: Chemical structure of ^{5Me}Bpy-Cu-^{5Me}Bpy (left), H-Cu-H (center) and S-Cu(en)-S (right) UBPs.

Only one metal-mediated UBP with a coordination number larger than four has been incorporated into DNA to date: Dit-Ag-Dit which can be seen in Figure 17. This has to do with the importance of mimicking the size and shape of canonical base pairs in order to maintain the structure integrity.



Dit-Ag-Dit

Figure 17: Chemical structure of Dit-Ag-Dit UBP.

In general terms, these types of UBPs present different properties to the UBPs previously studied and therefore different applications. The most important today is its use as metal-ion sensors[31].

6.2. Selection of the artificial DNA base pairs to study

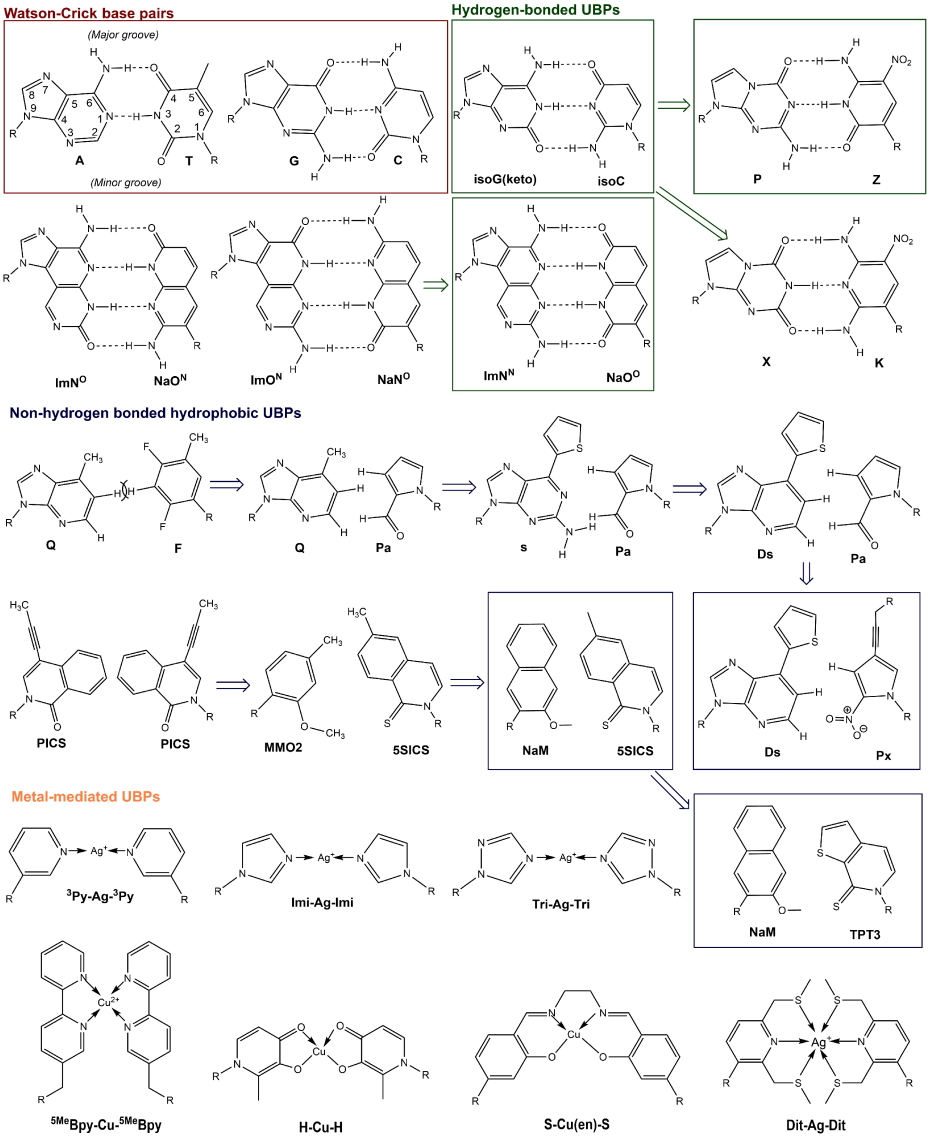


Figure 18: Chemical structures of Watson-Crick base pairs and the unnatural base pairs discussed in this work classified according to their interactions in: hydrogen-bonded, non-hydrogen-bonded and metal-mediated UBPs. The highlighted structures are the most significant bases from each research group, exhibiting a higher selectivity, and are the ones selected for the computational study of the non-covalent interactions.

6.3. Hydrogen bonds in natural and artificial DNA base pairs

W-C base pairs	ΔE	ΔE_{prep}	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}	ΔE_{σ}	ΔE_{π}	ΔE_{disp}
A-T	-16.5	1.8	-18.3	-31.0	38.0	-20.1	-18.6	-1.5	-5.3
G-C	-30.3	3.4	-33.7	-46.6	49.4	-30.3	-26.0	-4.3	-6.2
Hydrogen-bonded UBPs	**ΔE**	**ΔE_{prep}**	**ΔE_{int}**	**ΔV_{elstat}**	**ΔE_{Pauli}**	**ΔE_{oi}**	**ΔE_{σ}**	**ΔE_{π}**	**ΔE_{disp}**
isoG-isoC	-35.0	5.2	-40.2	-55.1	59.2	-37.9	-32.3	-5.5	-6.4
P-Z	-29.9	3.1	-33.0	-44.8	46.5	-28.4	-24.6	-3.9	-6.3
ImO^{N}-NaN^{O}	-29.4	2.8	-32.2	-52.7	62.2	-32.5	-29.4	-3.1	-9.0
ImN^{N}-NaO^{O}	-38.1	4.6	-42.7	-63.8	73.9	-43.4	-38.4	-5.0	-9.4
Non-hydrogen bonded UBPs	**ΔE**	**ΔE_{prep}**	**ΔE_{int}**	**ΔV_{elstat}**	**ΔE_{Pauli}**	**ΔE_{oi}**	**ΔE_{σ}**	**ΔE_{π}**	**ΔE_{disp}**
Ds-Pa	-1.9	0.0	-1.9	-0.7	3.3	-1.3	-1.3	-0.1	-3.2
Ds-Px (R=H)	-3.9	0.1	-4.0	-1.9	6.3	-2.2	-2.0	-0.2	-6.1
NaM-5SICS	-3.8	0.1	-3.9	-2.3	5.4	-2.1	-1.9	-0.2	-4.9
NaM-TPT3	-4.4	0.1	-4.5	-2.7	5.6	-2.1	-1.8	-0.3	-5.3

Table 1: Energy Decomposition Analysis (EDA) of the hydrogen bond energies ΔE (kcal mol^{-1}) obtained for W-C base pairs and the hydrogen-bonded UBPs, and of the total bonding energy ΔE (kcal mol^{-1}) obtained for the non-hydrogen-bonded UBPs.

In this second section, a quantum chemical analysis has been performed on the set of natural and unnatural base pairs selected in the previous section. The first step has been to compute the hydrogen bond energies of this set at the BLYP-D3(BJ)/TZ2P level of theory. First, by analyzing the results obtained for natural base pairs, it is observed that the stability of the G-C pair is almost double that of the A-T pair (ΔE = -16.5 and -30.3 kcal/mol for AT and GC, respectively). The G-C pair presents three hydrogen bonds while the A-T pair presents two, so an increase in the stability of G-C was expected. However, the number of hydrogen bonds in the G-C pair does not double compared to A-T. The increased stability of the G-C pair can be partly explained by the SEI model, which considers secondary electrostatic interactions. In this case, the A-T pair exhibits two

repulsive secondary interactions, whereas the G-C pair displays four secondary interactions, two repulsive and two attractive. Recent studies[10] suggest that this model is often predictive because it provides a measure of favorable charge accumulation in the monomers. When hydrogen bond donors and acceptors are grouped there is a stronger charge accumulation around the frontier atoms, resulting in a more favorable electrostatic interaction and an enhanced sigma orbital interaction. As observed in Figure 19, the G-C base pair exhibits a higher accumulation of charge in its monomers, resulting in a stronger electrostatic interaction (ΔV_{elstat}), as well as a stronger orbital interaction (ΔE_{oi}), as supported by the enclosed EDA data. The increase in the strength of the electrostatic interaction may be intuitive, as it directly depends on the accumulation of charge according to Coulomb's law (ΔV_{elstat} = -31.0 and -46.6 kcal/mol for AT and GC). On the other hand, the increase in the orbital interaction (ΔE_{oi} = -20.1 and -30.3 kcal/mol for AT and GC), primarily determined by the σ component, is due to a larger accumulation of negative charge destabilizing occupied orbitals (σ_{HOMO} becomes better electron donor), while a larger accumulation of positive charge stabilizes unoccupied orbitals (σ^*_{LUMO} becomes better electron acceptor).[33] In other words, it decreases the HOMO-LUMO energy gap ($\Delta\varepsilon$), facilitating the charge transfer. This phenomenon is depicted in Figure 20. It is worth mentioning that not only the HOMOs and LUMOs orbitals of the σ-system are involved in this interaction; for an accurate description other high-energy occupied and low-energy unoccupied orbitals must be considered.[11] In both cases, the π component, which accounts for polarization, has a small contribution to the overall orbital interaction energy. Similarly, the dispersion component contributes minimally to the overall interaction energy. The Pauli repulsion component exhibits a positive and greater value than any of the other interaction energy components in both cases (ΔE_{Pauli} = 38.0 and 49.4 kcal/mol for AT and GC), however its repulsive nature is compensated by attractive electrostatic and orbital interaction terms, thus giving rise to an attractive interaction. Finally, the preparation energies have a low positive value, as expected, that make that total bonding energies are determined by the interaction ones discussed above through the EDA.

It is noteworthy that these trends for both natural GC and AT hold true for the other bases with hydrogen bonds studied.

The results for the hydrogen-bonded UBPs are examined next. Firstly, the isoG-isoC pair, a constitutional isomer of the natural base pair G-C, is considered. According to the obtained results, this base pair exhibits stronger hydrogen bonding compared to the G-C base pair (ΔE = -35.0 kcal/mol). This increase in stability is attributed to a slight increase in charge

accumulation on the frontier atoms involved in the hydrogen bonds, resulting in enhanced electrostatic and orbital interactions for the same reasons explained above. The two primary concerns associated with this base pair are the possibility of tautomeric equilibrium, where the enol form can mispair with Thymine, and the absence of a keto group in the isoC base at position 2 to interact with the DNA polymerase, reducing its selectivity as detailed in section 6.1.1. Analyzing now the results for the P-Z base pair, which addresses these two concerns, it is observed that it exhibits a hydrogen bonding energy very similar to that obtained for the G-C pair (ΔE = -29.9 kcal/mol). Examining the different components obtained from the EDA analysis, all components are very similar to those of the G-C pair. This make sense as the charge distribution analysis of both base pairs reveals a similar accumulation of both positive and negative charges on the frontier atoms involved in the hydrogen bonds as observed in Figure 19. With this base pair a high selectivity is achieved, as mentioned in section 6.1.1.

Examining the results for the ImO^{N}-NaN^{O} pair, which presents four hydrogen bonds, interestingly, the hydrogen bonding energy is smaller compared to the base pairs with three hydrogen bonds studied previously (ΔE = -29.4 kcal/mol). The system under study is larger, and as expected, the Pauli repulsion term increases (due to a greater number of atoms and orbitals, resulting in higher repulsion), as does the dispersion (due to a larger number of electrons in motion, leading to a higher probability of instantaneous dipole formation). However, due to a less favorable charge distribution, there is no significant accumulation of positive/negative charge on the frontier atoms. Consequently, the electrostatic interaction and the orbital interaction energy are comparable to those of structures with only three hydrogen bonds with favorable charge accumulation. Analyzing the results for the ImN^{N}-NaO^{O} pair, which exhibits a donor-acceptor pattern with a greater accumulation of positive and negative charges on the frontier atoms, addressing the issue encountered in the previous base pair, it is observed that the hydrogen bonding energy surpasses that of structures with three hydrogen bonds (ΔE = -38.1 kcal/mol). This increase is attributed to a higher electrostatic and orbital interaction due to the charge accumulation in frontier orbitals. With this base pair, a good selectivity is achieved, as mentioned in section 6.1.1.

Finally, examining the results for the non-hydrogen bonded base pairs, we observe that the total bonding energy obtained in the four cases is negative but very close to zero, as expected. In all cases, it is observed that the preparation energy has values very close to zero, indicating that there is not a significant variation between the geometries presented by each of the

monomers in their equilibrium compared to when they form the dimer. Furthermore, from the results obtained from the EDA, it is seen that the Pauli repulsion term is also the component with the highest value contributing to the interaction energy. The electrostatic interaction terms are attractive but very close to zero due to the charge distribution which is not entirely neutral, as observed in Figure 19, and are comparable to those of the orbital interaction, which is described by the sigma component, as in the cases studied previously. In these base pairs, dispersion interactions play a key role in their stability, as without them, the system would be unstable, and the two bases would tend to separate. From a selectivity standpoint, it is clear that this interaction will not play a significant role in the case of these bases.

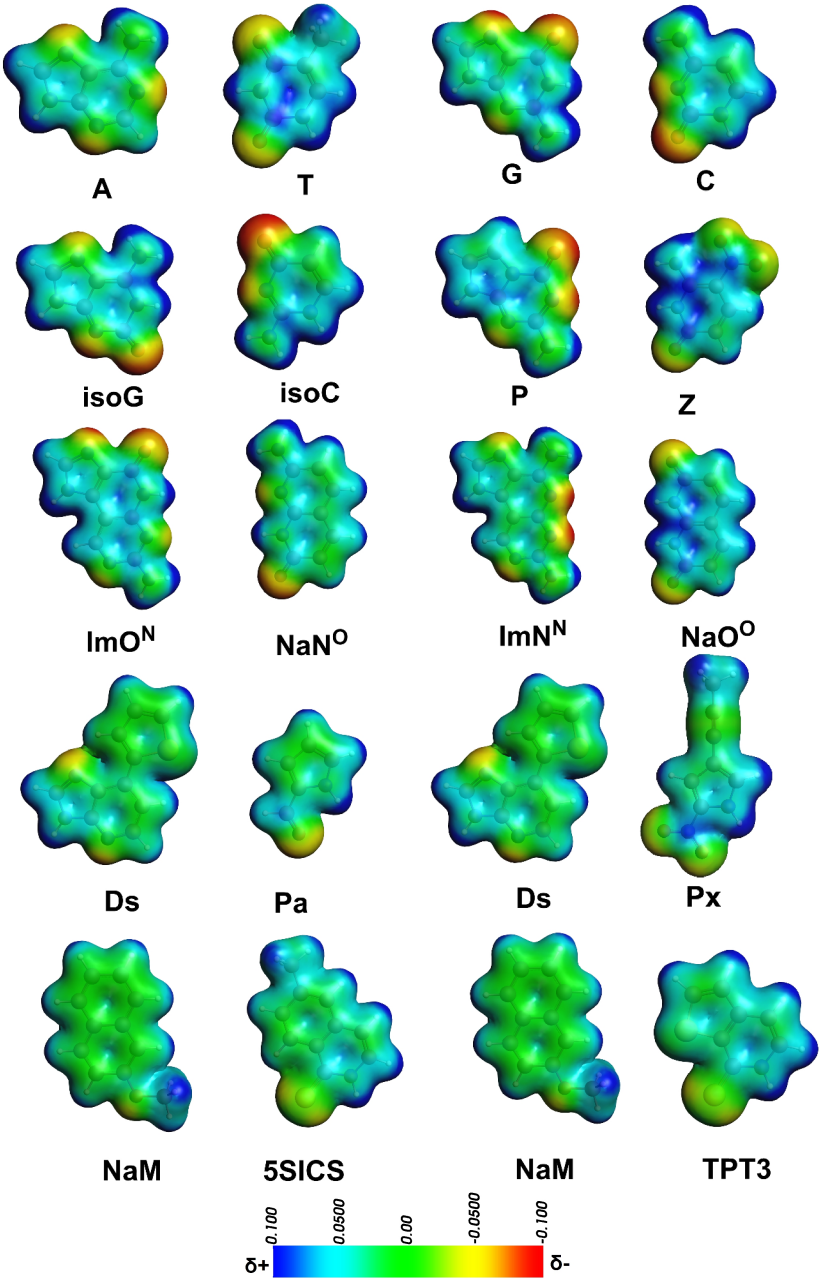


Figure 19: Electrostatic potential surfaces (at 0.01 au) from -0.1 (red, δ-) to 0.1 (blue, δ+) a.u. of the studied base pairs.

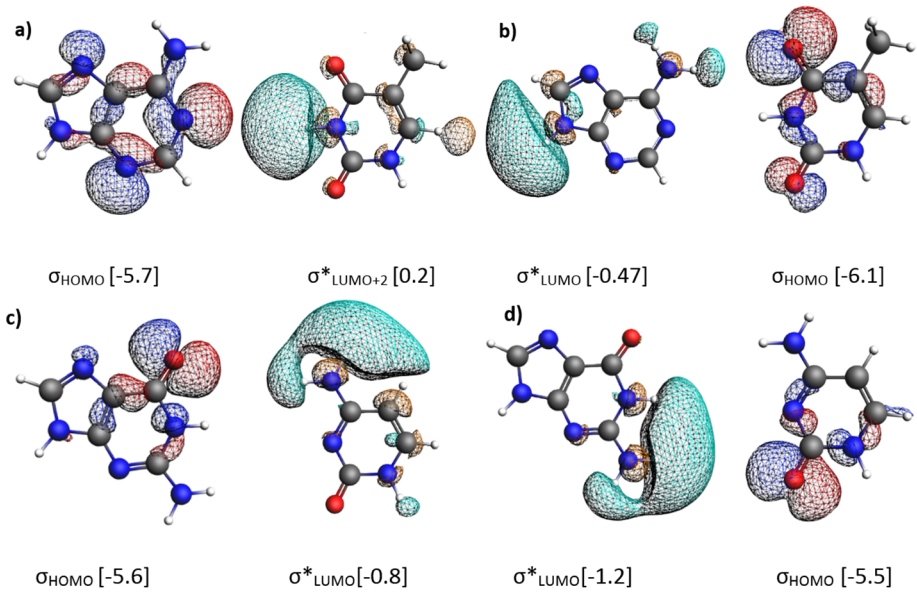


Figure 20: Isosurfaces (at 0.03 a.u.) and corresponding energies (in eV) of the most important σ_{HOMOs} and σ^*_{LUMOs} orbitals involved in charge transfer processes of the A-T (a and b) and G-C (c and d) base pairs. A larger accumulation of negative charge destabilizes occupied orbitals while a larger accumulation of positive charge stabilizes unoccupied orbitals (compare b and d).

6.4. π-π stacking interactions in natural and artificial DNA base pairs

W-C base pairs	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}	ΔE_{disp}
(A-T)//(A-T)'	-14.1	-6.0	17.4	-3.3	-22.2
A//A'	-6.0	-2.9	8.0	-1.3	-9.8
T//T'	-4.7	-1.9	9.0	-2.1	-9.6
A//T'	-1.7	-0.6	0.7	-0.2	-1.5
A'//T	-1.2	-0.3	0.6	-0.2	-1.3
(G-C)//(G-C)'	-12.5	-3.4	16.4	-3.2	-22.3
G//G'	-3.7	0.7	8.7	-2.0	-11.1
C//C'	-1.5	1.3	6.9	-1.7	-7.9

G//C'	-3.7	-2.1	0.9	-0.7	-1.8
G'//C	-5.6	-4.1	0.8	-0.7	-1.5
Hydrogen-bonded UBPs	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}	ΔE_{disp}
(isoG-isoC)//(isoG-isoC)'	-12.4	-2.8	16.4	-3.4	-22.5
isoG//isoG'	-3.8	0.9	8.8	-2.2	-11.3
isoC//isoC'	0.5	3.9	6.7	-2.1	-7.9
isoG//isoC'	-7.3	-5.5	1.0	-1.0	-1.8
isoG'//isoC	-4.7	-3.1	0.8	-0.8	-1.6
(P-Z)//(P-Z)'	-15.4	-4.3	17.6	-3.4	-25.3
P//P'	-4.1	0.7	8.1	-1.9	-10.9
Z//Z'	-4.6	-0.3	8.7	-2.1	-10.9
P//Z'	-5.0	-3.4	1.1	-0.7	-2.0
P'//Z	-4.0	-2.6	0.6	-0.7	-1.4
(ImO^N-NaN^O)//(ImO^N-NaN^O)'	-24.3	-10.6	29.4	-4.70	-38.4
ImO^N//$ImO^{N'}$	-10.3	-3.8	13.6	-2.7	-17.5
NaN^O//$NaN^{O'}$	-6.6	-3.2	13.9	-2.2	-15.1
ImO^N//$NaN^{O'}$	-3.8	-1.7	1.9	-0.6	-3.2
$ImO^{N'}$//NaN^O	-4.1	-2.2	1.4	-0.6	-2.7
(ImN^N-NaO^O)//(ImN^N-NaO^O)'	-24.6	-10.6	29.4	-4.6	-38.8
ImN^N//$ImN^{N'}$	-10.3	-4.1	14.9	-2.6	-18.5
NaO^O//$NaO^{O'}$	-6.3	-1.9	12.4	-2.7	-14.2
ImN^N//$NaO^{O'}$	-4.8	-2.6	1.9	-0.8	-3.3
$ImN^{N'}$//NaO^O	-4.6	-2.6	1.5	-0.7	-2.8
Non-hydrogen bonded UBPs	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}	ΔE_{disp}
(Ds-Pa)//(Ds-Pa)'	-17.5	-10.1	26.0	-4.4	-29.0
Ds//Ds'	-12.1	-8.0	19.9	-3.1	-20.8
Pa//Pa'	-3.4	-1.9	5.3	-1.1	-5.7
Ds//Pa'	-0.8	0.1	0.5	-0.1	-1.2
Ds'//Pa	-1.2	-0.3	0.6	-0.2	-1.3

(Ds-Px)//(Ds-Px)' (R=H)	-21.5	-12.7	33.1	-5.6	-36.3
Ds//Ds'	-11.3	-8.3	20.5	-3.2	-20.3
Px//Px'	-6.7	-4.4	10.8	-2.0	-11.1
Ds//Px'	-0.9	0.5	0.8	-0.3	-1.9
Ds'//Px	-2.4	-0.6	1.5	-0.4	-2.9
(NaM-5SICS)//(NaM-5SICS)'	-20.3	-15.2	41.9	-6.7	-40.3
NaM//NaM'	-7.3	-6.1	18.4	-2.8	-16.8
5SICS//5SICS'	-9.1	-7.1	20.3	-3.4	-19.0
NaM//5SICS'	-2.4	-1.6	3.0	-0.9	-2.9
NaM'//5SICS	-1.9	-0.7	0.6	-0.2	-1.6
(NaM-TPT3)//(NaM-TPT3)'	-19.3	-14.6	39.3	-6.3	-37.7
NaM//NaM'	-7.7	-6.2	18.9	-2.9	-17.4
TPT3//TPT3'	-7.6	-6.2	17.4	-2.9	-15.9
NaM//TPT3'	-2.5	-1.7	3.0	-1.0	-2.8
NaM'//TPT3	-2.0	-0.8	0.6	-0.2	-1.6

Table 2: Energy Decomposition Analysis (EDA) of π-π stacking interactions energies ΔE_{int} (kcal mol^{-1}) and the parameters contributing to the total energies obtained for W-C base pairs, the hydrogen-bonded UBPs and the non-hydrogen-bonded UBPs. The notation X//Y' denotes X "up" and Y' "down" following the scheme presented in Figure 4.

Next, the quantum chemical analysis has focused on the strength of the π-π stacking interaction. By analyzing the results obtained for the stacked systems of natural base pairs, it is observed that, unlike hydrogen bonding interactions, the π-π stacking interactions for both A-T and G-C stacked systems are comparable, being stronger for the stacked A-T system (ΔE = -14.1 and -12.5 kcal/mol for AT and GC, respectively). Analysis of the EDA results reveals that this difference is due to greater electrostatic interaction in the stacked A-T system. The other components exhibit similar behavior. It is worth noting that, in both cases, dispersion interactions contribute the most to the total interaction energy. If these were not considered, the systems would not be stable and would tend to separate. On the other hand, it is also worth mentioning that orbital interactions have a very small contribution to the total interaction energy because, in this case, they primarily account for the polarization of the π system, and this trend holds for all

the stacked systems studied. So, it is confirmed the electrostatic nature of this interaction. For a better understanding of the obtained results, the different components contributing to the total π-π stacking interaction energy are analyzed, including stacking between bases X//X' and cross interactions. In the case of the stacked A-T system, stacking interactions between bases have a greater contribution to total interaction energy, accounting for 76% of the total interaction. Within these interactions, dispersion forces play a crucial role. Regarding cross interactions, constituting 20.5% of the total interaction, dispersion forces also play a predominant role. It is important to note that when summing up all contributions, we do not obtain the total interaction energy. This is due to the existence of another parameter called "cooperativity", which relates to the influence of hydrogen bonding interactions on π-π stacking interactions and vice versa. Negative values indicate an increase in interaction forces due to the simultaneous occurrence of both phenomena, while a positive value indicate a decrease in interaction forces.[34] In this case, cooperativity has a negative value (-0.5 kcal/mol) and represents the 3.5% of the total interaction. In the case of the stacked G-C system, interestingly, cross interactions make a greater contribution to the total interaction energy, accounting for the 56% of the total interaction. Within these interactions, electrostatic interactions is the most significant component. The stacking interactions between bases represent the 32% of the total interaction, with dispersion interactions being the most significant component. The electrostatic component in the stacking between bases exhibits positive values, indicating that it is a repulsive interaction. In this case, the cooperativity has a positive value (2 kcal/mol) and represents the 12% of the total interaction.

Analyzing the results for the stacked systems of hydrogen-bonded UBPs, it is revealed that the isoG-isoC stacked system exhibits values very similar to the G-C (ΔE = -12.4 kcal/mol), with dispersion interactions predominating. Based on the EDA results, it can be observed that cross interactions also make a significant contribution to the total interaction energy, representing the 63% of the total interaction, with the electrostatic component being the most important for these interactions. On the other hand, interactions between bases represent the 22% of the total interaction, with electrostatic interactions being predominant. Similarly, the cooperativity value is positive (2.9 kcal/mol) representing the 15% of the total interaction. The results for the optimized P-Z stacked system show a higher π-π stacking interaction compared to its predecessor (ΔE = -15.4 kcal/mol). This increase can be mainly attributed to an enhancement in dispersion and electrostatic interactions caused by the nitro group added at the 5th position of the pyrimidine. From the results of the EDA, it can be observed how stacking between bases and cross

interactions have similar contributions to the total interaction, accounting for 43.5% and 45% respectively. As in previous cases, dispersion interactions predominate in stacking between bases, while electrostatic interactions predominate in cross interactions. Cooperativity value is positive (2.3 kcal/mol) and represents 11.5% of the total interaction. This increase in π-π stacking interactions is a favorable aspect from a selectivity standpoint. Analyzing the ImO^{N}-NaN^{O} stacked system, a significant increase in π-π stacking interaction forces is observed (ΔE = -24.3 kcal/mol). Upon examining the EDA results, it is noted that this increase is associated with higher dispersion and electrostatic interactions attributed to the enlarged size of the study system. Consequently, a substantial increase in Pauli repulsion values is also observed. However, orbital interactions experience a slight increase, with their contribution to the total interaction remaining minimal. Examining the different components influencing the total interaction, it is evident that stacking between bases makes the largest contribution to system stability, representing 67% of the total interaction, with dispersion interactions being the most important for these interactions. The cross interactions account for 31% of the total interaction energy, with dispersion interactions also being the predominant component in these interactions. Cooperativity is positive (0.5 kcal/mol), representing 2% of the total interaction. The results for the ImN^{N}-NaO^{O} stacked system are nearly identical to those obtained for the ImO^{N}-NaN^{O} stacked system (ΔE = -24.6 kcal/mol). In contrast to hydrogen bonding interactions, no significant differences are observed between these two pairs regarding π-π stacking energies.

Analyzing the results for the stacked systems of non-hydrogen bonded UBPs, in general, higher π-π stacking interaction values are observed compared to the stacked systems of natural base pairs. Examining the results of the Ds-Pa stacked system (ΔE = -17.5 kcal/mol) reveals that the total interaction is primarily determined by dispersion interactions. From the EDA results, it is observed that stacking between bases has the greatest contribution to the total interaction, representing 89% of the total interaction. Within these interactions, dispersion interactions is the most important component. On the other hand, cross interactions represent 11% of the total interaction, with dispersion interactions also being the most important component. As expected, due to the absence of hydrogen bonds, cooperativity is null. The results for the optimized Ds-Px stacked system exhibits a higher π-π stacking interaction compared to its predecessor (ΔE = -21.5 kcal/mol). This increase is primarily due to an increase in dispersion interactions, which can be attributed to the characteristic propynyl group of the Px base. Analyzing the EDA results, it is also observed that base stacking presents a higher contribution to the total interaction,

representing 84% of the total interaction. On the other hand, cross interactions represent 16% of the total interaction. In both types of interaction, dispersion interactions are the most significant component. This increase in π-π stacking interactions is a favorable aspect from a selectivity standpoint. For NaM-5SICS and NaM-TPT3 stacked systems, the results obtained are similar in both cases (ΔE = -20.3 and -19.3 kcal/mol for NaM-5SICS and NaM-TPT3, respectively). Following the same trend as the other non-hydrogen-bonded stacked systems studied, the total interaction is primarily determined by dispersion interactions in both cases. Analyzing the EDA, it is observed that stacking between bases presents a greater contribution to the total interaction, accounting for 78% and 75.5% respectively. On the other hand, cross interactions represent 20% and 22% of the total interaction. In both types of interactions, dispersion interactions are the most significant component. Although no hydrogen bonds are present, cooperativity in both cases is present, with values of 0.4 kcal mol^{-1} and 0.5 kcal mol^{-1}, representing 2% and 2.5% of the total interaction, respectively. This underscores the complexity of this parameter, which should be studied in more detail for each system under investigation to achieve a clearer understanding.

7. CONCLUSIONS

In this work, first an extensive bibliographic review of different artificial DNA base pairs has been conducted, classifying them into three distinct groups: hydrogen-bonded, non-hydrogen-bonded, and metal-mediated base pairs. The analysis has focused on their structure, their stability, and the methodology used in the different proposed unnatural base pairs with the aim to improve their selectivity. Next, the Watson-Crick base pairs and a set of 8 artificial DNA base pairs (4 hydrogen-bonded and 4 non-hydrogen-bonded) were analyzed by means of a Density Functional Theory analysis. The objective is to understand how these unnatural base pairs can be incorporated into DNA helix. For such, the quantum chemical analysis has focused on the analysis of the hydrogen bonding and π-π stacking interactions of the selected set of bases, and analyzed through an Energy Decomposition Analysis. Through the EDA analysis of hydrogen bonding interactions, it has been verified that despite the electrostatic component is the most significant attractive force, the orbital interaction component, primarily determined by charge transfer donor-acceptor interaction, plays a crucial role in all studied systems, leading to the conclusion that this type of interaction exhibits a significant covalent character. Changes in the hydrogen bond donor/acceptor pattern directly influence the total interaction and, consequently, the selectivity, due to the accumulation of positive/negative charges in monomers. This accumulation directly affects both the electrostatic component and the σ component of orbital interaction (charge transfer), surpassing even the effect of an increase in the number of hydrogen bonds where there is no such charge accumulation on the frontier atoms involved in the hydrogen bonds. In the case of non-hydrogen-bonded UBPs, the results revealed residual non-null interactions in each dimer, primarily driven by dispersion interactions. On the other hand, the analysis of π-π stacking interactions leads to the conclusion that such interactions significantly contribute to the selectivity of all examined base pairs, being the primary interaction in non-hydrogen-bonded UBPs. Additionally, the study underscored the importance of cross interactions across all studied systems, particularly pronounced in the G-C base pair and its derivatives, strengthening the stacking between bases. Moreover, the cooperativity parameter has been identified and quantified, emphasizing its complexity and significance in these interactions.

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APPENDICES

APPENDIX 1: CARTESIAN COORDINATES OF STUDIED SYSTEMS

Cartesian coordinates (Å) and total bonding energies (kcal mol^{-1}) of Watson-Crick base pairs optimized in Cs symmetry at BLYP-D3(BJ)/TZ2P level of theory in the gas phase.

A
Total bonding energy = -2307.00 kcal mol^{-1}

N	-1.45168254	-1.45594227	0.00000000
C	-2.20124417	-0.33423938	0.00000000
N	-1.79144521	0.94793477	0.00000000
C	-0.45136199	1.03450218	0.00000000
C	0.45959277	-0.03783736	0.00000000
C	-0.10543136	-1.33419680	0.00000000
N	0.34689576	2.16863137	0.00000000
C	1.66702801	1.73431824	0.00000000
N	1.77636423	0.41856631	0.00000000
N	0.65669465	-2.45901779	0.00000000
H	-3.27921080	-0.49136712	0.00000000
H	0.01383785	3.12595528	0.00000000
H	2.49446592	2.43324033	0.00000000
H	1.66466142	-2.38897878	0.00000000
H	0.20083546	-3.36156899	0.00000000

T
Total bonding energy = -2167.23 kcal mol^{-1}

N	1.11055531	-1.39236864	0.00000000
C	2.10692001	-0.41978227	0.00000000
N	1.58211068	0.87676317	0.00000000
C	0.22839942	1.16302389	0.00000000
C	-0.72514249	0.19817715	0.00000000
C	-0.29593286	-1.20783607	0.00000000
O	-1.04685699	-2.18028971	0.00000000
O	3.30791630	-0.65739292	0.00000000
C	-2.20056846	0.48666119	0.00000000
H	1.43542961	-2.35711395	0.00000000
H	2.27187129	1.61972642	0.00000000
H	-0.01770626	2.22158245	0.00000000
H	-2.68307461	0.04201450	-0.87890413
H	-2.39084635	1.56482029	0.00000000
H	-2.68307461	0.04201450	0.87890413

G
Total bonding energy = -2461.77 kcal mol^{-1}

N	-1.08119330	1.29370352	0.00000000
C	0.27591952	1.52743226	0.00000000
N	1.17604199	0.55942995	0.00000000
C	0.61923675	-0.68012531	0.00000000
C	-0.73810071	-1.04419674	0.00000000
C	-1.73727169	-0.00675010	0.00000000
N	1.30763782	-1.87499941	0.00000000
C	0.35286901	-2.89349700	0.00000000
N	-0.87735088	-2.42841337	0.00000000
O	-2.96061931	-0.05418804	0.00000000
N	0.69728996	2.82920644	0.00000000
H	-1.73784771	2.07076896	0.00000000
H	2.31676737	-1.97126382	0.00000000
H	0.63731181	-3.93824096	0.00000000
H	1.69252733	3.00317658	0.00000000
H	0.05678206	3.60795704	0.00000000

C
Total bonding energy = -1904.39 kcal mol^{-1}

N	1.33836758	0.27728827	0.00000000
C	1.36769460	-1.09812960	0.00000000
N	0.08242012	-1.75579280	0.00000000
C	-1.10006181	-1.08639839	0.00000000
C	-1.10792332	0.27714960	0.00000000
C	0.18007802	0.92570324	0.00000000
N	0.23783978	2.28939245	0.00000000
O	2.37608737	-1.79629848	0.00000000
H	0.11654601	-2.77043856	0.00000000
H	-2.00723887	-1.68440256	0.00000000
H	-2.03792988	0.83468003	0.00000000
H	1.15001058	2.72897055	0.00000000
H	-0.59589018	2.85827624	0.00000000

A-T
Total bonding energy = -4490.74 kcal mol^{-1}

N	1.26540244	-0.60369110	0.00000000
C	1.87747865	-1.80938847	0.00000000
N	3.19446042	-2.06250893	0.00000000
C	3.91468343	-0.92521780	0.00000000
C	3.41808014	0.38955004	0.00000000
C	2.00897920	0.53634184	0.00000000
N	5.29249635	-0.77739483	0.00000000
C	5.55308337	0.58827683	0.00000000
N	4.45470666	1.31994791	0.00000000
N	1.38621436	1.73060424	0.00000000
H	1.20479263	-2.66608739	0.00000000
H	5.96706248	-1.53396343	0.00000000
H	6.56573712	0.97264305	0.00000000
H	1.94806965	2.57111986	0.00000000
H	0.35882981	1.78506477	0.00000000
N	-1.55140060	-0.57632800	0.00000000
C	-2.16491838	-1.81879674	0.00000000
N	-3.56609366	-1.74274521	0.00000000
C	-4.26713612	-0.55449963	0.00000000
C	-3.64671256	0.65337345	0.00000000
C	-2.18044560	0.67118057	0.00000000

G-C
Total bonding energy = -4396.41 kcal mol^{-1}

N	-2.60282567	-0.57255291	0.00000000
O	1.37038223	1.81601623	0.00000000
N	-0.65936985	0.71373547	0.00000000
C	-2.03833665	0.65911156	0.00000000
N	-2.81072630	1.74686973	0.00000000
C	-2.09695489	2.89362281	0.00000000
C	-0.69898094	3.06727310	0.00000000
C	0.12410834	1.89594403	0.00000000
N	-2.61030653	4.17545039	0.00000000
C	-1.52148444	5.05128895	0.00000000
N	-0.36778176	4.42109767	0.00000000
H	-2.05090016	-1.43921256	0.00000000
H	-3.61217782	-0.61255400	0.00000000
H	-0.12336385	-0.17952228	0.00000000
H	-3.59585525	4.41145736	0.00000000
H	-1.65900447	6.12563197	0.00000000
O	-1.03453993	-3.01368714	0.00000000
N	2.83910019	-0.52094187	0.00000000
N	0.89111378	-1.74396255	0.00000000
C	3.01639010	-2.93710152	0.00000000
C	0.20418673	-2.91955428	0.00000000

O	-1.50883563	1.71850837	0.00000000
O	-1.56567873	-2.88983820	0.00000000
C	-4.38201218	1.96552153	0.00000000
H	-0.49056154	-0.58818551	0.00000000
H	-4.04759803	-2.63502361	0.00000000
H	-5.34961352	-0.65278849	0.00000000
H	-4.11168277	2.56296861	0.87918469
H	-5.46570459	1.80838775	0.00000000
H	-4.11168277	2.56296861	-0.87918469
N	0.97089898	-4.11681893	0.00000000
C	2.33602433	-4.11473023	0.00000000
C	2.23805893	-1.71973794	0.00000000
H	4.10060744	-2.91620005	0.00000000
H	0.44068280	-4.98219229	0.00000000
H	2.82567651	-5.08412273	0.00000000
H	2.27690625	0.36264852	0.00000000
H	3.84847184	-0.46725665	0.00000000

Cartesian coordinates (Å) and total bonding energies (kcal mol^{-1}) of stacked Watson-Crick base pairs with 3.4 Å distance between the base pairs and a twist angle of 36^{O} at BLYP-D3(BJ)/TZ2P level of theory in the gas phase.

A-T//A-T

Total bonding energy = -8995.51 kcal mol^{-1}

N	-0.18311350	-1.39002004	0.00000000
C	-1.14065789	-2.34472009	0.00000000
N	-0.97442000	-3.67546271	0.00000000
C	0.32976929	-4.00899321	0.00000000
C	1.42672895	-3.13040980	0.00000000
C	1.13090011	-1.74491401	0.00000000
N	0.89612489	-5.27369135	0.00000000
C	2.27548164	-5.09950858	0.00000000
N	2.63192512	-3.82879146	0.00000000
N	2.07426623	-0.78358208	0.00000000
H	-2.16329839	-1.96969219	0.00000000
H	0.38503779	-6.14903442	0.00000000
H	2.95396286	-5.94382384	0.00000000
H	3.04726692	-1.05820460	0.00000000
H	1.80858199	0.21034792	0.00000000
N	-1.02752965	1.29737451	0.00000000
C	-2.39877506	1.49692063	0.00000000
N	-2.75943273	2.85301873	0.00000000
C	-1.84597807	3.88693781	0.00000000
C	-0.50550108	3.67013325	0.00000000
C	-0.03546409	2.28113320	0.00000000
O	1.16814273	1.96603625	0.00000000
O	-3.23222079	0.59603985	0.00000000
C	0.51520582	4.77492080	0.00000000
H	-0.71098952	0.28479243	0.00000000
H	-3.75683295	3.03522741	0.00000000
H	-2.27396024	4.88606206	0.00000000
H	1.16694814	4.70244355	0.87918469
H	0.03088335	5.75701652	0.00000000
H	1.16694814	4.70244355	-0.87918469
N	0.66889135	-1.23218125	3.40000000
C	0.45538027	-2.56738028	3.40000000
N	1.37206043	-3.54626150	3.40000000
C	2.62321604	-3.04951011	3.40000000
C	2.99425669	-1.69394449	3.40000000
C	1.94055214	-0.74693868	3.40000000
N	3.82477827	-3.73977693	3.40000000
C	4.83831926	-2.78809456	3.40000000
N	4.37977931	-1.55055059	3.40000000
N	2.13869462	0.58529188	3.40000000
H	-0.59238914	-2.86506935	3.40000000
H	3.92581387	-4.74835381	3.40000000
H	5.88349815	-3.07235869	3.40000000
H	3.08728779	0.93503305	3.40000000
H	1.33953416	1.23323287	3.40000000
N	-1.59386655	0.44563125	3.40000000
C	-2.82051766	-0.19893037	3.40000000
N	-3.90939031	0.68618677	3.40000000
C	-3.77811234	2.05956006	3.40000000
C	-2.56620916	2.67207409	3.40000000
C	-1.36950751	1.82463026	3.40000000
O	-0.21055979	2.27717381	3.40000000
O	-2.96526498	-1.41764535	3.40000000
C	-2.38981776	4.16582246	3.40000000

G-C//G-C

Total bonding energy = -8805.24 kcal mol^{-1}

N	-2.60282567	-0.57255291	0.00000000
O	1.37038223	1.81601623	0.00000000
N	-0.65936985	0.71373547	0.00000000
C	-2.03833665	0.65911156	0.00000000
N	-2.81072630	1.74686973	0.00000000
C	-2.09695489	2.89362281	0.00000000
C	-0.69898094	3.06727310	0.00000000
C	0.12410834	1.89594403	0.00000000
N	-2.61030653	4.17545039	0.00000000
C	-1.52148444	5.05128895	0.00000000
N	-0.36778176	4.42109767	0.00000000
H	-2.05090016	-1.43921256	0.00000000
H	-3.61217782	-0.61255400	0.00000000
H	-0.12336385	-0.17952228	0.00000000
H	-3.59585525	4.41145736	0.00000000
H	-1.65900447	6.12563197	0.00000000
O	-1.03453993	-3.01368714	0.00000000
N	2.83910019	-0.52094187	0.00000000
N	0.89111378	-1.74396255	0.00000000
C	3.01639010	-2.93710152	0.00000000
C	0.20418673	-2.91955428	0.00000000
N	0.97089898	-4.11681893	0.00000000
C	2.33602433	-4.11473023	0.00000000
C	2.23805893	-1.71973794	0.00000000
H	4.10060744	-2.91620005	0.00000000
H	0.44068280	-4.98219229	0.00000000
H	2.82567651	-5.08412273	0.00000000
H	2.27690625	0.36264852	0.00000000
H	3.84847184	-0.46725665	0.00000000
N	-1.76919205	-1.99310757	3.40000000
O	0.04123495	2.27467846	3.40000000
N	-0.95296460	0.18985625	3.40000000
C	-2.03646504	-0.66487177	3.40000000
N	-3.30070961	-0.23885617	3.40000000
C	-3.39730096	1.10843087	3.40000000
C	-2.36838535	2.07062538	3.40000000
C	-1.01400219	1.60680000	3.40000000
N	-4.56605050	1.84371064	3.40000000
C	-4.19997992	3.19227249	3.40000000
N	-2.89619770	3.36056646	3.40000000
H	-0.81326517	-2.36983629	3.40000000
H	-2.56226304	-2.61875145	3.40000000
H	0.00571710	-0.21774803	3.40000000
H	-5.50209759	1.45535329	3.40000000
H	-4.94271894	3.98060201	3.40000000
O	0.93444047	-3.04621143	3.40000000
N	2.60308225	1.24733040	3.40000000
N	1.74600166	-0.88711180	3.40000000
C	4.16669581	-0.60317542	3.40000000
C	1.88126148	-2.24195108	3.40000000
N	3.20527922	-2.75989638	3.40000000
C	4.30846113	-1.95580603	3.40000000
C	2.82146430	-0.07579919	3.40000000
H	5.03156049	0.05102118	3.40000000

H	-0.74259939	-0.18750723	3.40000000
H	-4.82340361	0.24733955	3.40000000
H	-4.71162770	2.61630695	3.40000000
H	-1.81994609	4.49027166	4.27918469
H	-3.35890425	4.67567697	3.40000000
H	-1.81994609	4.49027166	2.52081531

A//A

Total bonding energy = -4618.98 kcal mol^{-1}

N	-0.18311350	-1.39002004	0.00000000
C	-1.14065789	-2.34472009	0.00000000
N	-0.97442000	-3.67546271	0.00000000
C	0.32976929	-4.00899321	0.00000000
C	1.42672895	-3.13040980	0.00000000
C	1.13090011	-1.74491401	0.00000000
N	0.89612489	-5.27369135	0.00000000
C	2.27548164	-5.09950858	0.00000000
N	2.63192512	-3.82879146	0.00000000
N	2.07426623	-0.78358208	0.00000000
H	-2.16329839	-1.96969219	0.00000000
H	0.38503779	-6.14903442	0.00000000
H	2.95396286	-5.94382384	0.00000000
H	3.04726692	-1.05820460	0.00000000
H	1.80858199	0.21034792	0.00000000
N	0.66889135	-1.23218125	3.40000000
C	0.45538027	-2.56738028	3.40000000
N	1.37206043	-3.54626150	3.40000000
C	2.62321604	-3.04951011	3.40000000
C	2.99425669	-1.69394449	3.40000000
C	1.94055214	-0.74693868	3.40000000
N	3.82477827	-3.73977693	3.40000000
C	4.83831926	-2.78809456	3.40000000
N	4.37977931	-1.55055059	3.40000000
N	2.13869462	0.58529188	3.40000000
H	-0.59238914	-2.86506935	3.40000000
H	3.92581387	-4.74835381	3.40000000
H	5.88349815	-3.07235869	3.40000000
H	3.08728779	0.93503305	3.40000000
H	1.33953416	1.23323287	3.40000000

G//G

Total bonding energy = -4923.81 kcal mol^{-1}

N	-2.60282567	-0.57255291	0.00000000
O	1.37038223	1.81601623	0.00000000
N	-0.65936985	0.71373547	0.00000000
C	-2.03833665	0.65911156	0.00000000
N	-2.81072630	1.74686973	0.00000000
C	-2.09695489	2.89362281	0.00000000
C	-0.69898094	3.06727310	0.00000000
C	0.12410834	1.89594403	0.00000000
N	-2.61030653	4.17545039	0.00000000
C	-1.52148444	5.05128895	0.00000000
N	-0.36778176	4.42109767	0.00000000
H	-2.05090016	-1.43921256	0.00000000
H	-3.61217782	-0.61255400	0.00000000
H	-0.12336385	-0.17952228	0.00000000
H	-3.59585525	4.41145736	0.00000000
H	-1.65900447	6.12563197	0.00000000
C	-2.03646504	-0.66487177	3.40000000
N	-3.30070961	-0.23885617	3.40000000
C	-3.39730096	1.10843087	3.40000000
C	-2.36838535	2.07062538	3.40000000
C	-1.01400219	1.60680000	3.40000000
N	-4.56605050	1.84371064	3.40000000
C	-4.19997992	3.19227249	3.40000000
N	-2.89619770	3.36056646	3.40000000
H	-0.81326517	-2.36983629	3.40000000
H	-2.56226304	-2.61875145	3.40000000
H	0.00571710	-0.21774803	3.40000000
H	-5.50209759	1.45535329	3.40000000
H	-4.94271894	3.98060201	3.40000000
N	-1.76919205	-1.99310757	3.40000000
O	0.04123495	2.27467846	3.40000000
H	3.28497902	-3.77165138	3.40000000
H	5.27439267	-2.45225071	3.40000000
H	1.62889640	1.63172074	3.40000000
H	3.38812568	1.88405643	3.40000000

T//T

Total bonding energy = -4336.51 kcal mol^{-1}

N	-1.59386655	0.44563125	3.40000000
C	-2.82051766	-0.19893037	3.40000000
N	-3.90939031	0.68618677	3.40000000
C	-3.77811234	2.05956006	3.40000000
C	-2.56620916	2.67207409	3.40000000
C	-1.36950751	1.82463026	3.40000000
O	-0.21055979	2.27717381	3.40000000
O	-2.96526498	-1.41764535	3.40000000
C	-2.38981776	4.16582246	3.40000000
H	-0.74259939	-0.18750723	3.40000000
H	-4.82340361	0.24733955	3.40000000
H	-4.71162770	2.61630695	3.40000000
H	-1.81994609	4.49027166	4.27918469
H	-3.35890425	4.67567697	3.40000000
H	-1.81994609	4.49027166	2.52081531
N	-1.02752965	1.29737451	0.00000000
C	-2.39877506	1.49692063	0.00000000
N	-2.75943273	2.85301873	0.00000000
C	-1.84597807	3.88693781	0.00000000
C	-0.50550108	3.67013325	0.00000000
C	-0.03546409	2.28113320	0.00000000
O	1.16814273	1.96603625	0.00000000
O	-3.23222079	0.59603985	0.00000000
C	0.51520582	4.77492080	0.00000000
H	-0.71098952	0.28479243	0.00000000
H	-3.75683295	3.03522741	0.00000000
H	-2.27396024	4.88606206	0.00000000
H	1.16694814	4.70244355	0.87918469
H	0.03088335	5.75701652	0.00000000
H	1.16694814	4.70244355	-0.87918469

C//C

Total bonding energy = -3806.79 kcal mol^{-1}

H	2.82567651	-5.08412273	0.00000000
H	2.27690625	0.36264852	0.00000000
H	3.84847184	-0.46725665	0.00000000
O	0.93444047	-3.04621143	3.40000000
N	2.60308225	1.24733040	3.40000000
N	1.74600166	-0.88711180	3.40000000
C	4.16669581	-0.60317542	3.40000000
C	1.88126148	-2.24195108	3.40000000
N	3.20527922	-2.75989638	3.40000000
C	4.30846113	-1.95580603	3.40000000
C	2.82146430	-0.07579919	3.40000000
H	5.03156049	0.05102118	3.40000000
H	3.28497902	-3.77165138	3.40000000
H	5.27439267	-2.45225071	3.40000000
H	1.62889640	1.63172074	3.40000000
H	3.38812568	1.88405643	3.40000000
O	-1.03453993	-3.01368714	0.00000000
N	2.83910019	-0.52094187	0.00000000
N	0.89111378	-1.74396255	0.00000000
C	3.01639010	-2.93710152	0.00000000
C	0.20418673	-2.91955428	0.00000000
N	0.97089898	-4.11681893	0.00000000
C	2.33602433	-4.11473023	0.00000000
C	2.23805893	-1.71973794	0.00000000
H	4.10060744	-2.91620005	0.00000000
H	0.44068280	-4.98219229	0.00000000

N -0.95296460 0.18985625 3.40000000

Cartesian coordinates (Å) and total bonding energies (kcal mol^{-1}) of hydrogen-bonded artificial DNA base pairs optimized in Cs symmetry at BLYP-D3(BJ)/TZ2P level of theory in the gas phase.

isoG
Total bonding energy = -2458.88 kcal mol^{-1}

N	1.75300601	0.43195842	0.00000000
C	1.97541098	-1.03636113	0.00000000
N	0.85673655	-1.82568679	0.00000000
C	-0.29932238	-1.17657157	0.00000000
C	-0.55694644	0.22096656	0.00000000
C	0.54958109	1.06819151	0.00000000
N	-1.57122248	-1.73464052	0.00000000
C	-2.49481132	-0.68687507	0.00000000
N	-1.92514268	0.49767176	0.00000000
N	0.46019184	2.42169842	0.00000000
O	3.14596139	-1.39903892	0.00000000
H	-1.76718837	-2.72914825	0.00000000
H	-3.56193837	-0.87203240	0.00000000
H	-0.46039333	2.84169376	0.00000000
H	1.27386375	3.01924853	0.00000000
H	2.62221376	0.95892571	0.00000000

P
Total bonding energy = -2462.06 kcal mol^{-1}

N	-1.68381076	-1.09033939	0.00000000
C	-1.81191991	0.24395512	0.00000000
N	-0.81940194	1.19370285	0.00000000
C	0.38335092	0.65396604	0.00000000
N	0.65093475	-0.69463010	0.00000000
C	-0.45487359	-1.66902608	0.00000000
N	1.60175228	1.28038223	0.00000000
C	2.62408700	0.31587444	0.00000000
C	2.03276836	-0.90843573	0.00000000
O	-0.17059210	-2.85782007	0.00000000
H	1.71250997	2.28634416	0.00000000
H	3.66608874	0.59595729	0.00000000
H	-3.23375335	1.73352582	0.00000000
N	-3.08072026	0.73582094	0.00000000
H	-3.85557138	0.08827949	0.00000000
H	2.43915134	-1.90755702	0.00000000

isoG-isoC
Total bonding energy = -4387.32 kcal mol^{-1}

N	-0.92683556	-0.16940991	0.00000000
C	-1.52423127	-1.47153992	0.00000000
N	-2.87967415	-1.57773249	0.00000000
C	-3.52272092	-0.40865932	0.00000000
C	-2.99555527	0.90331304	0.00000000
C	-1.59666758	1.02109778	0.00000000
N	-4.89615135	-0.21021709	0.00000000
C	-5.12114205	1.16822176	0.00000000
N	-4.00527806	1.86535798	0.00000000
N	-0.91247513	2.17613709	0.00000000
O	-0.74337809	-2.45646368	0.00000000
H	-5.59010650	-0.94870304	0.00000000
H	-6.12272853	1.58012981	0.00000000
H	-1.44601238	3.03558497	0.00000000
H	0.12274378	2.20328266	0.00000000
N	1.94072568	-0.09544178	0.00000000
C	2.61003455	-1.23883902	0.00000000
N	4.00035851	-1.25397275	0.00000000
C	4.71224403	-0.06582590	0.00000000
C	4.06040724	1.11771494	0.00000000
C	2.59276749	1.13066605	0.00000000
O	1.94144772	2.19618929	0.00000000
H	4.49666828	-2.13710118	0.00000000
H	0.11571344	-0.14684442	0.00000000

isoC
Total bonding energy = -1893.49 kcal mol^{-1}

N	1.30649503	0.42620684	0.00000000
C	0.64062192	-0.69226689	0.00000000
N	-0.74672444	-0.76759477	0.00000000
C	-1.48791450	0.40849835	0.00000000
C	-0.85531793	1.59966288	0.00000000
C	0.62306882	1.66267302	0.00000000
O	1.23459507	2.73140807	0.00000000
H	-1.22176661	-1.66163420	0.00000000
H	-2.56645387	0.28292503	0.00000000
N	1.31217643	-1.88814199	0.00000000
H	2.32212200	-1.84687459	0.00000000
H	0.85117778	-2.78557811	0.00000000
H	-1.41207964	2.53071633	0.00000000

Z
Total bonding energy = -2343.15 kcal mol^{-1}

H	-2.03493565	1.41951884	0.00000000
N	-1.38444078	0.63617738	0.00000000
C	-2.03931601	-0.64657801	0.00000000
C	-1.11705827	-1.76068017	0.00000000
C	0.23296651	-1.55656884	0.00000000
C	0.81029262	-0.25569940	0.00000000
C	-0.04041328	0.87850860	0.00000000
N	0.38997539	2.15350011	0.00000000
H	-1.54863512	-2.75565820	0.00000000
H	0.92387727	-2.39362286	0.00000000
H	-0.25457348	2.93213646	0.00000000
H	1.40718517	2.27160689	0.00000000
O	-3.26781889	-0.67368908	0.00000000
N	2.23687663	-0.12636664	0.00000000
O	2.75364264	1.03909903	0.00000000
O	2.93237527	-1.16168410	0.00000000

P-Z
Total bonding energy = -4835.10 kcal mol^{-1}

N	-1.11800546	-0.51647112	0.00000000
C	-1.77038124	-1.71076886	0.00000000
N	-3.13364929	-1.87847279	0.00000000
C	-3.79508461	-0.74314719	0.00000000
N	-3.22918315	0.51791248	0.00000000
C	-1.79416392	0.65169557	0.00000000
N	-5.14835807	-0.54002745	0.00000000
C	-5.42075920	0.83822178	0.00000000
C	-4.23259183	1.49642119	0.00000000
O	-1.30729231	1.78964623	0.00000000
H	0.73877311	-0.38002492	0.00000000
H	-5.82335275	-1.29448217	0.00000000
H	-6.43130847	1.21622011	0.00000000
H	-1.49250832	-3.71321428	0.00000000
N	-1.01915799	-2.81961915	0.00000000
N	1.78173906	-0.32739741	0.00000000
C	2.44907696	-1.56764794	0.00000000
C	3.88631621	-1.49114429	0.00000000
C	4.51428690	-0.27500647	0.00000000
C	3.79445006	0.94610875	0.00000000
C	2.36835181	0.91059660	0.00000000
N	1.57019029	1.98283956	0.00000000
H	4.43691034	-2.42543586	0.00000000
H	0.01727895	-2.76304916	0.00000000

H	5.79310730	-0.16692530	0.00000000
N	1.95334108	-2.40887491	0.00000000
H	0.89204898	-2.41459550	0.00000000
H	2.45498456	-3.28663461	0.00000000
H	4.59636424	2.06008548	0.00000000

ImO^{N}

Total bonding energy = -3325.82 kcal mol^{-1}

N	1.63962358	1.07749667	0.00000000
C	1.06332620	-0.17071040	0.00000000
C	-0.36068322	-0.29246963	0.00000000
C	-1.08330050	0.94105140	0.00000000
C	-0.47294096	2.20073393	0.00000000
C	0.97909333	2.34819357	0.00000000
N	-2.43956670	1.20485734	0.00000000
C	-2.58424021	2.59037954	0.00000000
N	-1.42424302	3.21063246	0.00000000
H	-3.55992210	3.06008430	0.00000000
C	1.27328184	-2.44386159	0.00000000
H	3.08496242	-3.42337912	0.00000000
H	-3.18894791	0.52317785	0.00000000
N	-0.06784213	-2.68521057	0.00000000
N	1.87562976	-1.23566567	0.00000000
N	2.08198827	-3.53916846	0.00000000
C	-0.85156729	-1.60624221	0.00000000
H	1.66577155	-4.45939070	0.00000000
H	-1.92651421	-1.79609550	0.00000000
O	1.63862861	3.38020132	0.00000000
H	2.65746265	1.11538548	0.00000000

ImN^{N}

Total bonding energy = -3437.64 kcal mol^{-1}

N	1.65774757	0.77810715	0.00000000
C	1.03000100	-0.43457736	0.00000000
C	-0.41150419	-0.59175242	0.00000000
C	-1.14732896	0.62223373	0.00000000
C	-0.50275500	1.86082517	0.00000000
C	0.93032282	1.89406153	0.00000000
N	-2.49810813	0.93249125	0.00000000
C	-2.59990134	2.32162132	0.00000000
N	-1.41983281	2.90859872	0.00000000
N	1.56739984	3.09575145	0.00000000
C	1.21342067	-2.72934624	0.00000000
H	-3.27055015	0.27809696	0.00000000
N	-0.13605745	-2.98205496	0.00000000
N	1.81902707	-1.53559812	0.00000000
N	2.01312335	-3.83668707	0.00000000
C	-0.91166025	-1.90491056	0.00000000
H	-1.98928063	-2.08830959	0.00000000
H	1.03073557	3.95208110	0.00000000
H	3.01629052	-3.72303073	0.00000000
H	1.59119927	-4.75356076	0.00000000
H	2.57827179	3.11476742	0.00000000
H	-3.56056053	2.82119203	0.00000000
H	5.59721780	-0.20309303	0.00000000
H	0.54339780	1.90147665	0.00000000
H	2.05277484	2.88094415	0.00000000
O	1.77593807	-2.62178154	0.00000000
N	4.52315072	2.17794159	0.00000000
O	3.88195915	3.27660389	0.00000000
O	5.77390717	2.13714853	0.00000000
H	-3.98992261	2.54700662	0.00000000

NaN^{O}

Total bonding energy = -2869.68 kcal mol^{-1}

C	0.50753124	2.15941776	0.00000000
C	-0.89238783	1.89918747	0.00000000
C	0.87710773	-0.23493888	0.00000000
C	1.11238461	-2.66708721	0.00000000
C	1.67469778	-1.42466104	0.00000000
C	1.37566594	1.08517359	0.00000000
O	-0.92908492	-3.93618083	0.00000000
H	2.45163299	1.24817290	0.00000000
H	-2.08428713	-1.72961057	0.00000000
H	0.87426528	3.18264316	0.00000000
N	-1.06954439	-1.64238752	0.00000000
H	1.71021491	-3.57302586	0.00000000
C	-0.33602146	-2.85375980	0.00000000
H	2.75913723	-1.31758587	0.00000000
N	-1.40377080	0.65498592	0.00000000
C	-0.54016815	-0.37257672	0.00000000
N	-1.79862144	2.92590541	0.00000000
H	-2.78522050	2.70618030	0.00000000
H	-1.50353111	3.89014775	0.00000000

NaO^{O}

Total bonding energy = -2748.64 kcal mol^{-1}

H	-1.38296775	-3.35075795	0.00000000
H	-2.55221616	-1.15699889	0.00000000
N	1.39152697	1.11729480	0.00000000
C	0.65659943	-0.03138166	0.00000000
C	-0.74825729	0.03572713	0.00000000
C	-1.34304593	1.33477448	0.00000000
C	-0.60053257	2.48307817	0.00000000
C	0.84963975	2.44972542	0.00000000
H	2.40935026	1.08448823	0.00000000
H	-2.43044973	1.39496053	0.00000000
N	1.27876360	-1.24445382	0.00000000
C	0.61227866	-2.51992199	0.00000000
C	-0.83431223	-2.41463078	0.00000000
C	-1.46405380	-1.20072220	0.00000000
H	2.29499273	-1.30874460	0.00000000
H	-1.05813889	3.46685764	0.00000000
O	1.29486933	-3.54344024	0.00000000
O	1.62595364	3.40414569	0.00000000

ImO^{N}-NaN^{O}
Total bonding energy = -6224.85 kcal mol^{-1}

C	-3.75885381	2.45872121	0.00000000
C	-2.33865074	2.28000303	0.00000000
C	-4.00990059	0.05306461	0.00000000
C	-4.13742286	-2.38133155	0.00000000
C	-4.75548183	-1.16266153	0.00000000
C	-4.57229210	1.35132150	0.00000000
O	-2.06320603	-3.56675315	0.00000000
H	-5.65507630	1.46141576	0.00000000
H	-0.96003780	-1.32038812	0.00000000
H	-4.17139328	3.46432912	0.00000000
N	-1.99917323	-1.26757254	0.00000000
H	-4.69008478	-3.31521877	0.00000000
C	-2.69165847	-2.48507565	0.00000000
H	-5.84336579	-1.10160440	0.00000000
N	-1.77143888	1.04806543	0.00000000
C	-2.58809671	-0.02416548	0.00000000
N	-1.51108070	3.35023887	0.00000000
H	-0.48404825	3.24344921	0.00000000
H	-1.90360130	4.28055961	0.00000000
N	1.21892431	0.80765836	0.00000000
C	1.78456027	-0.44778308	0.00000000
C	3.20485618	-0.59622580	0.00000000
C	3.95113222	0.61803192	0.00000000
C	3.35675978	1.88527136	0.00000000
C	1.91415193	2.03764382	0.00000000
N	5.31002548	0.86458171	0.00000000
C	5.47227059	2.25003410	0.00000000
N	4.32161288	2.88547137	0.00000000
H	6.45435776	2.70638097	0.00000000
C	1.53561973	-2.73936885	0.00000000
H	-0.30503927	-3.72115565	0.00000000
H	6.05062442	0.17340684	0.00000000
N	2.88533810	-2.98457163	0.00000000
N	0.95981108	-1.50621872	0.00000000
N	0.72631601	-3.81299159	0.00000000
C	3.67699871	-1.92045846	0.00000000
H	1.16543195	-4.72383213	0.00000000
H	4.75078403	-2.12119528	0.00000000
O	1.29193686	3.11045163	0.00000000
H	0.17839040	0.86847197	0.00000000

ImN^{N}-NaO^{O}
Total bonding energy = -6224.41 kcal mol^{-1}

N	-1.03385679	0.81844772	0.00000000
C	-1.65483562	-0.39947472	0.00000000
C	-3.08872048	-0.56588350	0.00000000
C	-3.83546849	0.64099482	0.00000000
C	-3.20426052	1.88329145	0.00000000
C	-1.77151719	1.95128489	0.00000000
N	-5.18855684	0.93523513	0.00000000
C	-5.30482657	2.32431088	0.00000000
N	-4.13088449	2.92155981	0.00000000
N	-1.16529017	3.14842288	0.00000000
C	-1.44908827	-2.71717853	0.00000000
H	4.74964512	-3.33753573	0.00000000
H	-5.95370974	0.27210915	0.00000000
H	5.88808982	-1.11568515	0.00000000
N	1.86382185	1.04010897	0.00000000
C	2.64205666	-0.08009237	0.00000000
C	4.04990054	0.02591599	0.00000000
C	4.61173474	1.33459367	0.00000000
C	3.82510150	2.45319021	0.00000000
C	2.38333109	2.35182419	0.00000000
H	0.81322523	0.94366259	0.00000000
N	-2.80342171	-2.95407581	0.00000000
N	-0.85578417	-1.49802091	0.00000000
N	-0.66473473	-3.81302121	0.00000000
C	-3.57958546	-1.88220285	0.00000000
H	5.69669323	1.42880127	0.00000000
H	-4.65679559	-2.06826862	0.00000000
H	-1.75322327	3.97253879	0.00000000
N	2.03898734	-1.30274443	0.00000000
C	2.74861672	-2.52385606	0.00000000
C	4.19047611	-2.40764024	0.00000000
C	4.80121908	-1.18482680	0.00000000
H	0.36506987	-3.74978197	0.00000000
H	-1.12858821	-4.71094671	0.00000000
H	0.98444706	-1.36280020	0.00000000
H	4.23977831	3.45580888	0.00000000
H	-0.13269600	3.23271975	0.00000000
O	2.12705329	-3.60520874	0.00000000
H	-6.27038428	2.81418015	0.00000000
O	1.60698098	3.33024340	0.00000000

Cartesian coordinates (Å) and total bonding energies (kcal mol^{-1}) of stacked hydrogen-bonded artificial DNA base pairs with 3.4 Å distance between the base pairs and a twist angle of 36^{O} at BLYP-D3(BJ)/TZ2P level of theory in the gas phase.

isoG-isoC//isoG-isoC
Total bonding energy = -8787.06 kcal mol^{-1}

N	-0.92683556	-0.16940991	0.00000000
C	-1.52423127	-1.47153992	0.00000000
N	-2.87967415	-1.57773249	0.00000000
C	-3.52272092	-0.40865932	0.00000000
C	-2.99555527	0.90331304	0.00000000
C	-1.59666758	1.02109778	0.00000000
N	-4.89615135	-0.21021709	0.00000000
C	-5.12114205	1.16822176	0.00000000
N	-4.00527806	1.86535798	0.00000000
N	-0.91247513	2.17613709	0.00000000
O	-0.74337809	-2.45646368	0.00000000
H	-5.59010650	-0.94870304	0.00000000
H	-6.12272853	1.58012981	0.00000000
H	-1.44601238	3.03558497	0.00000000
H	0.12274378	2.20328266	0.00000000
N	1.94072568	-0.09544178	0.00000000
C	2.61003455	-1.23883902	0.00000000
N	4.00035851	-1.25397275	0.00000000

P-Z//P-Z
Total bonding energy = -9685.49 kcal mol^{-1}

N	-1.11800546	-0.51647112	0.00000000
C	-1.77038124	-1.71076886	0.00000000
N	-3.13364929	-1.87847279	0.00000000
C	-3.79508461	-0.74314719	0.00000000
N	-3.22918315	0.51791248	0.00000000
C	-1.79416392	0.65169557	0.00000000
N	-5.14835807	-0.54002745	0.00000000
C	-5.42075920	0.83822178	0.00000000
C	-4.23259183	1.49642119	0.00000000
O	-1.30729231	1.78964623	0.00000000
H	0.73877311	-0.38002492	0.00000000
H	-5.82335275	-1.29448217	0.00000000
H	-6.43130847	1.21622011	0.00000000
H	-1.49250832	-3.71321428	0.00000000
N	-1.01915799	-2.81961915	0.00000000
N	1.78173906	-0.32739741	0.00000000
C	2.44907696	-1.56764794	0.00000000

C	4.71224403	-0.06582590	0.00000000
C	4.06040724	1.11771494	0.00000000
C	2.59276749	1.13066605	0.00000000
O	1.94144772	2.19618929	0.00000000
H	4.49666828	-2.13710118	0.00000000
H	0.11571344	-0.14684442	0.00000000
H	5.79310730	-0.16692530	0.00000000
N	1.95334108	-2.40887491	0.00000000
H	0.89204898	-2.41459550	0.00000000
H	2.45498456	-3.28663461	0.00000000
H	4.59636424	2.06008548	0.00000000
N	-0.65024907	-0.68183577	3.40000000
C	-0.36817954	-2.08642146	3.40000000
N	-1.40233744	-2.96904240	3.40000000
C	-2.60973717	-2.40121574	3.40000000
C	-2.95440920	-1.02994761	3.40000000
C	-1.89191742	-0.11241220	3.40000000
N	-3.83750714	-3.04795475	3.40000000
C	-4.82975447	-2.06502052	3.40000000
N	-4.33676793	-0.84513707	3.40000000
N	-2.01730917	1.22419246	3.40000000
O	0.84246761	-2.42426754	3.40000000
H	-3.96485750	-4.05329904	3.40000000
H	-5.88216843	-2.32049766	3.40000000
H	-2.95412066	1.60589508	3.40000000
H	-1.19575525	1.85464010	3.40000000
N	1.62617933	1.06351592	3.40000000
C	2.83973362	0.53189799	3.40000000
N	3.97342471	1.33686647	3.40000000
C	3.85097700	2.71653327	3.40000000
C	2.62796210	3.29089788	3.40000000
C	1.43300413	2.43871854	3.40000000
O	0.27977652	2.91790879	3.40000000
H	4.89403761	0.91412413	3.40000000
H	0.17992712	-0.05078498	3.40000000
H	4.78483849	3.27005763	3.40000000
N	2.99618728	-0.80067566	3.40000000
H	2.14094641	-1.42911556	3.40000000
H	3.91795958	-1.21593953	3.40000000
H	2.50764892	4.36831928	3.40000000

C	3.88631621	-1.49114429	0.00000000
C	4.51428690	-0.27500647	0.00000000
C	3.79445006	0.94610875	0.00000000
C	2.36835181	0.91059660	0.00000000
N	1.57019029	1.98283956	0.00000000
H	4.43691034	-2.42543586	0.00000000
H	0.01727895	-2.76304916	0.00000000
H	5.59721780	-0.20309303	0.00000000
H	0.54339780	1.90147665	0.00000000
H	2.05277484	2.88094415	0.00000000
O	1.77593807	-2.62178154	0.00000000
N	4.52315072	2.17794159	0.00000000
O	3.88195915	3.27660389	0.00000000
O	5.77390717	2.13714853	0.00000000
H	-3.98992261	2.54700662	0.00000000
N	-0.60091131	-1.07498104	3.40000000
C	-0.42670380	-2.42464507	3.40000000
N	-1.43103693	-3.36162924	3.40000000
C	-2.63347698	-2.83191347	3.40000000
N	-2.91688536	-1.47906624	3.40000000
C	-1.83456614	-0.52735030	3.40000000
N	-3.84768900	-3.46302033	3.40000000
C	-4.87818072	-2.50810665	3.40000000
C	-4.30381303	-1.27722489	3.40000000
O	-2.10954936	0.67944707	3.40000000
H	0.82105305	0.12679332	3.40000000
H	-3.95031381	-4.47013894	3.40000000
H	-5.91791409	-2.79628554	3.40000000
H	0.97510800	-3.88132784	3.40000000
N	0.83281442	-2.88016585	3.40000000
N	1.63389655	0.78240988	3.40000000
C	2.90278522	0.17127750	3.40000000
C	4.02056848	1.07795829	3.40000000
C	3.81377957	2.43094636	3.40000000
C	2.51366581	2.99573984	3.40000000
C	1.38080161	2.12877039	3.40000000
N	0.10482678	2.52708560	3.40000000
H	5.01517130	0.64573164	3.40000000
H	1.63805852	-2.22519741	3.40000000
H	4.64761941	3.12565636	3.40000000
H	-0.67804187	1.85772814	3.40000000
H	-0.03264675	3.53732355	3.40000000
O	2.97780861	-1.07719562	3.40000000
N	2.37914386	4.42063305	3.40000000
O	1.21463148	4.93258657	3.40000000
O	3.41500464	5.12280696	3.40000000
H	-4.72500813	-0.28464603	3.40000000

isoG//isoG

Total bonding energy = -4916.49 kcal mol^{-1}

N	-0.92683556	-0.16940991	0.00000000
C	-1.52423127	-1.47153992	0.00000000
N	-2.87967415	-1.57773249	0.00000000
C	-3.52272092	-0.40865932	0.00000000
C	-2.99555527	0.90331304	0.00000000
C	-1.59666758	1.02109778	0.00000000
N	-4.89615135	-0.21021709	0.00000000
C	-5.12114205	1.16822176	0.00000000
N	-4.00527806	1.86535798	0.00000000
N	-0.91247513	2.17613709	0.00000000
O	-0.74337809	-2.45646368	0.00000000
H	-5.59010650	-0.94870304	0.00000000
H	-6.12272853	1.58012981	0.00000000
H	-1.44601238	3.03558497	0.00000000
H	0.12274378	2.20328266	0.00000000
C	-2.60973717	-2.40121574	3.40000000
C	-2.95440920	-1.02994761	3.40000000
C	-1.89191742	-0.11241220	3.40000000
N	-3.83750714	-3.04795475	3.40000000
C	-4.82975447	-2.06502052	3.40000000
N	-4.33676793	-0.84513707	3.40000000
N	-2.01730917	1.22419246	3.40000000

isoC//isoC

Total bonding energy = -3781.10 kcal mol^{-1}

H	0.89204898	-2.41459550	0.00000000
H	2.45498456	-3.28663461	0.00000000
N	1.62617933	1.06351592	3.40000000
C	2.83973362	0.53189799	3.40000000
N	3.97342471	1.33686647	3.40000000
C	3.85097700	2.71653327	3.40000000
C	2.62796210	3.29089788	3.40000000
C	1.43300413	2.43871854	3.40000000
O	0.27977652	2.91790879	3.40000000
H	4.89403761	0.91412413	3.40000000
H	4.59636424	2.06008548	0.00000000
H	4.78483849	3.27005763	3.40000000
N	2.99618728	-0.80067566	3.40000000
H	2.14094641	-1.42911556	3.40000000
H	3.91795958	-1.21593953	3.40000000
N	1.94072568	-0.09544178	0.00000000
C	2.61003455	-1.23883902	0.00000000
N	4.00035851	-1.25397275	0.00000000
C	4.71224403	-0.06582590	0.00000000
C	4.06040724	1.11771494	0.00000000
C	2.59276749	1.13066605	0.00000000
O	1.94144772	2.19618929	0.00000000

H	0.17992712	-0.05078498	3.40000000
H	0.11571344	-0.14684442	0.00000000
O	0.84246761	-2.42426754	3.40000000
H	-3.96485750	-4.05329904	3.40000000
H	-5.88216843	-2.32049766	3.40000000
H	-2.95412066	1.60589508	3.40000000
H	-1.19575525	1.85464010	3.40000000
N	-0.65024907	-0.68183577	3.40000000
C	-0.36817954	-2.08642146	3.40000000
N	-1.40233744	-2.96904240	3.40000000

P//P

Total bonding energy = -4925.01 kcal mol^{-1}

N	-1.11800546	-0.51647112	0.00000000
C	-1.77038124	-1.71076886	0.00000000
N	-3.13364929	-1.87847279	0.00000000
C	-3.79508461	-0.74314719	0.00000000
N	-3.22918315	0.51791248	0.00000000
C	-1.79416392	0.65169557	0.00000000
N	-5.14835807	-0.54002745	0.00000000
C	-5.42075920	0.83822178	0.00000000
C	-4.23259183	1.49642119	0.00000000
O	-1.30729231	1.78964623	0.00000000
N	-0.60091131	-1.07498104	3.40000000
H	-5.82335275	-1.29448217	0.00000000
H	-6.43130847	1.21622011	0.00000000
H	-1.49250832	-3.71321428	0.00000000
N	-1.01915799	-2.81961915	0.00000000
C	-0.42670380	-2.42464507	3.40000000
N	-1.43103693	-3.36162924	3.40000000
C	-2.63347698	-2.83191347	3.40000000
N	-2.91688536	-1.47906624	3.40000000
C	-1.83456614	-0.52735030	3.40000000
N	-3.84768900	-3.46302033	3.40000000
H	1.63805852	-2.22519741	3.40000000
C	-4.87818072	-2.50810665	3.40000000
H	0.01727895	-2.76304916	0.00000000
C	-4.30381303	-1.27722489	3.40000000
O	-2.10954936	0.67944707	3.40000000
N	0.83281442	-2.88016585	3.40000000
H	-3.95031381	-4.47013894	3.40000000
H	-5.91791409	-2.79628554	3.40000000
H	0.97510800	-3.88132784	3.40000000
H	-4.72500813	-0.28464603	3.40000000
H	-3.98992261	2.54700662	0.00000000

ImO^{N}-NaN^{O}//ImO^{N}-NaN^{O}

Total bonding energy = -12473.94 kcal mol^{-1}

C	1.17683312	4.33466905	0.00000000
C	1.44572892	2.92874871	0.00000000
C	-1.18865999	3.83003995	0.00000000
C	-3.54331487	3.19905105	0.00000000
C	-2.57528153	4.16344981	0.00000000
C	-0.12773284	4.76608950	0.00000000
O	-4.02974955	0.86003820	0.00000000
H	-0.35762570	5.82989947	0.00000000
H	-1.55243172	0.50502784	0.00000000
H	2.00574137	5.03776733	0.00000000
N	-1.82331163	1.50962527	0.00000000
H	-4.60227632	3.43607675	0.00000000
C	-3.19521560	1.79198872	0.00000000
H	-2.85338738	5.21695663	0.00000000
N	0.44936474	2.00860852	0.00000000
C	-0.82274860	2.45395870	0.00000000
N	2.71931689	2.47240389	0.00000000
H	2.93512437	1.46263817	0.00000000
H	3.48280896	3.13319809	0.00000000
N	1.14479707	-0.90968575	0.00000000
C	0.12559243	-1.83559026	0.00000000
C	0.42331059	-3.23224326	0.00000000
C	1.80875029	-3.56676768	0.00000000
C	2.83029543	-2.60988737	0.00000000
C	2.61003455	-1.23883902	0.00000000
N	4.00035851	-1.25397275	0.00000000
C	4.71224403	-0.06582590	0.00000000
C	4.06040724	1.11771494	0.00000000
C	2.59276749	1.13066605	0.00000000
O	1.94144772	2.19618929	0.00000000
H	4.49666828	-2.13710118	0.00000000
H	2.50764892	4.36831928	3.40000000

Z//Z

Total bonding energy = -4688.00 kcal mol^{-1}

C	4.02056848	1.07795829	3.40000000
C	3.81377957	2.43094636	3.40000000
C	2.51366581	2.99573984	3.40000000
C	1.38080161	2.12877039	3.40000000
N	0.10482678	2.52708560	3.40000000
H	5.01517130	0.64573164	3.40000000
H	0.82105305	0.12679332	3.40000000
H	4.64761941	3.12565636	3.40000000
H	-0.67804187	1.85772814	3.40000000
H	-0.03264675	3.53732355	3.40000000
H	0.73877311	-0.38002492	0.00000000
O	2.97780861	-1.07719562	3.40000000
N	2.37914386	4.42063305	3.40000000
O	1.21463148	4.93258657	3.40000000
O	3.41500464	5.12280696	3.40000000
N	1.78173906	-0.32739741	0.00000000
C	2.44907696	-1.56764794	0.00000000
C	3.88631621	-1.49114429	0.00000000
C	4.51428690	-0.27500647	0.00000000
C	3.79445006	0.94610875	0.00000000
C	2.36835181	0.91059660	0.00000000
N	1.57019029	1.98283956	0.00000000
H	4.43691034	-2.42543586	0.00000000
C	2.90278522	0.17127750	3.40000000
H	5.59721780	-0.20309303	0.00000000
H	0.54339780	1.90147665	0.00000000
H	2.05277484	2.88094415	0.00000000
O	1.77593807	-2.62178154	0.00000000
N	4.52315072	2.17794159	0.00000000
O	3.88195915	3.27660389	0.00000000
O	5.77390717	2.13714853	0.00000000
N	1.63389655	0.78240988	3.40000000

ImN^{N}-NaO^{O}// ImN^{N}-NaO^{O}

Total bonding energy = -12473.42 kcal mol^{-1}

N	-1.03385679	0.81844772	0.00000000
C	-1.65483562	-0.39947472	0.00000000
C	-3.08872048	-0.56588350	0.00000000
C	-3.83546849	0.64099482	0.00000000
C	-3.20426052	1.88329145	0.00000000
C	-1.77151719	1.95128489	0.00000000
N	-5.18855684	0.93523513	0.00000000
C	-5.30482657	2.32431088	0.00000000
N	-4.13088449	2.92155981	0.00000000
N	-1.16529017	3.14842288	0.00000000
C	-1.44908827	-2.71717853	0.00000000
H	4.74964512	-3.33753573	0.00000000
H	-5.95370974	0.27210915	0.00000000
H	5.88808982	-1.11568515	0.00000000
N	1.86382185	1.04010897	0.00000000
C	2.64205666	-0.08009237	0.00000000
C	4.04990054	0.02591599	0.00000000
C	4.61173474	1.33459367	0.00000000
C	3.82510150	2.45319021	0.00000000
C	2.38333109	2.35182419	0.00000000
H	0.81322523	0.94366259	0.00000000
N	-2.80342171	-2.95407581	0.00000000
N	-0.85578417	-1.49802091	0.00000000
N	-0.66473473	-3.81302121	0.00000000

C	2.52941991	-1.19080010	0.00000000
N	2.46315418	-4.78296389	0.00000000
C	3.83093420	-4.50913983	0.00000000
N	4.07969817	-3.21843840	0.00000000
H	4.56842749	-5.30214129	0.00000000
C	-2.13076200	-2.30697268	0.00000000
H	-3.63329165	-0.85979075	0.00000000
H	2.03466548	-5.70090012	0.00000000
N	-1.94687779	-3.66640296	0.00000000
N	-1.13590119	-1.37828176	0.00000000
N	-3.40192651	-1.86904678	0.00000000
C	-0.69020944	-4.09048789	0.00000000
H	-4.13249305	-2.56813606	0.00000000
H	-0.54930359	-5.17374950	0.00000000
O	3.35744574	-0.26752256	0.00000000
H	0.88109159	0.09871325	0.00000000
C	-1.59577655	4.19854608	3.40000000
C	-0.55185604	3.21918561	3.40000000
C	-3.21288713	2.39989060	3.40000000
C	-4.74695697	0.50537845	3.40000000
C	-4.53066092	1.85458915	3.40000000
C	-2.90477516	3.78076792	3.40000000
O	-3.76565364	-1.67284184	3.40000000
H	-3.71605420	4.50628064	3.40000000
H	-1.55279156	-0.50392037	3.40000000
H	-1.33844649	5.25458458	3.40000000
N	-2.36242556	0.14959681	3.40000000
H	-5.74299499	0.07469434	3.40000000
C	-3.63828826	-0.42835128	3.40000000
H	-5.37488905	2.54342755	3.40000000
N	-0.81708676	1.88912839	3.40000000
C	-2.10801833	1.50169479	3.40000000
N	0.74673103	3.59859113	3.40000000
H	1.51484835	2.90852195	3.40000000
H	0.97600401	4.58195424	3.40000000
N	1.46086015	-0.06305639	3.40000000
C	1.18053929	-1.41120233	3.40000000
C	2.24233038	-2.36612400	3.40000000
C	3.55980316	-1.82241892	3.40000000
C	3.82381041	-0.44783733	3.40000000
C	2.74627843	0.52337820	3.40000000
N	4.80408923	-2.42169337	3.40000000
C	5.74969677	-1.39620412	3.40000000
N	5.19229578	-0.20578494	3.40000000
H	6.81245594	-1.60426811	3.40000000
C	-0.36781815	-3.11881058	3.40000000
H	-2.43402237	-2.83118058	3.40000000
H	4.99698397	-3.41617872	3.40000000
N	0.58000037	-4.11052835	3.40000000
N	-0.10882968	-1.78271934	3.40000000
N	-1.65361823	-3.51169284	3.40000000
C	1.84593728	-3.71496915	3.40000000
H	-1.83374461	-4.50668418	3.40000000
H	2.59665771	-4.50852382	3.40000000
O	2.87347647	1.75702680	3.40000000
H	0.65479588	0.59775334	3.40000000

ImO^N// ImO^N

Total bonding energy = -6658.99 kcal mol^{-1}

C	3.82381041	-0.44783733	3.40000000
C	2.74627843	0.52337820	3.40000000
N	4.80408923	-2.42169337	3.40000000
C	5.74969677	-1.39620412	3.40000000
N	5.19229578	-0.20578494	3.40000000
H	6.81245594	-1.60426811	3.40000000
C	-0.36781815	-3.11881058	3.40000000
H	-2.43402237	-2.83118058	3.40000000
H	4.99698397	-3.41617872	3.40000000
N	0.58000037	-4.11052835	3.40000000
N	-0.10882968	-1.78271934	3.40000000
N	-1.65361823	-3.51169284	3.40000000
C	1.84593728	-3.71496915	3.40000000
H	-1.83374461	-4.50668418	3.40000000
C	-3.57958546	-1.88220285	0.00000000
H	5.69669323	1.42880127	0.00000000
H	-4.65679559	-2.06826862	0.00000000
H	-1.75322327	3.97253879	0.00000000
N	2.03898734	-1.30274443	0.00000000
C	2.74861672	-2.52385606	0.00000000
C	4.19047611	-2.40764024	0.00000000
C	4.80121908	-1.18482680	0.00000000
H	0.36506987	-3.74978197	0.00000000
H	-1.12858821	-4.71094671	0.00000000
H	0.98444706	-1.36280020	0.00000000
H	4.23977831	3.45580888	0.00000000
H	-0.13269600	3.23271975	0.00000000
O	2.12705329	-3.60520874	0.00000000
H	-6.27038428	2.81418015	0.00000000
O	1.60698098	3.33024340	0.00000000
N	-1.31747921	0.05445235	3.40000000
C	-1.10398479	-1.29586981	3.40000000
C	-2.16620939	-2.27331372	3.40000000
C	-3.47972650	-1.73585611	3.40000000
C	-3.69927216	-0.35980229	3.40000000
C	-2.58012399	0.53735096	3.40000000
N	-4.74734807	-2.29313607	3.40000000
C	-5.65789051	-1.23769182	3.40000000
N	-5.05920553	-0.06448145	3.40000000
N	-2.79333609	1.86218724	3.40000000
C	0.42478043	-3.04999632	3.40000000
H	5.80429790	0.09164823	3.40000000
H	-4.97659411	-3.27936185	3.40000000
H	5.41934801	2.55832411	3.40000000
N	0.89650283	1.93699283	3.40000000
C	2.18454585	1.48816585	3.40000000
C	3.26120532	2.40143829	3.40000000
C	2.94651730	3.79041862	3.40000000
C	1.65262309	4.23301082	3.40000000
C	0.54578778	3.30355261	3.40000000
H	0.10324208	1.24144087	3.40000000
N	-0.53165361	-4.03770747	3.40000000
N	0.18817066	-1.71494169	3.40000000
N	1.70345594	-3.47552023	3.40000000
C	-1.78961439	-3.62676164	3.40000000
H	3.76889332	4.50435678	3.40000000
H	-2.55172898	-4.41046024	3.40000000
H	-3.75338713	2.18333261	3.40000000
N	2.41530937	0.14454431	3.40000000
C	3.70716301	-0.42624607	3.40000000
C	4.80534181	0.51527819	3.40000000
C	4.58069155	1.86354075	3.40000000
H	2.49941428	-2.81905465	3.40000000
H	1.85597796	-4.47460345	3.40000000
H	1.59746826	-0.52388506	3.40000000
H	1.39877921	5.28788728	3.40000000
H	-2.00749832	2.53732846	3.40000000
O	3.83991078	-1.66642458	3.40000000
H	-6.72698103	-1.40891984	3.40000000
O	-0.65739303	3.63878323	3.40000000

NaN^O// NaN^O

Total bonding energy = -5743.28 kcal mol^{-1}

C	1.17683312	4.33466905	0.00000000
C	1.44572892	2.92874871	0.00000000
C	-1.18865999	3.83003995	0.00000000
C	-3.54331487	3.19905105	0.00000000
C	-2.57528153	4.16344981	0.00000000
C	-0.12773284	4.76608950	0.00000000
O	-4.02974955	0.86003820	0.00000000
H	-0.35762570	5.82989947	0.00000000
H	-1.55243172	0.50502784	0.00000000
H	2.00574137	5.03776733	0.00000000
N	-1.82331163	1.50962527	0.00000000
H	-4.60227632	3.43607675	0.00000000
C	-3.19521560	1.79198872	0.00000000
H	-2.85338738	5.21695663	0.00000000

H	2.59665771	-4.50852382	3.40000000
O	2.87347647	1.75702680	3.40000000
H	0.65479588	0.59775334	3.40000000
N	1.46086015	-0.06305639	3.40000000
C	1.18053929	-1.41120233	3.40000000
N	1.14479707	-0.90968575	0.00000000
C	0.12559243	-1.83559026	0.00000000
C	0.42331059	-3.23224326	0.00000000
C	1.80875029	-3.56676768	0.00000000
C	2.83029543	-2.60988737	0.00000000
C	2.52941991	-1.19080010	0.00000000
N	2.46315418	-4.78296389	0.00000000
C	3.83093420	-4.50913983	0.00000000
N	4.07969817	-3.21843840	0.00000000
H	4.56842749	-5.30214129	0.00000000
C	-2.13076200	-2.30697268	0.00000000
H	-3.63329165	-0.85979075	0.00000000
H	2.03466548	-5.70090012	0.00000000
N	-1.94687779	-3.66640296	0.00000000
N	-1.13590119	-1.37828176	0.00000000
N	-3.40192651	-1.86904678	0.00000000
C	-0.69020944	-4.09048789	0.00000000
H	-4.13249305	-2.56813606	0.00000000
H	-0.54930359	-5.17374950	0.00000000
O	3.35744574	-0.26752256	0.00000000
H	0.88109159	0.09871325	0.00000000
C	2.24233038	-2.36612400	3.40000000
C	3.55980316	-1.82241892	3.40000000

ImN^{N}// ImN^{N}

Total bonding energy = -6882.17 kcal mol^{-1}

N	-1.03385679	0.81844772	0.00000000
C	-1.65483562	-0.39947472	0.00000000
C	-3.08872048	-0.56588350	0.00000000
C	-3.83546849	0.64099482	0.00000000
C	-3.20426052	1.88329145	0.00000000
C	-1.77151719	1.95128489	0.00000000
N	-5.18855684	0.93523513	0.00000000
C	-5.30482657	2.32431088	0.00000000
N	-4.13088449	2.92155981	0.00000000
N	-1.16529017	3.14842288	0.00000000
C	-1.44908827	-2.71717853	0.00000000
C	-3.69927216	-0.35980229	3.40000000
H	-5.95370974	0.27210915	0.00000000
C	-2.58012399	0.53735096	3.40000000
N	-4.74734807	-2.29313607	3.40000000
C	-5.65789051	-1.23769182	3.40000000
N	-5.05920553	-0.06448145	3.40000000
N	-2.79333609	1.86218724	3.40000000
C	0.42478043	-3.04999632	3.40000000
N	0.18817066	-1.71494169	3.40000000
H	-4.97659411	-3.27936185	3.40000000
N	-2.80342171	-2.95407581	0.00000000
N	-0.85578417	-1.49802091	0.00000000
N	-0.66473473	-3.81302121	0.00000000
C	-3.57958546	-1.88220285	0.00000000
N	1.70345594	-3.47552023	3.40000000
H	-4.65679559	-2.06826862	0.00000000
H	-1.75322327	3.97253879	0.00000000
C	-1.78961439	-3.62676164	3.40000000
H	-6.72698103	-1.40891984	3.40000000
H	-2.55172898	-4.41046024	3.40000000
H	-3.75338713	2.18333261	3.40000000
H	0.36506987	-3.74978197	0.00000000
H	-1.12858821	-4.71094671	0.00000000
H	2.49941428	-2.81905465	3.40000000
H	1.85597796	-4.47460345	3.40000000
H	-0.13269600	3.23271975	0.00000000
H	-2.00749832	2.53732846	3.40000000
H	-6.27038428	2.81418015	0.00000000
N	-0.53165361	-4.03770747	3.40000000
N	-1.31747921	0.05445235	3.40000000
C	-1.10398479	-1.29586981	3.40000000
N	0.44936474	2.00860852	0.00000000
C	-0.82274860	2.45395870	0.00000000
N	2.71931689	2.47240389	0.00000000
H	2.93512437	1.46263817	0.00000000
H	3.48280896	3.13319809	0.00000000
H	1.51484835	2.90852195	3.40000000
H	0.97600401	4.58195424	3.40000000
C	-1.59577655	4.19854608	3.40000000
C	-0.55185604	3.21918561	3.40000000
C	-3.21288713	2.39989060	3.40000000
C	-4.74695697	0.50537845	3.40000000
C	-4.53066092	1.85458915	3.40000000
C	-2.90477516	3.78076792	3.40000000
O	-3.76565364	-1.67284184	3.40000000
H	-3.71605420	4.50628064	3.40000000
H	-1.55279156	-0.50392037	3.40000000
H	-1.33844649	5.25458458	3.40000000
N	-2.36242556	0.14959681	3.40000000
H	-5.74299499	0.07469434	3.40000000
C	-3.63828826	-0.42835128	3.40000000

NaO^{O}// NaO^{O}

Total bonding energy = -5497.85 kcal mol^{-1}

C	1.65262309	4.23301082	3.40000000
C	0.54578778	3.30355261	3.40000000
H	0.10324208	1.24144087	3.40000000
H	5.80429790	0.09164823	3.40000000
O	2.12705329	-3.60520874	0.00000000
O	-0.65739303	3.63878323	3.40000000
O	1.60698098	3.33024340	0.00000000
H	3.76889332	4.50435678	3.40000000
C	2.94651730	3.79041862	3.40000000
H	5.41934801	2.55832411	3.40000000
N	2.41530937	0.14454431	3.40000000
H	4.74964512	-3.33753573	0.00000000
C	3.70716301	-0.42624607	3.40000000
H	5.88808982	-1.11568515	0.00000000
N	1.86382185	1.04010897	0.00000000
C	2.64205666	-0.08009237	0.00000000
C	4.04990054	0.02591599	0.00000000
C	4.61173474	1.33459367	0.00000000
C	3.82510150	2.45319021	0.00000000
C	2.38333109	2.35182419	0.00000000
H	0.81322523	0.94366259	0.00000000
C	4.80534181	0.51527819	3.40000000
C	4.58069155	1.86354075	3.40000000
N	0.89650283	1.93699283	3.40000000
C	2.18454585	1.48816585	3.40000000
H	5.69669323	1.42880127	0.00000000
H	1.59746826	-0.52388506	3.40000000
H	1.39877921	5.28788728	3.40000000
N	2.03898734	-1.30274443	0.00000000
C	2.74861672	-2.52385606	0.00000000
C	4.19047611	-2.40764024	0.00000000
C	4.80121908	-1.18482680	0.00000000
C	3.26120532	2.40143829	3.40000000
O	3.83991078	-1.66642458	3.40000000
H	0.98444706	-1.36280020	0.00000000
H	4.23977831	3.45580888	0.00000000

C -2.16620939 -2.27331372 3.40000000
C -3.47972650 -1.73585611 3.40000000

Cartesian coordinates (Å) and total bonding energies (kcal mol^{-1}) of non-hydrogen-bonded artificial DNA base pairs optimized in Cs symmetry at BLYP-D3(BJ)/TZ2P level of theory in the gas phase.

NaM
Total bonding energy = -3146.61 kcal mol^{-1}

C	1.87420800	-1.00932209	0.00000000
C	2.05831597	-2.37899565	0.00000000
C	0.94386445	-3.25411876	0.00000000
C	-0.33880966	-2.73927878	0.00000000
C	-2.05668695	0.59156863	0.00000000
C	-0.93514277	1.46925781	0.00000000
C	0.35244383	0.96099217	0.00000000
C	0.56777561	-0.44706142	0.00000000
C	-0.56242897	-1.33701609	0.00000000
C	-1.86961445	-0.77000559	0.00000000
H	3.06523164	-2.79094159	0.00000000
H	1.10202907	-4.33010684	0.00000000
H	-1.19967153	-3.40594895	0.00000000
H	-3.05172837	1.02907516	0.00000000
H	-2.73067495	-1.43590695	0.00000000
H	1.21883046	1.61469926	0.00000000
O	-1.25764896	2.80803034	0.00000000
C	-0.17367366	3.75210354	0.00000000
H	2.73333710	-0.34048309	0.00000000
H	0.45054652	3.63745149	0.89679406
H	-0.64104888	4.73855589	0.00000000
H	0.45054652	3.63745149	-0.89679406

TPT3
Total bonding energy = -2135.13 kcal mol^{-1}

H	-0.89075687	3.00134916	0.00000000
H	1.44369514	2.07169703	0.00000000
S	-3.19844948	-1.16640303	0.00000000
H	-2.71970261	1.52535848	0.00000000
N	-1.78811907	1.11655206	0.00000000
C	-0.68384099	1.93644932	0.00000000
C	0.57991018	1.41565856	0.00000000
C	0.72123312	-0.00668099	0.00000000
C	-0.44215722	-0.80591539	0.00000000
C	-1.77139915	-0.28022433	0.00000000
S	-0.06916942	-2.50647135	0.00000000
C	1.91293103	-0.80254210	0.00000000
C	1.63879654	-2.14616975	0.00000000
H	2.91684874	-0.38916810	0.00000000
H	2.35018006	-2.96348957	0.00000000

Px
Total bonding energy = -2437.65 kcal mol^{-1}

C	-0.83060925	1.34168652	0.00000000
C	-0.01149616	0.19529268	0.00000000
C	-0.88189937	-0.93710746	0.00000000
C	-2.17810463	-0.44140975	0.00000000
N	-2.13427334	0.93813474	0.00000000
O	-3.43780662	-2.35617379	0.00000000
H	-0.60038764	-1.97943104	0.00000000
H	-2.97148264	1.51014421	0.00000000
H	-0.55695694	2.38707611	0.00000000
N	-3.43665622	-1.10909153	0.00000000
O	-4.46687675	-0.38501565	0.00000000
C	1.40407481	0.18268698	0.00000000

5SICS
Total bonding energy = -2992.31 kcal mol^{-1}

C	-0.76081282	1.10513136	0.00000000
C	-1.89418627	0.30105428	0.00000000
C	-1.72222417	-1.10513501	0.00000000
C	-0.46045155	-1.67295716	0.00000000
N	3.07290721	-0.55069588	0.00000000
C	2.94169053	0.81915181	0.00000000
C	1.70966179	1.39417440	0.00000000
C	0.54238400	0.55565668	0.00000000
C	0.69808850	-0.86639324	0.00000000
C	2.03111836	-1.46817803	0.00000000
S	2.39221911	-3.10942005	0.00000000
H	-2.60081157	-1.74792415	0.00000000
H	-0.32856549	-2.75119282	0.00000000
H	3.99988641	-0.96973024	0.00000000
H	3.87017388	1.38049891	0.00000000
H	1.61063081	2.47496963	0.00000000
C	-3.28369843	0.89554504	0.00000000
H	-0.86713791	2.18899827	0.00000000
H	-3.25291254	1.98973358	0.00000000
H	-3.84897993	0.56835632	0.88275768
H	-3.84897993	0.56835632	-0.88275768

Ds
Total bonding energy = -3166.82 kcal mol^{-1}

C	-1.56383933	-1.26796487	0.00000000
C	-1.26052612	-2.63735591	0.00000000
N	-0.00972889	-3.14552026	0.00000000
C	0.93194863	-2.20174179	0.00000000
C	0.76311811	-0.78898101	0.00000000
C	-0.55755033	-0.27606972	0.00000000
N	2.30922516	-2.39540768	0.00000000
C	2.89139558	-1.14226632	0.00000000
N	2.00891832	-0.15987513	0.00000000
H	3.96738558	-1.01439496	0.00000000
H	-2.06976010	-3.36619753	0.00000000
H	2.77531308	-3.29523030	0.00000000
C	0.03624148	2.21482640	0.00000000
C	-0.60349285	3.48400525	0.00000000
C	-1.97666146	3.39227125	0.00000000
S	-2.51215139	1.74410454	0.00000000
C	-0.85103319	1.14877862	0.00000000
H	-2.61037875	-0.97464457	0.00000000
H	1.10872310	2.05959022	0.00000000
H	-0.07072802	4.42995887	0.00000000
H	-2.70641861	4.19211489	0.00000000

Pa
Total bonding energy = -1721.03 kcal mol^{-1}

C	0.61644307	0.28311685	0.00000000
C	1.74468973	-0.53970570	0.00000000
C	1.28921450	-1.87860676	0.00000000
C	-0.11205837	-1.85082619	0.00000000
N	-0.49167225	-0.51673093	0.00000000
C	-1.09506118	-2.91038823	0.00000000
H	-0.67031178	-3.93952893	0.00000000
O	-2.31433178	-2.72061289	0.00000000
H	0.53213580	1.36153396	0.00000000
H	2.77183041	-0.19906569	0.00000000
H	1.89541927	-2.77550885	0.00000000
H	-1.46335666	-0.22567000	0.00000000

C	2.61679770	0.15983137	0.00000000
C	4.07466450	0.12928940	0.00000000
H	4.46047988	-0.39070381	-0.88719479
H	4.49005275	1.14549481	0.00000000
H	4.46047988	-0.39070381	0.88719479

NaM-5SICS

Total bonding energy = -6142.72 kcal mol^{-1}

C	-1.90496064	-2.48342685	0.00000000
C	-2.25242206	-3.82093657	0.00000000
C	-3.61510492	-4.20865850	0.00000000
C	-4.60565171	-3.24445293	0.00000000
C	-4.93440577	0.48738992	0.00000000
C	-3.56378865	0.87912561	0.00000000
C	-2.56400620	-0.08047303	0.00000000
C	-2.89799918	-1.46504544	0.00000000
C	-4.28109220	-1.86232850	0.00000000
C	-5.27678409	-0.84296180	0.00000000
H	-1.47642310	-4.58359918	0.00000000
H	-3.87719553	-5.26415683	0.00000000
H	-5.65533551	-3.53403579	0.00000000
H	-5.68963771	1.26921469	0.00000000
H	-6.32570676	-1.13413223	0.00000000
H	-1.51627490	0.20064223	0.00000000
O	-3.35932428	2.23541032	0.00000000
C	-1.99631184	2.70802389	0.00000000
H	-0.85659115	-2.19330561	0.00000000
H	-1.46050439	2.37278645	0.89648319
H	-2.05779574	3.79626714	0.00000000
H	-1.46050439	2.37278645	-0.89648319
C	4.19529445	-0.21432690	0.00000000
C	3.05527994	-1.00866130	0.00000000
C	1.79077355	-0.37024313	0.00000000
C	1.68282869	1.00794565	0.00000000
N	3.93048779	3.95371996	0.00000000
C	5.17592169	3.36792913	0.00000000
C	5.30138718	2.01429973	0.00000000
C	4.11869919	1.19839875	0.00000000
C	2.83326484	1.82569846	0.00000000
C	2.71741508	3.28226099	0.00000000
S	1.29289894	4.17746086	0.00000000
H	0.89040804	-0.97955650	0.00000000
H	0.71402069	1.49621934	0.00000000
H	3.85001240	4.96782337	0.00000000
H	6.01779029	4.05219658	0.00000000
H	6.28541218	1.55654262	0.00000000
C	3.13996225	-2.51710729	0.00000000
H	5.17907552	-0.68104250	0.00000000
H	4.17862331	-2.86200292	0.00000000
H	2.63913235	-2.93584417	-0.88250366
H	2.63913235	-2.93584417	0.88250366

Ds-Px

Total bonding energy = -5608.35 kcal mol^{-1}

H	6.90638804	-0.97307686	0.00000000
H	2.01377990	3.28012524	0.00000000
H	6.55467340	1.57666213	0.00000000
C	2.11506873	-2.68420891	0.00000000
C	1.08182487	-3.66122023	0.00000000
C	-0.17931302	-3.11021503	0.00000000
S	-0.12235034	-1.37899177	0.00000000
C	1.64112666	-1.38072838	0.00000000
H	0.70703463	1.22775117	0.00000000
H	3.17671826	-2.90169393	0.00000000
H	1.26241194	-4.73188473	0.00000000
H	-1.13624390	-3.61406198	0.00000000
C	1.78846610	1.13675158	0.00000000
C	2.53458669	2.32505003	0.00000000
N	3.88420296	2.37713988	0.00000000
C	4.45032227	1.17050778	0.00000000
C	3.81433615	-0.10212816	0.00000000
C	2.39802212	-0.13716539	0.00000000
N	5.81242830	0.88678278	0.00000000
C	5.93692098	-0.48904304	0.00000000

NaM-TPT3

Total bonding energy = -5286.12 kcal mol^{-1}

C	-1.48024420	-2.33261681	0.00000000
C	-1.83118070	-3.66899972	0.00000000
C	-3.19569726	-4.05200346	0.00000000
C	-4.18408343	-3.08532637	0.00000000
C	-4.49750867	0.65036534	0.00000000
C	-3.12481113	1.03415190	0.00000000
C	-2.13139914	0.06896591	0.00000000
C	-2.47167087	-1.31247451	0.00000000
C	-3.85601016	-1.70395565	0.00000000
C	-4.84645933	-0.67905679	0.00000000
H	-1.05853795	-4.43520342	0.00000000
H	-3.46079634	-5.10676241	0.00000000
H	-5.23434234	-3.37295746	0.00000000
H	-5.24954383	1.43535040	0.00000000
H	-5.89696036	-0.96457640	0.00000000
H	-1.08362769	0.34413419	0.00000000
O	-2.90294373	2.38771761	0.00000000
C	-1.52889291	2.83155385	0.00000000
H	-0.43235974	-2.03928047	0.00000000
H	-0.99825098	2.48212661	0.89358211
H	-1.56946746	3.92178591	0.00000000
H	-0.99825098	2.48212661	-0.89358211
H	6.68593605	2.82306966	0.00000000
H	6.56382723	0.31298180	0.00000000
S	1.99652321	3.65645834	0.00000000
H	4.69865254	4.07474825	0.00000000
N	4.61242554	3.06095513	0.00000000
C	5.74591795	2.28171566	0.00000000
C	5.66307710	0.91718805	0.00000000
C	4.36364703	0.32263581	0.00000000
C	3.23147417	1.16551375	0.00000000
C	3.29795410	2.59220831	0.00000000
S	1.74379065	0.26114290	0.00000000
C	3.99469206	-1.06215583	0.00000000
C	2.63495073	-1.23755490	0.00000000
H	4.70911575	-1.87953026	0.00000000
H	2.09105507	-2.17444150	0.00000000

Ds-Pa

Total bonding energy = -4889.71 kcal mol^{-1}

C	-1.82516695	5.56396435	0.00000000
C	-0.58922292	4.91419996	0.00000000
C	-0.84367687	3.52257540	0.00000000
C	-2.23447725	3.34683080	0.00000000
N	-2.80497768	4.61139550	0.00000000
C	-3.05159250	2.15572170	0.00000000
H	-2.47948490	1.20250547	0.00000000
O	-4.28549873	2.16019132	0.00000000
H	-2.06447392	6.61889610	0.00000000
H	0.37709956	5.40112091	0.00000000
H	-0.11047150	2.72609703	0.00000000
H	-3.80843289	4.75815542	0.00000000
C	-0.54690638	-1.12688444	0.00000000
C	-1.76412606	-1.82312574	0.00000000
N	-1.87378202	-3.16879330	0.00000000
C	-0.69234310	-3.78561851	0.00000000
C	0.60607876	-3.20310627	0.00000000
C	0.70026847	-1.78998223	0.00000000
N	-0.46560653	-5.15775688	0.00000000
C	0.90399028	-5.33932447	0.00000000
C	3.77306123	0.66652248	0.00000000

N	4.77417491	-1.11579139	0.00000000
C	-4.74260007	1.72328403	0.00000000
C	-3.70966000	0.76417805	0.00000000
C	-2.47784354	1.48287388	0.00000000
C	-2.80084428	2.83119708	0.00000000
N	-4.17535187	2.96525147	0.00000000
O	-0.73174615	3.81304158	0.00000000
H	-1.48611926	1.06379643	0.00000000
H	-4.63897244	3.86733126	0.00000000
H	-5.81454320	1.58639063	0.00000000
N	-1.96903981	3.98553738	0.00000000
O	-2.54183403	5.10589057	0.00000000
C	-3.86564102	-0.64277233	0.00000000
C	-3.97109627	-1.85077122	0.00000000
C	-4.09575017	-3.30314313	0.00000000
H	-3.62183144	-3.74184451	0.88853572
H	-5.14987467	-3.60895747	0.00000000
H	-3.62183144	-3.74184451	-0.88853572
N	1.57860494	-4.20375649	0.00000000
H	1.34717717	-6.32811386	0.00000000
H	-2.70199908	-1.27031227	0.00000000
H	-1.18547752	-5.87107752	0.00000000
C	3.25463788	-1.60794189	0.00000000
C	4.27262130	-0.61547244	0.00000000
S	2.04000880	0.68028910	0.00000000
C	1.97106558	-1.08316936	0.00000000
H	-0.57743153	-0.04067646	0.00000000
H	3.42872552	-2.67762528	0.00000000
H	5.33510807	-0.83855484	0.00000000
H	4.31670074	1.60282669	0.00000000

Cartesian coordinates (Å) and total bonding energies (kcal mol^{-1}) of stacked non-hydrogen-bonded artificial DNA base pairs with 3.4 Å distance between the base pairs and a twist angle of 36^{O} at BLYP-D3(BJ)/TZ2P level of theory in the gas phase.

NaM-5SICS//NaM-5SICS
Total bonding energy = -12305.85 kcal mol^{-1}

C	-3.00086721	-0.88942676	0.00000000
C	-4.06813789	-1.76726215	0.00000000
C	-5.39846871	-1.27997089	0.00000000
C	-5.63309209	0.08231659	0.00000000
C	-3.70553752	3.29467767	0.00000000
C	-2.36642851	2.80596997	0.00000000
C	-2.12162545	1.44198098	0.00000000
C	-3.20566269	0.51815452	0.00000000
C	-4.55812557	1.00970745	0.00000000
C	-4.76448852	2.41964545	0.00000000
H	-3.88862338	-2.84038991	0.00000000
H	-6.23091082	-1.97983398	0.00000000
H	-6.65251665	0.46502780	0.00000000
H	-3.85698792	4.37110139	0.00000000
H	-5.78423047	2.80062490	0.00000000
H	-1.10875762	1.05356700	0.00000000
O	-1.40380921	3.78304621	0.00000000
C	-0.02331370	3.36424001	0.00000000
H	-1.98218949	-1.27092987	0.00000000
H	0.21311601	2.77808750	0.89648319
H	0.56659811	4.28078662	0.00000000
H	0.21311601	2.77808750	-0.89648319
C	3.26808632	-2.63932631	0.00000000
C	1.87889716	-2.61187262	0.00000000
C	1.23114278	-1.35212327	0.00000000
C	1.95389260	-0.17369673	0.00000000
N	5.50376970	0.88834388	0.00000000
C	6.16702768	-0.31761853	0.00000000
C	5.47288800	-1.48647449	0.00000000
C	4.03649875	-1.45138569	0.00000000
C	3.36527804	-0.18833021	0.00000000
C	4.12769958	1.05814841	0.00000000
S	3.50142710	2.61968990	0.00000000
H	0.14458637	-1.31584657	0.00000000
H	1.45711053	0.79077604	0.00000000
H	6.03473877	1.75607302	0.00000000
H	7.25031600	-0.25887249	0.00000000
H	5.99991807	-2.43520315	0.00000000
C	1.06076428	-3.88200608	0.00000000
H	3.78965337	-3.59515917	0.00000000
H	1.69833416	-4.77154216	0.00000000
H	0.40945702	-3.92639090	-0.88250366
H	0.40945702	-3.92639090	0.88250366
C	-1.90496064	-2.48342685	3.40000000
C	-2.25242206	-3.82093657	3.40000000

NaM-TPT3//NaM-TPT3
Total bonding energy = -10591.65 kcal mol^{-1}

C	-2.56862047	-1.01706093	0.00000000
C	-3.63804023	-1.89194212	0.00000000
C	-4.96708127	-1.39975594	0.00000000
C	-5.19850394	-0.03673893	0.00000000
C	-3.25628579	3.16972588	0.00000000
C	-1.92016607	2.67336436	0.00000000
C	-1.68380098	1.30859957	0.00000000
C	-2.77107690	0.39099750	0.00000000
C	-4.12113775	0.88797683	0.00000000
C	-4.32000753	2.29930884	0.00000000
H	-3.46332235	-2.96596194	0.00000000
H	-5.80152269	-2.09725253	0.00000000
H	-6.21724656	0.34788933	0.00000000
H	-3.40329237	4.24682731	0.00000000
H	-5.33770493	2.68578763	0.00000000
H	-0.67439622	0.91535078	0.00000000
O	-0.94506561	3.63801164	0.00000000
C	0.42744525	3.18943589	0.00000000
H	-1.54844536	-1.39567788	0.00000000
H	0.65135541	2.59483981	0.89358211
H	1.03544207	4.09530128	0.00000000
H	0.65135541	2.59483981	-0.89358211
H	7.06839460	-1.64598328	0.00000000
H	5.49421386	-3.60491325	0.00000000
S	3.76443349	1.78461004	0.00000000
H	6.19636668	0.53474191	0.00000000
N	5.53071493	-0.23475099	0.00000000
C	5.98970408	-1.53141909	0.00000000
C	5.12063522	-2.58665248	0.00000000
C	3.71990518	-2.30386952	0.00000000
C	3.29938931	-0.95649243	0.00000000
C	4.19176273	0.15865179	0.00000000
S	1.56425222	-0.81370538	0.00000000
C	2.60745423	-3.20732320	0.00000000
C	1.40430340	-2.54998813	0.00000000
H	2.70499450	-4.28852071	0.00000000
H	0.41359444	-2.98825146	0.00000000
C	-1.48024420	-2.33261681	3.40000000
C	-1.83118070	-3.66899972	3.40000000
C	-3.19569726	-4.05200346	3.40000000
C	-4.18408343	-3.08532637	3.40000000
C	-4.49750867	0.65036534	3.40000000
C	-3.12481113	1.03415190	3.40000000
C	-2.13139914	0.06896591	3.40000000
C	-2.47167087	-1.31247451	3.40000000

C	-3.61510492	-4.20865850	3.40000000
C	-4.60565171	-3.24445293	3.40000000
C	-4.93440577	0.48738992	3.40000000
C	-3.56378865	0.87912561	3.40000000
C	-2.56400620	-0.08047303	3.40000000
C	-2.89799918	-1.46504544	3.40000000
C	-4.28109220	-1.86232850	3.40000000
C	-5.27678409	-0.84296180	3.40000000
H	-1.47642310	-4.58359918	3.40000000
H	-3.87719553	-5.26415683	3.40000000
H	-5.65533551	-3.53403579	3.40000000
H	-5.68963771	1.26921469	3.40000000
H	-6.32570676	-1.13413223	3.40000000
H	-1.51627490	0.20064223	3.40000000
O	-3.35932428	2.23541032	3.40000000
C	-1.99631184	2.70802389	3.40000000
H	-0.85659115	-2.19330561	3.40000000
H	-1.46050439	2.37278645	4.29648319
H	-2.05779574	3.79626714	3.40000000
H	-1.46050439	2.37278645	2.50351681
C	4.19529445	-0.21432690	3.40000000
C	3.05527994	-1.00866130	3.40000000
C	1.79077355	-0.37024313	3.40000000
C	1.68282869	1.00794565	3.40000000
N	3.93048779	3.95371996	3.40000000
C	5.17592169	3.36792913	3.40000000
C	5.30138718	2.01429973	3.40000000
C	4.11869919	1.19839875	3.40000000
C	2.83326484	1.82569846	3.40000000
C	2.71741508	3.28226099	3.40000000
S	1.29289894	4.17746086	3.40000000
H	0.89040804	-0.97955650	3.40000000
H	0.71402069	1.49621934	3.40000000
H	3.85001240	4.96782337	3.40000000
H	6.01779029	4.05219658	3.40000000
H	6.28541218	1.55654262	3.40000000
C	3.13996225	-2.51710729	3.40000000
H	5.17907552	-0.68104250	3.40000000
H	4.17862331	-2.86200292	3.40000000
H	2.63913235	-2.93584417	2.51749634
H	2.63913235	-2.93584417	4.28250366

NaM//NaM

Total bonding energy = -6300.44 kcal mol^{-1}

C	-3.00086721	-0.88942676	0.00000000
C	-4.06813789	-1.76726215	0.00000000
C	-5.39846871	-1.27997089	0.00000000
C	-5.63309209	0.08231659	0.00000000
C	-3.70553752	3.29467767	0.00000000
C	-2.36642851	2.80596997	0.00000000
C	-2.12162545	1.44198098	0.00000000
C	-3.20566269	0.51815452	0.00000000
C	-4.55812557	1.00970745	0.00000000
C	-4.76448852	2.41964545	0.00000000
H	-3.88862338	-2.84038991	0.00000000
H	-6.23091082	-1.97983398	0.00000000
H	-6.65251665	0.46502780	0.00000000
H	-3.85698792	4.37110139	0.00000000
H	-5.78423047	2.80062490	0.00000000
H	-1.10875762	1.05356700	0.00000000
O	-1.40380921	3.78304621	0.00000000
C	-0.02331370	3.36424001	0.00000000
H	-1.98218949	-1.27092987	0.00000000
H	0.21311601	2.77808750	0.89648319
H	0.56659811	4.28078662	0.00000000
H	0.21311601	2.77808750	-0.89648319
C	-2.25242206	-3.82093657	3.40000000
C	-3.61510492	-4.20865850	3.40000000
C	-4.60565171	-3.24445293	3.40000000
C	-4.93440577	0.48738992	3.40000000
C	-3.56378865	0.87912561	3.40000000
C	-2.56400620	-0.08047303	3.40000000
C	-2.89799918	-1.46504544	3.40000000
C	-3.85601016	-1.70395565	3.40000000
C	-4.84645933	-0.67905679	3.40000000
H	-1.05853795	-4.43520342	3.40000000
H	-3.46079634	-5.10676241	3.40000000
H	-5.23434234	-3.37295746	3.40000000
H	-5.24954383	1.43535040	3.40000000
H	-5.89696036	-0.96457640	3.40000000
H	-1.08362769	0.34413419	3.40000000
O	-2.90294373	2.38771761	3.40000000
C	-1.52889291	2.83155385	3.40000000
H	-0.43235974	-2.03928047	3.40000000
H	-0.99825098	2.48212661	4.29358211
H	-1.56946746	3.92178591	3.40000000
H	-0.99825098	2.48212661	2.50641789
H	6.68593605	2.82306966	3.40000000
H	6.56382723	0.31298180	3.40000000
S	1.99652321	3.65645834	3.40000000
H	4.69865254	4.07474825	3.40000000
N	4.61242554	3.06095513	3.40000000
C	5.74591795	2.28171566	3.40000000

5SICS//5SICS

Total bonding energy = -5993.72 kcal mol^{-1}

H	0.40945702	-3.92639090	0.88250366
H	2.63913235	-2.93584417	4.28250366
C	4.19529445	-0.21432690	3.40000000
C	3.05527994	-1.00866130	3.40000000
C	1.79077355	-0.37024313	3.40000000
C	1.68282869	1.00794565	3.40000000
N	3.93048779	3.95371996	3.40000000
C	5.17592169	3.36792913	3.40000000
C	5.30138718	2.01429973	3.40000000
C	4.11869919	1.19839875	3.40000000
C	2.83326484	1.82569846	3.40000000
C	2.71741508	3.28226099	3.40000000
S	1.29289894	4.17746086	3.40000000
H	0.89040804	-0.97955650	3.40000000
H	0.71402069	1.49621934	3.40000000
H	3.85001240	4.96782337	3.40000000
H	6.01779029	4.05219658	3.40000000
H	6.28541218	1.55654262	3.40000000
C	3.13996225	-2.51710729	3.40000000
H	5.17907552	-0.68104250	3.40000000
H	4.17862331	-2.86200292	3.40000000
H	2.63913235	-2.93584417	2.51749634
C	3.26808632	-2.63932631	0.00000000
C	1.87889716	-2.61187262	0.00000000
C	1.23114278	-1.35212327	0.00000000
C	1.95389260	-0.17369673	0.00000000
N	5.50376970	0.88834388	0.00000000
C	6.16702768	-0.31761853	0.00000000
C	5.47288800	-1.48647449	0.00000000

C	-4.28109220	-1.86232850	3.40000000
C	-5.27678409	-0.84296180	3.40000000
H	-1.47642310	-4.58359918	3.40000000
H	-3.87719553	-5.26415683	3.40000000
H	-5.65533551	-3.53403579	3.40000000
H	-5.68963771	1.26921469	3.40000000
H	-6.32570676	-1.13413223	3.40000000
H	-1.51627490	0.20064223	3.40000000
O	-3.35932428	2.23541032	3.40000000
C	-1.99631184	2.70802389	3.40000000
H	-0.85659115	-2.19330561	3.40000000
H	-1.46050439	2.37278645	4.29648319
H	-2.05779574	3.79626714	3.40000000
H	-1.46050439	2.37278645	2.50351681
C	-1.90496064	-2.48342685	3.40000000

TPT3//TPT3

Total bonding energy = -4277.84 kcal mol^{-1}

C	3.29938931	-0.95649243	0.00000000
C	4.19176273	0.15865179	0.00000000
S	1.56425222	-0.81370538	0.00000000
C	2.60745423	-3.20732320	0.00000000
C	1.40430340	-2.54998813	0.00000000
H	2.70499450	-4.28852071	0.00000000
H	0.41359444	-2.98825146	0.00000000
C	3.23147417	1.16551375	3.40000000
C	3.29795410	2.59220831	3.40000000
S	1.74379065	0.26114290	3.40000000
C	3.99469206	-1.06215583	3.40000000
C	2.63495073	-1.23755490	3.40000000
H	4.70911575	-1.87953026	3.40000000
H	2.09105507	-2.17444150	3.40000000
H	6.68593605	2.82306966	3.40000000
C	4.36364703	0.32263581	3.40000000
H	6.56382723	0.31298180	3.40000000
S	1.99652321	3.65645834	3.40000000
H	4.69865254	4.07474825	3.40000000
N	4.61242554	3.06095513	3.40000000
C	5.74591795	2.28171566	3.40000000
C	5.66307710	0.91718805	3.40000000
H	7.06839460	-1.64598328	0.00000000
H	5.49421386	-3.60491325	0.00000000
S	3.76443349	1.78461004	0.00000000
H	6.19636668	0.53474191	0.00000000
N	5.53071493	-0.23475099	0.00000000
C	5.98970408	-1.53141909	0.00000000
C	5.12063522	-2.58665248	0.00000000
C	3.71990518	-2.30386952	0.00000000
C	4.03649875	-1.45138569	0.00000000
C	3.36527804	-0.18833021	0.00000000
C	4.12769958	1.05814841	0.00000000
S	3.50142710	2.61968990	0.00000000
H	0.14458637	-1.31584657	0.00000000
H	1.45711053	0.79077604	0.00000000
H	6.03473877	1.75607302	0.00000000
H	7.25031600	-0.25887249	0.00000000
H	5.99991807	-2.43520315	0.00000000
C	1.06076428	-3.88200608	0.00000000
H	3.78965337	-3.59515917	0.00000000
H	1.69833416	-4.77154216	0.00000000
H	0.40945702	-3.92639090	-0.88250366

Ds-Pa//Ds-Pa

Total bonding energy = -9796.93 kcal mol^{-1}

C	1.79382511	5.57414793	0.00000000
C	2.41180291	4.32200782	0.00000000
C	1.38796894	3.34572418	0.00000000
C	0.15948772	4.02103577	0.00000000
N	0.44123566	5.37942184	0.00000000
C	-1.20168877	3.53769656	0.00000000
H	-1.29913044	2.43025202	0.00000000
O	-2.19731270	4.26658444	0.00000000
H	2.22029503	6.56826675	0.00000000
H	3.47977917	4.14794504	0.00000000
H	1.51298631	2.27039234	0.00000000
H	-0.28431335	6.08796928	0.00000000
C	-1.10482261	-0.59020516	0.00000000
C	-2.49881439	-0.43801243	0.00000000
N	-3.37849147	-1.46222619	0.00000000
C	-2.78524806	-2.65568065	0.00000000
C	-1.39241061	-2.94761156	0.00000000
C	-0.48559606	-1.85973352	0.00000000
N	-3.40833702	-3.89903632	0.00000000
C	-2.40703268	-4.85095639	0.00000000
N	-1.19378785	-4.32879114	0.00000000
H	-2.62968278	-5.91140253	0.00000000
H	-2.93263399	0.56049100	0.00000000
H	-4.41000424	-4.05299529	0.00000000
C	1.68793283	-3.21388046	0.00000000
C	3.09485762	-3.00931145	0.00000000
C	3.44424274	-1.67852173	0.00000000
S	2.05026569	-0.64872164	0.00000000
C	0.95795458	-2.03486570	0.00000000
H	-0.49106094	0.30649779	0.00000000
H	1.20002856	-4.18159865	0.00000000
H	3.82330293	-3.81430296	0.00000000
H	4.43440215	-1.24057900	0.00000000
C	-1.82516695	5.56396435	3.40000000
C	-0.58922292	4.91419996	3.40000000
C	-0.84367687	3.52257540	3.40000000
C	-2.23447725	3.34683080	3.40000000
N	-2.80497768	4.61139550	3.40000000
C	-3.05159250	2.15572170	3.40000000
H	-2.47948490	1.20250547	3.40000000
O	-4.28549873	2.16019132	3.40000000
H	-2.06447392	6.61889610	3.40000000
H	0.37709956	5.40112091	3.40000000
H	-0.11047150	2.72609703	3.40000000
H	-3.80843289	4.75815542	3.40000000
C	-0.54690638	-1.12688444	3.40000000
C	-1.76412606	-1.82312574	3.40000000
N	-1.87378202	-3.16879330	3.40000000
C	-0.69234310	-3.78561851	3.40000000
C	0.60607876	-3.20310627	3.40000000
C	0.70026847	-1.78998223	3.40000000
N	-0.46560653	-5.15775688	3.40000000
C	0.90399028	-5.33932447	3.40000000
N	1.57860494	-4.20375649	3.40000000
H	1.34717717	-6.32811386	3.40000000

Ds-Px//Ds-Px

Total bonding energy = -11238.24 kcal mol^{-1}

H	6.90638804	-0.97307686	0.00000000
H	2.01377990	3.28012524	0.00000000
H	6.55467340	1.57666213	0.00000000
C	2.11506873	-2.68420891	0.00000000
C	1.08182487	-3.66122023	0.00000000
C	-0.17931302	-3.11021503	0.00000000
S	-0.12235034	-1.37899177	0.00000000
C	1.64112666	-1.38072838	0.00000000
H	0.70703463	1.22775117	0.00000000
H	3.17671826	-2.90169393	0.00000000
H	1.26241194	-4.73188473	0.00000000
H	-1.13624390	-3.61406198	0.00000000
C	1.78846610	1.13675158	0.00000000
C	2.53458669	2.32505003	0.00000000
N	3.88420296	2.37713988	0.00000000
C	4.45032227	1.17050778	0.00000000
C	3.81433615	-0.10212816	0.00000000
C	2.39802212	-0.13716539	0.00000000
N	5.81242830	0.88678278	0.00000000
C	5.93692098	-0.48904304	0.00000000
N	4.77417491	-1.11579139	0.00000000
C	-4.74260007	1.72328403	0.00000000
C	-3.70966000	0.76417805	0.00000000
C	-2.47784354	1.48287388	0.00000000
C	-2.80084428	2.83119708	0.00000000
N	-4.17535187	2.96525147	0.00000000
O	-0.73174615	3.81304158	0.00000000
H	-1.48611926	1.06379643	0.00000000
H	-4.63897244	3.86733126	0.00000000
H	-5.81454320	1.58639063	0.00000000
N	-1.96903981	3.98553738	0.00000000
O	-2.54183403	5.10589057	0.00000000
C	-3.86564102	-0.64277233	0.00000000
C	-3.97109627	-1.85077122	0.00000000
C	-4.09575017	-3.30314313	0.00000000
H	-3.62183144	-3.74184451	0.88853572
H	-5.14987467	-3.60895747	0.00000000
H	-3.62183144	-3.74184451	-0.88853572
H	6.15934552	3.27223732	3.40000000
H	-0.29882708	3.83734719	3.40000000
H	4.37610342	5.12828682	3.40000000
C	3.28886496	-0.92836442	3.40000000
C	3.02722596	-2.32610868	3.40000000
C	1.68307125	-2.62161436	3.40000000
S	0.71156752	-1.18754350	3.40000000
C	2.13927114	-0.15240268	3.40000000
H	-0.14965100	1.40885609	3.40000000
H	4.27559196	-0.48029156	3.40000000
H	3.80264477	-3.08614804	3.40000000
H	1.20505171	-3.59170497	3.40000000
C	0.77873365	1.97088534	3.40000000
C	0.68389359	3.37079766	3.40000000
N	1.74513844	4.20622378	3.40000000
C	2.91237914	3.56279448	3.40000000
C	3.14589219	2.15938712	3.40000000
C	2.02066444	1.29855291	3.40000000
N	4.18111543	4.13388197	3.40000000
C	5.09052225	3.09399047	3.40000000
H	-2.70199908	-1.27031227	3.40000000
H	-1.18547752	-5.87107752	3.40000000
C	3.25463788	-1.60794189	3.40000000
C	4.27262130	-0.61547244	3.40000000
C	3.77306123	0.66652248	3.40000000
S	2.04000880	0.68028910	3.40000000
C	1.97106558	-1.08316936	3.40000000
H	-0.57743153	-0.04067646	3.40000000
H	3.42872552	-2.67762528	3.40000000
H	5.33510807	-0.83855484	3.40000000
H	4.31670074	1.60282669	3.40000000

Ds//Ds

Total bonding energy = -6345.72 kcal mol^{-1}

H	1.34717717	-6.32811386	3.40000000
H	-2.70199908	-1.27031227	3.40000000
H	-1.18547752	-5.87107752	3.40000000
C	3.25463788	-1.60794189	3.40000000
C	4.27262130	-0.61547244	3.40000000
C	3.77306123	0.66652248	3.40000000
S	2.04000880	0.68028910	3.40000000
C	1.97106558	-1.08316936	3.40000000
H	-0.57743153	-0.04067646	3.40000000
H	3.42872552	-2.67762528	3.40000000
H	5.33510807	-0.83855484	3.40000000
H	4.31670074	1.60282669	3.40000000
C	-1.10482261	-0.59020516	0.00000000
C	-2.49881439	-0.43801243	0.00000000
N	-3.37849147	-1.46222619	0.00000000
C	-2.78524806	-2.65568065	0.00000000
C	-1.39241061	-2.94761156	0.00000000
C	-0.48559606	-1.85973352	0.00000000
N	-3.40833702	-3.89903632	0.00000000
C	-2.40703268	-4.85095639	0.00000000
N	-1.19378785	-4.32879114	0.00000000
H	-2.62968278	-5.91140253	0.00000000
H	-2.93263399	0.56049100	0.00000000
H	-4.41000424	-4.05299529	0.00000000
C	1.68793283	-3.21388046	0.00000000
C	3.09485762	-3.00931145	0.00000000
C	3.44424274	-1.67852173	0.00000000
S	2.05026569	-0.64872164	0.00000000
C	0.95795458	-2.03486570	0.00000000
H	-0.49106094	0.30649779	0.00000000
H	1.20002856	-4.18159865	0.00000000
H	3.82330293	-3.81430296	0.00000000
H	4.43440215	-1.24057900	0.00000000
N	-0.46560653	-5.15775688	3.40000000
C	0.90399028	-5.33932447	3.40000000
N	1.57860494	-4.20375649	3.40000000
C	-0.54690638	-1.12688444	3.40000000
C	-1.76412606	-1.82312574	3.40000000
N	-1.87378202	-3.16879330	3.40000000
C	-0.69234310	-3.78561851	3.40000000
C	0.60607876	-3.20310627	3.40000000
C	0.70026847	-1.78998223	3.40000000

N	4.51823436	1.90349541	3.40000000
C	-4.84976499	-1.39346431	3.40000000
C	-3.45035057	-1.56225041	3.40000000
C	-2.87622893	-0.25676972	3.40000000
C	-3.93006651	0.64419159	3.40000000
N	-5.12086170	-0.05527142	3.40000000
O	-2.83324468	2.65470584	3.40000000
H	-1.82757959	-0.01288959	3.40000000
H	-6.02616782	0.40201713	3.40000000
H	-5.63652128	-2.13428576	3.40000000
N	-3.93562676	2.06699491	3.40000000
O	-5.05755410	2.63669969	3.40000000
C	-2.74955718	-2.79218052	3.40000000
C	-2.12482834	-3.83145719	3.40000000
C	-1.37199267	-5.07972047	3.40000000
H	-0.73072217	-5.15607491	4.28853572
H	-2.04504415	-5.94672831	3.40000000
H	-0.73072217	-5.15607491	2.51146428

Pa//Pa

Total bonding energy = -3445.46 kcal mol^{-1}

C	1.79382511	5.57414793	0.00000000
C	2.41180291	4.32200782	0.00000000
C	1.38796894	3.34572418	0.00000000
C	0.15948772	4.02103577	0.00000000
N	0.44123566	5.37942184	0.00000000
C	-1.20168877	3.53769656	0.00000000
H	-1.29913044	2.43025202	0.00000000
O	-2.19731270	4.26658444	0.00000000
H	2.22029503	6.56826675	0.00000000
H	3.47977917	4.14794504	0.00000000
H	1.51298631	2.27039234	0.00000000
H	-0.28431335	6.08796928	0.00000000
C	-2.23447725	3.34683080	3.40000000
N	-2.80497768	4.61139550	3.40000000
C	-3.05159250	2.15572170	3.40000000
H	-2.47948490	1.20250547	3.40000000
O	-4.28549873	2.16019132	3.40000000
H	-2.06447392	6.61889610	3.40000000
H	0.37709956	5.40112091	3.40000000
H	-0.11047150	2.72609703	3.40000000
H	-3.80843289	4.75815542	3.40000000
C	-1.82516695	5.56396435	3.40000000
C	-0.58922292	4.91419996	3.40000000
C	-0.84367687	3.52257540	3.40000000

Px//Px

Total bonding energy = -4881.89 kcal mol^{-1}

C	-4.09575017	-3.30314313	0.00000000
H	-3.62183144	-3.74184451	0.88853572
H	-5.14987467	-3.60895747	0.00000000
H	-3.62183144	-3.74184451	-0.88853572
C	-1.37199267	-5.07972047	3.40000000
H	-0.73072217	-5.15607491	4.28853572
H	-2.04504415	-5.94672831	3.40000000
H	-0.73072217	-5.15607491	2.51146428
C	-4.84976499	-1.39346431	3.40000000
C	-3.45035057	-1.56225041	3.40000000
C	-2.87622893	-0.25676972	3.40000000
C	-3.93006651	0.64419159	3.40000000
N	-5.12086170	-0.05527142	3.40000000
O	-2.83324468	2.65470584	3.40000000
H	-1.82757959	-0.01288959	3.40000000
H	-6.02616782	0.40201713	3.40000000
H	-5.63652128	-2.13428576	3.40000000
N	-3.93562676	2.06699491	3.40000000
O	-5.05755410	2.63669969	3.40000000
C	-2.74955718	-2.79218052	3.40000000
C	-2.12482834	-3.83145719	3.40000000
C	-4.74260007	1.72328403	0.00000000
C	-3.70966000	0.76417805	0.00000000
C	-2.47784354	1.48287388	0.00000000
C	-2.80084428	2.83119708	0.00000000
N	-4.17535187	2.96525147	0.00000000
O	-0.73174615	3.81304158	0.00000000
H	-1.48611926	1.06379643	0.00000000
H	-4.63897244	3.86733126	0.00000000
H	-5.81454320	1.58639063	0.00000000
N	-1.96903981	3.98553738	0.00000000
O	-2.54183403	5.10589057	0.00000000
C	-3.86564102	-0.64277233	0.00000000
C	-3.97109627	-1.85077122	0.00000000