

Symmetry-Adapted Perturbation-Theory Interaction-Energy Decomposition for Hydrogen-Bonded and Stacking Structures

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Abstract: This letter reports the computational *ab initio* studies on the stacked and hydrogen-bonded geometries of the uracil dimer and pyrimidine...*p*-benzoquinone complex with a special regard to the ratios of different interaction-energy terms calculated by means of the symmetry-adapted perturbation theory (SAPT). In the hydrogen-bonded systems the absolute value of the dispersion term constitutes approximately half of the absolute value of the total SAPT0 interaction energy, while in the stacking complexes the ratio of the dispersion to the total interaction energy is much larger, ca. 1.2–2.0. Our SAPT results are compared with the DFT-SAPT results published recently by the Hobza group (*J. Chem. Phys.* **2007**, 127, 075104), and the role of the dispersion contribution in stacking and hydrogen-bonded arrangements is discussed. The methodological part of this letter presents the influence of counterpoise corrections in the optimization procedure on the geometries of the systems and the calculated SAPT contributions.

Noncovalent interactions make an important contribution to the stabilization of the structure of various forms of molecular systems, among them DNA and RNA. There are two main types of noncovalent interactions: hydrogen bonds and stacking interactions. It is well-known that the helical structure of DNA is stabilized not only by hydrogen bonds in Watson–Crick adenine–thymine (AT) and guanine–cytosine (GC) pairs but also by stacking interactions between pyrimidine and purine bases along the DNA helical backbone. It was also shown that stacking interactions play an important role in the long-distance DNA radiation-induced damage repair.¹

The origin of the stabilization of hydrogen bonding and stacking interaction is different.² It is widely and intuitively accepted that

the former bonding originates mainly in electrostatic interactions, while the stacking bonding is mainly due to the dispersion energy.^{3–8} For a long time they were believed to be much weaker than the hydrogen bonding. However, the recently calculated interaction energies have shown that the stacked pairs are about as stable as the AT planar pair, the weakest hydrogen-bonding interaction in DNA.^{6,9} This finding changes the widely spread opinion about stabilization of a DNA double helix where a dominant contribution was expected to originate in the hydrogen bonding.^{6,9}

Despite the great importance of these molecular systems from a biological point of view, relatively little attention has been devoted to the discussion of the nature of interactions binding them. Inspiration for this study has been the recent paper published by Hobza and co-workers.¹⁰ They authors have found that dispersion energy in stacked and hydrogen-bonded complexes is of similar magnitude. A partial explanation has been drawn from comparison of the results with dispersion energies calculated by the empirical C_6/r^6 formula. The DFT-SAPT and empirical dispersion energies agreed well, and the authors argued that “our intuitive perception of the dispersion interaction is not accurate and very close contacts in the hydrogen-bonded complexes can bring as much dispersion stabilization as is found in the stacking molecules”.¹⁰

The supermolecular *ab initio* calculations have become very popular tools for the investigation of intermolecular interactions. However, this method does not provide the information on the character of these interactions. To get more insight into the physical nature of the interaction one can use the interaction-energy decomposition scheme^{11–15} or the perturbation scheme known as the symmetry-adapted perturbation-theory (SAPT) method.¹⁶ The first step in such an investigation is to find the optimal structure on the intermolecular potential energy surface (IPES) by a supermolecular method, while the second stage is to perform the SAPT calculations for the minimal configuration.

The basis-set superposition error (BSSE) arising from the use of an incomplete basis set can strongly influence calculated binding energies of weakly bound complexes. The Boys–Bernardi counterpoise (CP) correction is a simple procedure for estimating the size of the basis-set superposition error in the interaction energy calculations.¹⁷ The effectiveness of the CP procedure tested on a broad range of interacting systems supports this approach for hydrogen-bonded complexes.¹⁸

The counterpoise correction in the geometry optimization procedure increases the H-bond distance.^{19,20} BSSE introduces a nonphysical attraction between the two units. Thus, the counterpoise correction generally makes intermolecular complexes less stable with longer intermolecular distances than

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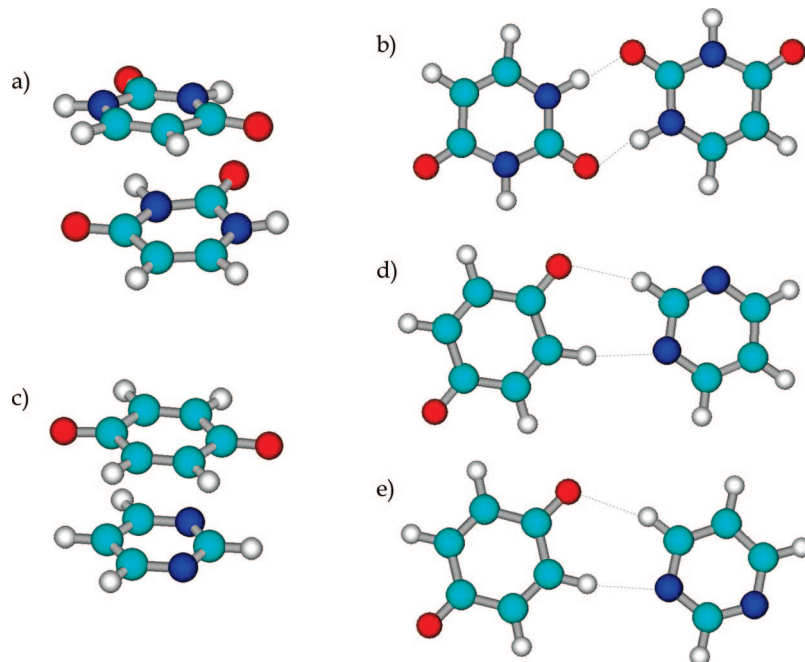


Figure 1. The structures of the uracil dimer: stacked (a) and hydrogen-bonded (b) and of the pyrimidine...*p*-benzoquinone complex: stacked (c) and hydrogen-bonded: planar A (d) and planar B (e) are optimized at the MP2/aug-cc-pVDZ level.

apparent from the normally optimized structure.^{21,22} Optimization on the standard IPES using medium-size basis sets leads sometimes to a completely wrong geometric structure, while optimization on a counterpoise-corrected IPES yields the correct structure.²⁰ Counterpoise-corrected surfaces lead to noticeable improvements in the geometrically optimized transition states obtained with relatively small basis sets.²³ The geometries and associated activation energies become closer to those obtained with larger basis sets.

The object of this Letter is 2-fold. The first goal is to investigate the systems with hydrogen bonds and stacking arrangement in terms of physically meaningful contributions to interaction energy with special regards to the ratios of electrostatic and dispersion terms. The second purpose, a methodological one, is to study how counterpoise correction influences the geometries of the interacting systems and the calculated SAPT decomposition of the total interaction energy.

As model systems we have chosen two dimers which can form hydrogen-bonded as well as stacking conformers. Since all the calculations are time-consuming, we have selected two relatively small systems: the uracil dimer and the pyrimidine...*p*-benzoquinone complex, Figure 1. The uracil dimer is well-known to form several different structures among them the hydrogen-bonded and *face-to-face* stacked are the most studied.^{3,24–28} The *face-to-face* stacked structure is lower in energy than the second possible stacked structure of the dimer, the *face-to-back*.^{26,28} The pyrimidine...*p*-benzoquinone complex was studied previously²⁹ in a search for a system forming a stable stacked complex. Quinone was selected as one of the components in the complex because it can form only weak C–H...O and C–H...N hydrogen bond interactions with pyrimidine in the planar dimers which are presumably not strong competitors with the stacking interactions. The symmetrical quinone molecule was also chosen since it can form a very limited number of different dimer conformers with pyrimidine.²⁹

However, a limited analysis of harmonic frequencies with an experimental infrared data has not confirmed undoubtedly the presence of a stacking structure in low-temperature argon matrices since the energy differences between all conformers are rather small.²⁹

The structures of the uracil dimer and the pyrimidine...*p*-benzoquinone dimer were optimized by means of the frozen-core Møller–Plesset (MP2) perturbation theory with the aug-cc-pVDZ basis set.^{30,31} We employed two optimization procedures: with counterpoise corrections (CP) and without (no CP) for the basis-set superposition error. At each stationary point vibrational frequencies were calculated in order to confirm the nature of the stationary points on the potential energy surface. Geometry optimization and vibrational analysis were carried out with the Gaussian 03 program package.³²

The interaction energy components were calculated by means of the SAPT method^{16,33} implemented in the SAPT2002 program.³⁴ In this study we have employed the SAPT0 approach which is recommended for large systems since it takes much less time than the full SAPT calculation.

In this work we employed the following approximation to the intermolecular interaction energy

$$E_{\text{int}}^{\text{SAPT0}} = E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind, resp}}^{(20)} + E_{\text{exch-ind, } r}^{(20)} + E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)} \quad (1)$$

where $E_{\text{elst}}^{(10)}$ is the classical (Coulombic) electrostatic energy, $E_{\text{exch}}^{(10)}$ is the exchange term that results from the antisymmetrization (symmetry adaptation) of the wave function, $E_{\text{ind, resp}}^{(20)}$ denotes the induction (with response) energy, $E_{\text{exch-ind, } r}^{(20)}$ is the second-order exchange-induction (with response) energy term, $E_{\text{disp}}^{(20)}$ is the dispersion energy, and $E_{\text{exch-disp}}^{(20)}$ denotes the exchange-dispersion contribution. This level of theory may introduce about 20–30% errors with respect to the exact interaction energies, but we believe such an accuracy can be acceptable for large systems.

Table 1. Calculated SAPT and SAPT(DFT) Decomposition (See Definitions in Text) of Interaction Energy (kJ/mol) for Stacked and Hydrogen-Bonded Systems^{a,b}

uracil dimer	stacked			hydrogen-bonded		
	SAPT0		SAPT(DFT)	SAPT0		SAPT(DFT)
	CP	no CP	CP	CP	no CP	CP
$E_{\text{elst}}^{(10)}$	-39.99	-53.64	-37.55	-128.00	-142.02	-119.34
$E_{\text{exch}}^{(10)}$	46.89	79.27	49.07	109.20	133.88	123.81
$E_{\text{ind,resp}}^{(20)}$	-19.72	-34.79	-20.93	-57.68	-69.68	-67.62
$E_{\text{exch-ind,r}}^{(20)}$	14.83	28.15	15.83	26.86	33.58	32.67
$E_{\text{disp}}^{(20)}$	-55.98	-75.01	-48.92	-38.52	-43.56	-40.39
$E_{\text{exch-disp}}^{(20)}$	5.59	9.19	4.74	6.56	7.80	7.10
$E_{\text{int}}^{\text{SAPT}}$	-48.39	-46.87	-37.76	-81.58	-80.00	-63.77
$E_{\text{int}}^{\text{MP2}}$	-42.21	-39.80		-79.70	-80.68	

pyrimidine... <i>p</i> -benzoquinone	stacked			hydrogen-bonded					
	SAPT0		SAPT(DFT)	planar A			planar B		
	CP	no CP	CP	SAPT0		SAPT(DFT)	SAPT0		SAPT(DFT)
dimer	CP	no CP	CP	CP	no CP	CP	CP	no CP	CP
$E_{\text{elst}}^{(10)}$	-18.22	-30.56	-15.07	-24.52	-29.30	-23.19	-28.91	-33.84	-27.21
$E_{\text{exch}}^{(10)}$	37.39	68.11	33.36	20.90	29.56	25.09	23.18	32.27	27.61
$E_{\text{ind,resp}}^{(20)}$	-16.23	-31.32	-13.38	-7.38	-10.08	-8.95	-8.40	-11.34	-10.07
$E_{\text{exch-ind,r}}^{(20)}$	14.65	28.78	11.89	3.65	5.43	5.10	4.07	5.93	5.48
$E_{\text{disp}}^{(20)}$	-47.10	-64.93	-36.23	-15.73	-18.93	-16.34	-16.83	-20.16	-17.44
$E_{\text{exch-disp}}^{(20)}$	5.36	9.01	3.54	1.73	2.36	1.95	1.92	2.55	2.11
$E_{\text{int}}^{\text{SAPT}}$	-24.13	-20.93	-15.88	-21.32	-20.98	-16.35	-25.02	-24.60	-19.52
$E_{\text{int}}^{\text{MP2}}$	-24.35	-22.07		-17.35	-16.92		-20.64	-20.20	

^a The CP and no CP abbreviations refer to the counterpoise corrected and standard optimized geometries, respectively. ^b The total MP2 interaction energies ($E_{\text{int}}^{\text{MP2}}$) are counterpoise corrected.

To compare our results with previously published literature^{6–8} we performed the SAPT(DFT)³⁵ (accordingly to the original notation) calculations where the total interaction energy is defined as a sum:

$$E_{\text{int}}^{\text{SAPT(DFT)}} = E_{\text{elst}}^{(1)}(\text{KS}) + E_{\text{exch}}^{(1)}(\text{KS}) + E_{\text{ind}}^{(2)}(\text{CKS}) + \tilde{E}_{\text{exch-ind}}^{(2)}(\text{CKS}) + E_{\text{disp}}^{(2)}(\text{CKS}) + \tilde{E}_{\text{exch-disp}}^{(2)}(\text{CKS}) \quad (2)$$

The corrections $E_{\text{elst}}^{(1)}(\text{KS})$ and $E_{\text{exch}}^{(1)}(\text{KS})$ are obtained by using Kohn–Sham orbitals in the expressions for $E_{\text{elst}}^{(10)}$ and $E_{\text{exch}}^{(10)}$, respectively. The second-order induction and dispersion energies, $E_{\text{ind}}^{(2)}(\text{CKS})$ and $E_{\text{disp}}^{(2)}(\text{CKS})$, are calculated in the coupled Kohn–Sham approximation. The exchange-induction energy is estimated by scaling the SAPT(KS) result $E_{\text{exch-ind}}^{(2)}(\text{KS})$ using $E_{\text{ind}}^{(2)}(\text{UCKS})$ calculated in the uncoupled KS approximation:

$$\tilde{E}_{\text{exch-ind}}^{(2)}(\text{CKS}) = E_{\text{exch-ind}}^{(2)}(\text{KS}) \frac{E_{\text{ind}}^{(2)}(\text{CKS})}{E_{\text{ind}}^{(2)}(\text{UCKS})} \quad (3)$$

The exchange-dispersion term, $E_{\text{exch-disp}}^{(2)}(\text{CKS})$, is estimated similarly as the exchange-induction energy.

Because of the system size the SAPT and SAPT(DFT) calculations were carried out in aug-cc-pVDZ basis set. This basis set is large enough to provide a reliable estimation of the energy terms.³⁶ The dispersion term is underestimated by about 10–15% in this basis but should serve well enough for a qualitative purpose. Also our previous calculations for dihydrogen-bonded systems³⁷ proved using of this basis set to recognize the correct proportion between the most important contributions to the total interaction energy.

The hydrogen-bonded structures of both dimers are minima on the standard and CP-corrected PESs. The stacked structure

of the uracil dimer is also a minimum, while the stacked structure of the pyrimidine...*p*-benzoquinone dimer turned out to be a transition state with one imaginary frequency (-51 cm^{-1} for the CP-corrected and -68 cm^{-1} for the standard PES).

The differences between intramolecular geometric parameters (tables in the Supporting Information) for the CP-corrected and standard optimized structures are small, especially, for bond lengths. The intermolecular distances differ significantly, and, as expected,^{19,20,22} the CP-corrected optimized are longer than the standard ones. The largest deviations are ca. $+0.20 \text{ \AA}$ for the stacking structures, and the differences in hydrogen bond lengths are smaller.

The calculated decomposition of the interaction energy is presented in Table 1 along with the all-electron MP2 counterpoise-corrected supermolecular energies for the complexes. The SAPT0 interaction energies agree reasonably with the MP2 ones. However, at this level of SAPT one cannot expect accurate agreement of the results, and the SAPT0 energies are mostly lower than the respective total MP2 calculated energies. The following discussion shall be given with respect to the results for the CP-optimized structures.

The interaction-energy decomposition for hydrogen-bonded structures is similar, and the dominant attraction energy originates in the electrostatic term which is larger for the uracil dimer than for the pyrimidine...*p*-benzoquinone complex. The exchange repulsion compensates the attractive electrostatic term, but the first-order energy is still attractive and for the hydrogen-bonded uracil dimer it arises to ca. -18.8 kJ/mol . This sum in the pyrimidine...*p*-benzoquinone complexes is much smaller with values of ca. -3.6 and -5.7 kJ/mol . The second-order induction energy is attractive, and in the case of the uracil dimer

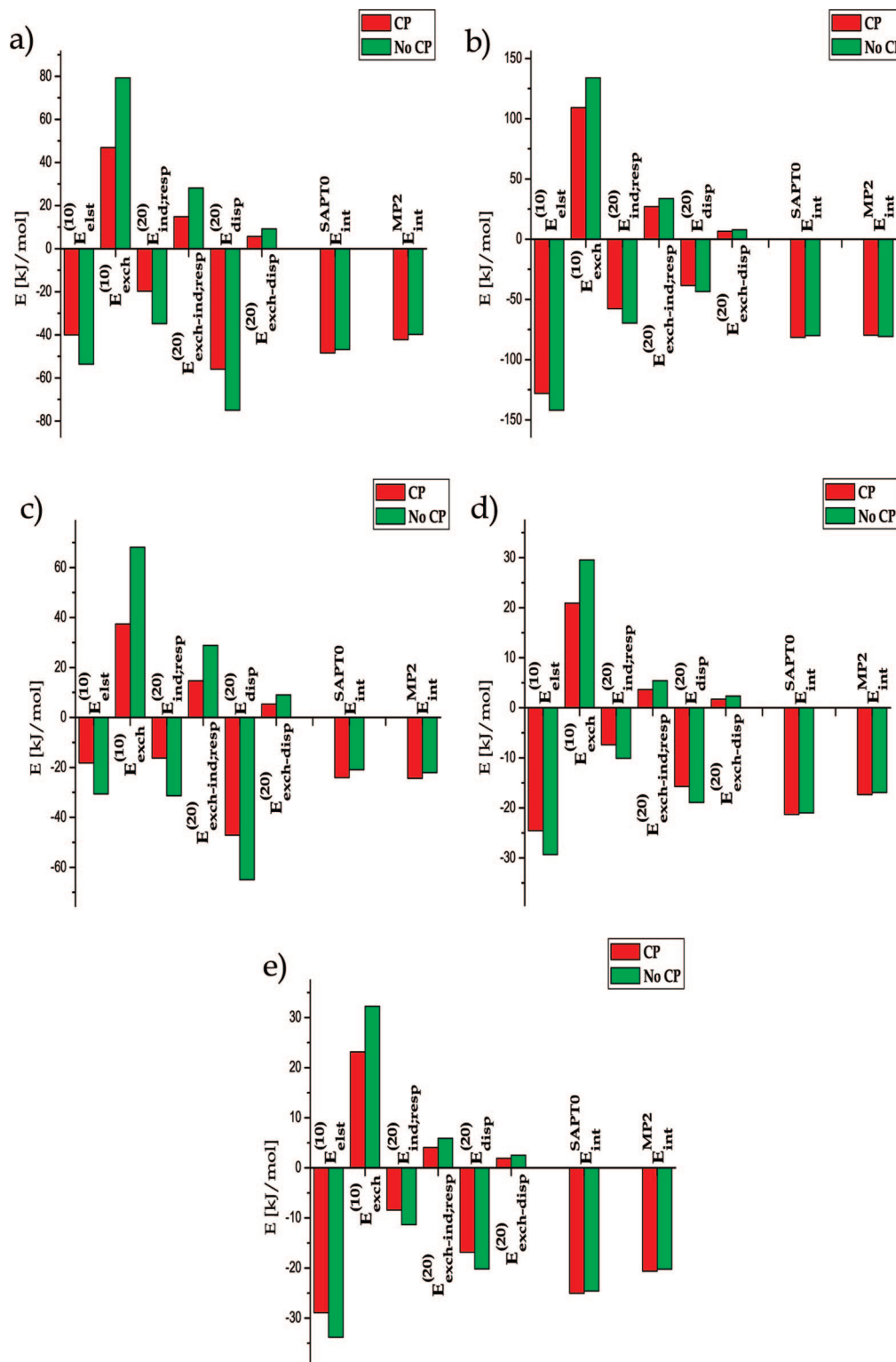


Figure 2. The SAPT0 decomposition of the total interaction energy for the uracil dimer: stacked (a) and hydrogen-bonded (b) and for the pyrimidine...*p*-benzoquinone complex: stacked (c) and hydrogen-bonded: planar A (d) and planar B (e) level.

this attractive contribution to the total interaction energy is approximately twice as large as that for both the pyrimidine...*p*-benzoquinone complexes (71% vs ca. 35%). However, this contribution is reduced by the repulsive $E^{(20)}_{\text{exch-ind},r}$ term which is approximately half of the $E^{(20)}_{\text{ind,resp}}$ absolute value in both systems. The dispersion effect, as it is usual for the hydrogen-bonded systems,¹³ constitutes ca. 50% of the total interaction energy

(the ratio of $E^{(20)}_{\text{disp}}/E_{\text{int}}^{\text{SAPT0}}$ is 0.5 and 0.7 for the uracil dimer and the pyrimidine...*p*-benzoquinone complex, respectively).

Now, let us discuss the stacked systems. Electrostatic terms are attractive here, but, in contrary to the hydrogen-bonded structures, they are not dominant and the exchange contribution is much larger. Thus, the first-order energies are repulsive, and the inclusion of the second-order terms makes the systems stable.

Comparing results for the two stacked structures the first-order energy for the weaker pyrimidine...*p*-benzoquinone complex is almost three times larger than for the uracil dimer. The largest attraction comes from dispersion, and this term is significantly larger in absolute value than for the hydrogen-bonded complexes. The dispersion energy is about twice as much as the electrostatic ($E_{\text{disp}}^{(20)}/E_{\text{elst}}^{(10)} = 2.6$) or total interaction energy ($E_{\text{disp}}^{(20)}/E_{\text{int}}^{\text{SAPT0}} = 2.0$) for the pyrimidine...*p*-benzoquinone complex. This is the most noticeable difference between the hydrogen-bonded and the stacking structures (it can be easily identified from Figure 2). $E_{\text{ind,resp}}^{(20)}$, the third attractive term, despite being quite substantial is roughly compensated by the repulsive $E_{\text{exch-ind,r}}^{(20)}$ contribution.

Our second goal has been the methodological one. The supermolecular counterpoise-corrected MP2 interaction energies for geometries obtained for the CP-corrected structures are systematically lower than for the noncorrected (no CP) ones. The one exception is the hydrogen-bonded uracil dimer; however, the energy differences result from slight differences between both geometries (vide infra). The difference between each pair of $E_{\text{int}}^{\text{SAPT0}}$ for CP-corrected and standard optimized structures is also small, and the calculated interaction energies are close to each other. The most noticeable differences between the geometries obtained within the counterpoise-corrected and standard procedures are observed for intermolecular bond lengths. Thus, the changes in energetic terms arise mainly due to a variation in a separation between two subunits. These discrepancies are greater for stacked structures, and it is also reflected in the values of SAPT terms.

Similarly, all the energetic terms for the CP-optimized structures are smaller than for these optimized without counterpoise corrections (see Figure 2). The differences are much larger for the stacking structures than for the hydrogen-bonded structures. The largest terms remain dominant, but the order of smaller terms can vary in pairs (CP vs no CP) and the contributions of similar magnitude can change their places in the sequence of increasing energy (for instance, the $E_{\text{elst}}^{(10)}$ and $E_{\text{ind,resp}}^{(20)}$ terms in the stacked pyrimidine...*p*-benzoquinone complex). On the other hand, relations between some terms are maintained: the ratios $E_{\text{elst}}^{(10)}/E_{\text{disp}}^{(20)}$, $E_{\text{exch}}^{(10)}/E_{\text{ind,resp}}^{(20)}$, $E_{\text{exch}}^{(10)}/E_{\text{exch-disp}}^{(20)}$, and $E_{\text{ind,resp}}^{(20)}/E_{\text{exch-disp}}^{(20)}$ are approximately constant and do not depend on the optimization procedure (CP or no CP).

In conclusion, we would like to stress several points. First, previous studies^{7,10} have shown that for Watson—Crick (WC) structures of DNA pairs (for instance, mAmT WC and mCmG WC) the DFT-SAPT calculated sum of first-order electrostatic and exchange energies is repulsive. Our observations are in contrast with these findings since the electrostatic term usually overcompensates exchange energy and this first-order sum is attractive for hydrogen-bonded complexes. The SAPT(DFT) results for our model systems presented in Table 1 show that the first-order energy for these hydrogen-bonded geometries is repulsive. Intramonomer correlation contained in the SAPT-(DFT) (or DFT-SAPT) approach affects the values of interaction-energy contributions. Thus, one cannot compare directly the terms calculated by means of these two methods. The electrostatic-exchange sum in SAPT(DFT) (or DFT-SAPT) is not the Heitler—London energy in its pure form as in the original SAPT approach. The value of the Heitler—London energy tells

us whether a system is bonded at an uncorrelated level (by electrostatic interaction) or an inclusion of correlation terms makes it stable (among others, by dispersion). The electrostatic-exchange sum along with the induction terms ($E_{\text{ind,resp}}^{(20)}$ and $E_{\text{exch-ind,r}}^{(20)}$) provides a good approximation to the supermolecular Hartree—Fock interaction energy.³⁸ In the SAPT-DFT (or DFT-SAPT) approximation such a picture is indistinct because of the intramonomer correlation integrated within the monomers' electron density.

Second, the comparison of the percentage of dispersion contribution to the total interaction energy makes clear a distinction between hydrogen-bonded and stacking interactions. In the hydrogen-bonded systems the absolute value of the dispersion term constitutes approximately half of the absolute value of the total SAPT0 interaction energy, E_{int} , while in the stacking complexes the absolute value of the dispersion energy is larger than the absolute value of E_{int} . Similar ratios of the dispersion energy to the total interaction energy one can find for the components presented in Table 1 of ref 10, even though the absolute values of the dispersion terms for both hydrogen-bonded and stacking complexes are similar. This observation is also in line with previous works on stacked interactions in the DNA pairs.⁷ Thus, the statement in the paper “the similarity of magnitudes of the dispersion energy in stacked and H-bonded complexes is indeed puzzling” seems to be unjustified. The dispersion energies (in absolute values) in our model systems are larger for stacked than for hydrogen-bonded arrangements. However, this cannot be a general trend since the total interaction energies can differ largely (stacking vs hydrogen bonded), and the values of individual terms maintain their relative proportion. The ratio of these energy terms to the total interaction energy seems to be the valid criterion for a discrimination between hydrogen-bonded and stacking systems.

Finally, we would like to compare the SAPT terms calculated for two sets of optimized geometries. The absolute values of the SAPT terms differ for geometries obtained by means of two optimization methods (with CP or without CP optimized geometry). It is especially meaningful for weak systems where the difference between the calculated bond lengths by means of standard and counterpoise-corrected optimization procedures becomes substantial and the interaction-energy terms are well-known to be distance sensitive.^{16,27} However, the sequence of individual interaction-energy terms is approximately maintained. The comparison between two sets of differently obtained geometries^{7,10} (taken from geometry optimization⁷ and in experimental crystal geometries)¹⁰ indicates that despite differences in the total interaction energy which are greater for stacked structures, the sequence of the individual SAPT terms is still maintained.

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Supporting Information Available: The MP2/aug-cc-pVDZ optimized bond lengths and bond angles for the studied

systems. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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