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Interplay between π–π interactions and the H-bonding ability of aromatic nitrogen bases

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Abstract

The influence of π–π interactions on the hydrogen bonding ability of pyrimidine and imidazole stacked with substituted benzenes in the T-shaped, parallel-displaced and parallel-sandwich arrangements is studied at the MP2 level of theory. While the dispersion is the major source of the stabilization of the complexes, it appears that the hydrogen bonding ability of the heterocycles is directly related to the electrostatic interaction between the cycles. The dispersion interaction can successfully be modeled by London's formula involving the polarizability. The reactivity descriptor local hardness, introduced in a conceptual DFT context, is found to be an excellent tool for the estimation of the interaction energy.

1. Introduction

Noncovalent interactions between aromatic systems such as hydrogen bonding and π–π interactions have been the subject of many studies. Hydrogen bonding is mostly monitored by electrostatics. Although aromatic stacking is stabilized by dispersion forces, the role of electrostatics is still the subject of considerable debate [1,2].

In 1990, Hunter and Sanders [3] proposed a model for aromatic interactions. The aromatic ring was described as 'a positively charged σ-framework between two regions of negatively charged π-electron density'. According to this electrostatics based model, an electron-donating substituent on one of the interacting molecules should increase the negative charge of the π cloud on the latter, leading to an increase in the repulsion between the two stacked aromatic cycles. Experimental measurements of the rotational barrier in a system of benzene parallel stacked to a variety of substituted benzenes confirm this model [4,5]. In contrast, high level calculation studies on the substituent effects in the parallel stacked benzene dimer revealed that substituted benzenes bind stronger than unsubstituted benzene, for electron-withdrawing as well as for electron-donating substituents [2,6]. This has also been observed in our previous MP2 study on pyridine stacked with substituted benzenes in a parallel-displaced conformation [7]. In addition to binding energies, that work dealt with the influence of parallel stacking on the hydrogen bonding capacity of the pyridine base.

The present study on imidazole and pyrimidine complexed with substituted benzenes also takes into account conformational effects by comparing the T-shaped, parallel-sandwich, and parallel-displaced arrangements between the interacting partners. Imidazole and pyrimi-

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dine are chosen as prototypes of aromatic nitrogen bases capable of both aromatic stacking and hydrogen bonding. Histidine is one of the most occurring amino acids in enzyme active sites. Due to its neutral pK_a, the imidazole side chain of histidine often plays an important function as a hydrogen bond donor and acceptor. Moreover, histidine residues are often involved in aromatic stacking interactions in proteins [8]. Pyrimidine and purine are the scaffold from which DNA/RNA bases are derived.

A series of mono-substituted benzenes comprising electron-withdrawing and electron-donating groups is used to correlate aromatic stacking interactions with the hydrogen bonding capacity of the nitrogen bases. Interaction energy components (electrostatic and correlation) are obtained by comparing MP2 and HF results supplemented by a distributed multipole analysis [9] to estimate electrostatic effects. The MEP around the unprotonated nitrogen of pyrimidine or imidazole is used as a measure of their hydrogen bonding capacity [10–14]. The relative changes in the MEP and in the charge transfer between the interacting cycles are related with intrinsic properties of the substituted benzene such as the global hardness. Furthermore, another DFT based reactivity descriptor, the local hardness of the isolated substituted benzenes is used in order to assess the magnitude of the stacking interaction. This work is part of our ongoing interest in the development/use of reactivity descriptors in a conceptual DFT context [15], and their application to systems of biological interest [16–21].

2. Theory and computational details

All optimizations were carried out at the MP2/6-31G* level of theory. First, pyrimidine, imidazole and six substituted benzenes Ph–X (X = H, F, CH_3, OH, CHO, NO_2) were separately optimized. Then, for the parallel-sandwich geometry, the optimum intermolecular distance was computed, while the partners were kept fixed (Fig. 1a). For the T-shaped geometry, the twist angle ϕ was also optimized (Fig. 1b). For the parallel-displaced geometry, both the horizontal and vertical centers of mass distances were varied (respectively, R_1 and R_2 in Fig. 1c). Unconstrained geometry optimizations of aromatic complexes are very rarely reported in computational studies [7]. Here, full optimizations in the series of benzenes stacked with pyrimidine were carried out for the parallel-displaced conformations (data not shown). No fundamental differences were found compared to the results for the partial optimizations presented in Table 1, giving confidence in the applied methodology.

After the optimization procedure, single point calculations were carried out on the optimized complexes at the MP2/6-31G*(0.25) level of theory to obtain interaction energies. The MP2/6-31G*(0.25) level has been shown by Hobza and Sponer [22] to be a good compromise between computational cost and quality. Basis set superposition errors were corrected by the counterpoise method [23]. The Correlation interaction energy was calculated as the difference between the MP2 and Hartree–Fock energies. The electrostatic interaction

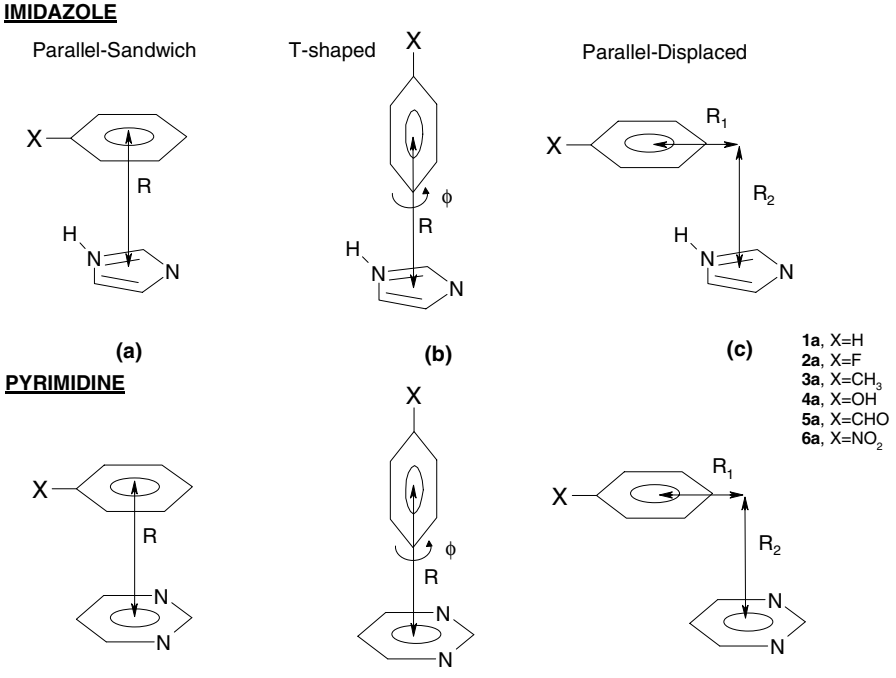

Fig. 1. Geometries and optimization parameters for parallel-sandwich, T-shaped and parallel-displaced conformations.

Table 1
Properties for the optimized complexes of pyrimidine and substituted benzenes in the parallel-displaced, parallel-sandwich, and T-shaped conformations (see Fig. 1)

Conformation	Benzene substituent	Complex properties							
		ΔE_{MP2}	ΔE_{HF}	ΔE_{Corr}	ΔE_{Elec}	Δq	MEP N_1	MEP N_3	R
Parallel-displaced	NO_2	−4.66	4.99	−9.65	−0.79	−0.0118	−0.0883	−0.0883	3.52
	CHO	−4.44	4.85	−9.29	−0.66	−0.0215	−0.0922	−0.0929	3.53
	F	−4.18	4.55	−8.73	−0.67	−0.0231	−0.0944	−0.0944	3.55
	H	−4.08	4.83	−8.90	−0.61	−0.0314	−0.0978	−0.0978	3.57
	CH_3	−4.15	5.20	−9.35	−0.44	−0.0341	−0.0983	−0.0983	3.55
	OH	−4.17	4.81	−8.98	−0.62	−0.0293	−0.0983	−0.0977	3.55
Parallel-sandwich	NO_2	−4.35	3.81	−8.16	−0.91	−0.0048	−0.0895	−0.0895	3.50
	CHO	−3.81	4.34	−8.14	−0.56	−0.0124	−0.0924	−0.0934	3.52
	F	−3.36	3.99	−7.35	−0.43	−0.0128	−0.0951	−0.0951	3.54
	H	−2.81	4.35	−7.16	−0.02	−0.0216	−0.0982	−0.0982	3.58
	CH_3	−3.17	4.86	−8.03	0.11	−0.0249	−0.0983	−0.0983	3.55
	OH	−3.20	4.50	−7.70	−0.08	−0.0220	−0.0977	−0.0986	3.53
T-shaped	NO_2	−1.81	1.23	−3.04	−0.02	0.0396	−0.0815	−0.0815	4.89
	CHO	−1.72	1.44	−3.16	−0.01	0.0293	−0.0845	−0.0850	4.91
	F	−1.65	1.53	−3.18	−0.05	0.0250	−0.0870	−0.0870	4.92
	H	−1.58	1.40	−2.98	−0.02	0.0207	−0.0897	−0.0908	4.99
	CH_3	−1.57	1.69	−3.26	−0.04	0.0155	−0.0908	−0.0909	4.94
	OH	−1.58	1.67	−3.26	−0.08	0.0204	−0.0896	−0.0908	4.93

ΔE_i (kcal/mol) interaction energies at the MP2, Hartree–Fock (HF) levels and their correlation (ΔE_{Corr}), and electrostatic (ΔE_{Elec}) components; Δq (a.u.): charge transfer to the pyrimidine; MEP (a.u.): molecular electrostatic potential minimum around the pyrimidine nitrogen atoms; and R (Å): distance between the geometrical centers of each ring.

was computed from a distributed multipole analysis using the ORIENT program version 3.2 [9,24]. Multipoles were computed at the nuclear positions with GDMA version 1.3 from the MP2/6-31G*(0.25) wave function [25].

The MEP minimum around the nitrogen atom, used as the measure of the H-bonding capacity [26], was computed according to:

$$V(\underline{r}) = \sum_A \frac{Z_A}{|\,\underline{r} - \underline{R_A}\,|} - \int \frac{\rho(\underline{r}')}{|\,\underline{r} - \underline{r}'\,|}\,\mathrm{d}\underline{r}', \tag{1}$$

where the summation runs over all nuclei A, with charge Z_A at position R_A; ρ being the electron density.

Charge transfer to pyrimidine or imidazole was calculated as the sum of atomic CHelpG charges on the molecule.

In order to relate the dispersion energy to an intrinsic property of the stacked partners, a simple model was used, based on the London dispersion energy expression:

$$\Delta E_{disp} = -\frac{C\alpha_1\alpha_2}{r^6}, \tag{2}$$

where α_1 and α_2 being the polarizabilities, r the distance between the interacting partners and C a constant. Neglecting directional effects, the dispersion interaction of the systems studied here was approximated by a similar expression, a procedure which proved to be successful in our previous study [7]. The polarizability was computed analytically using the 6-31G*(0.25) Pople basis set, as the trace of the corresponding tensor. α_1 being the polarizability of pyrimidine or imidazole and α_2 that of the substituted benzene, we can approximate the dispersion energy as:

$$\Delta E_{disp} = -\frac{C'\alpha_2}{r^6}. \tag{3}$$

For the parallel-displaced and T-shaped conformations, the benzene substituent is located as far as possible from the nitrogen atom of pyrimidine or imidazole avoiding direct interactions with the π-electrons of pyrimidine or imidazole (see Fig. 1b and c). Hence, for the parallel-displaced and T-shaped conformations, α_2 was computed as α_{bz}, the polarizability of the benzene ring in the substituted benzene (i.e., excluding the polarizability of the substituent as was also done in [7]). In a first approximation, the polarizability is an additive property, at least considering its isotropic part [27,28]. The benzene ring polarizability can then be expressed as:

$$\alpha_{bz} = \alpha_{total} - \alpha_{subst.}, \tag{4}$$

where α_{total} is the polarizability of the substituted benzene and $\alpha_{subst.}$ can be approximated by the polarizability of the radical corresponding to the substituent (e.g., CH_3 in the case of toluene), this procedure being in line with our approach to obtain group softness and hardness [29]. For the parallel-sandwich arrangement, α_2 was computed as the polarizability of the substituted benzene, α_{total}.

When interpreting interaction energies use can be made of descriptors within the context of conceptual DFT [15]. The hardness, η, is a global property that has been sharply defined by Parr and Pearson [30] as the second partial energy derivative with respect to the number of electrons. Considering the variation in energy when one electron is added or removed from the system and using a finite difference approximation, one gets

$$\eta = \frac{(I - A)}{2}, \tag{5}$$

with I the vertical ionization energy and A the vertical electron affinity. For the substituted benzenes considered in this study, the calculated electron affinity values were found to be negative; hence the hardness was taken as half the ionization energy.

In a previous study on substituted benzene/pyridine complexes, the local counterpart of the hardness, $\eta(\underline{r})$, was used for the estimation of the interaction energy [7]. $\eta(\underline{r})$ indeed mirrors the accumulation of negative charge at a defined point independently of the number of electrons of the system. Although a debate in the literature on the exact formulation of the local hardness is still going on, proposal (6) [15,31] received by far the most attention and will thus be used here:

$$\eta(\underline{r}) = -\frac{V_{\mathrm{el}}(\underline{r})}{2N}, \tag{6}$$

where N is the number of electrons of the system and $V_{\mathrm{el}}(\underline{r})$ the electronic part of the electrostatic potential (Eq. (1)). For the parallel-displaced and parallel-sandwich conformations, we used $V_{\mathrm{el}}(\underline{r})$ evaluated at a distance of 1.7 Å above the isolated benzene rings (Fig. 2). For the T-shaped geometries, $V_{\mathrm{el}}(\underline{r})$ was computed at a distance of 2 Å from the carbon atom in para position with the benzene substituent (Fig. 2).

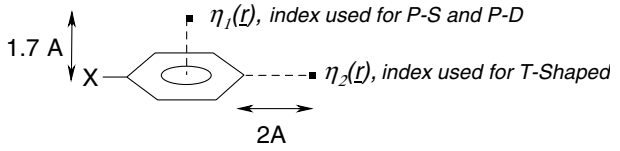

Fig. 2. Local hardnesses evaluation for isolated substituted benzenes.

All calculations were carried out using the GAUSSIAN 03 package [32].

3. Results and discussion

The dispersion energy (corresponding to the correlation part of the interaction) is found to be the major contribution to the stabilization of the complexes with pyrimidine (Table 1) and imidazole (Table 2), regardless of the stacking conformation. The Hartree–Fock terms are all positive and incorporate a small negative contribution from electrostatics, so that the sum of exchange and induction terms must be repulsive. It has to be mentioned that the dispersion component is larger for the

Table 2
Properties for the optimized complexes of imidazole and substituted benzenes in parallel-displaced, parallel-sandwich and T-shaped conformations (see Fig. 1)

Conformation	Benzene substituent	Complex properties						
		ΔE_{MP2}	ΔE_{HF}	ΔE_{Corr}	ΔE_{Elec}	Δq	MEP N	R
Parallel-displaced	NO_2	−3.67	3.85	−7.52	−1.17	0.0015	−0.1170	3.50
	CHO	−3.58	4.15	−7.73	−1.19	−0.0051	−0.1214	3.48
	F	−3.08	4.08	−7.17	−0.89	−0.0074	−0.1237	3.52
	H	−2.92	4.12	−7.04	−0.95	−0.0143	−0.1267	3.60
	CH_3	−2.81	4.69	−7.50	−0.67	−0.0181	−0.1276	3.54
	OH	−2.82	4.45	−7.27	−0.64	−0.0123	−0.1265	3.52
Parallel-sandwich	NO_2	−3.44	2.86	−6.30	−1.16	0.0060	−0.1191	3.55
	CHO	−2.87	3.53	−6.40	−0.66	−0.0018	−0.1232	3.58
	F	−2.30	3.64	−5.93	−0.30	−0.0018	−0.1255	3.60
	H	−1.52	4.28	−5.80	0.49	−0.0084	−0.1285	3.65
	CH_3	−1.65	4.49	−6.14	0.64	−0.0136	−0.1288	3.65
	OH	−2.27	4.02	−6.29	−0.15	−0.0083	−0.1280	3.58
T-shaped	NO_2	−2.56	0.23	−2.79	−0.63	0.0473	−0.1104	4.87
	CHO	−2.41	0.54	−2.94	−0.60	0.0410	−0.1142	4.88
	F	−2.17	0.76	−2.93	−0.49	0.0352	−0.1166	4.91
	H	−2.00	0.99	−2.99	−0.40	0.0333	−0.1197	4.92
	CH_3	−1.96	1.12	−3.07	−0.40	0.0286	−0.1202	4.90
	OH	−2.08	0.94	−3.02	−0.54	0.0320	−0.1186	4.90

ΔE_{i} (kcal/mol) interaction energy at the MP2, Hartree–Fock (HF) levels and its correlation (ΔE_{Corr}) and electrostatic (ΔE_{Elec}) components (kcal/mol); Δq (a.u.): charge transfer to the pyrimidine; MEP (a.u.): molecular electrostatic potential minimum around the pyrimidine nitrogen atoms; and R (Å) distance between the geometrical centers of each ring.

parallel-displaced than for the parallel-sandwich conformations, as was also observed from coupled cluster calculations with large basis sets on the benzene dimer [33]. For the parallel-sandwich arrangements, the inter-ring distances are larger in the case of imidazole, concomitant with smaller stabilization energies than for pyrimidine. These differences in interaction energies arise from both the correlation and the Hartree–Fock parts of the interaction. For the T-shaped structures, the correlation component is more important in the case of pyrimidine, but the more repulsive Hartree–Fock and electrostatic terms result in a weaker total interaction than for imidazole.

From Tables 1 and 2, it is clear that substituted benzenes bind stronger than unsubstituted benzene, in agreement with previous theoretical studies on substituent effects on parallel π–π interactions [2,7]. Hunter and Sanders [3] formulated a set of rules governing parallel π–π interactions, stating that electrostatics control substituent effects on the magnitude of the stacking interaction. Accordingly, electron-withdrawing substituents decrease the π electron density over the substituted benzene ring and thus the repulsion between the rings, while electron-donating substituents have the opposite effect.

Our results appear to violate the Hunter–Sanders rules, since the expected trend in the substituent effects is not found for electron-donating substituents. One can wonder whether the electron-withdrawing or electron-donating character of a particular substituent portraits the actual π-electron density of the substituted benzene. The latter can be described directly by the local hardness computed above the ring, $\eta_1(\underline{r})$, which mirrors the accumulation of negative charge (Table 3, Fig. 2). Going from electron-withdrawing to electron-donating character of the substituent, the local hardness increases gradually until it reaches a maximum value for unsubstituted benzene which persists for electron donating-substituents. Apparently, there exists a threshold for the substituent effect since the π-cloud density in unsubstituted benzene cannot be increased by the hydroxyl and methyl substituents. In line with this finding, the electrostatic potentials of the π clouds were found to be similar for benzene, toluene and phenol [2,34]. However $\eta_2(\underline{r})$ computed for amino benzene in a previous study displays a value larger than benzene [7]. Hence, we assume that the relative large value for unsubstituted benzene is not only due to the number of electrons of the system but also to the substituent effect.

We find that, regardless of the stacking conformation, the local hardness correlates with the total interaction energy, rather than with the electrostatic component thereof (Fig. 3a). London's formula (Eq. (3)) relates the dispersion energy component to the benzene's polarizability and is most obvious for parallel-stacking interactions (Fig. 3b). The data in Fig. 3b suggest that substituent effects also emerge in the dispersion

Table 3
Substituted benzenes properties (see Fig. 2): total, substituent and benzene polarizabilities, α_i (a.u.), global (η) and local hardnesses ($\eta_1(\underline{r})$, $\eta_2(\underline{r})$) (a.u.) (see Fig. 2)

Benzene substituent	α	α_{subst}	α_{bz}	η	$\eta_1(\underline{r})$	$\eta_2(\underline{r})$
NO_2	76.840	18.083	58.757	0.3923	0.0887	0.1369
CHO	64.905	9.644	55.261	0.3592	0.0970	0.1452
F	59.448	2.411	57.036	0.3461	0.1033	0.1545
H	58.384	0.257	58.127	0.3432	0.1062	0.1543
CH_3	70.713	12.122	58.591	0.3305	0.1057	0.1537
OH	63.944	5.583	58.360	0.3258	0.1050	0.1543

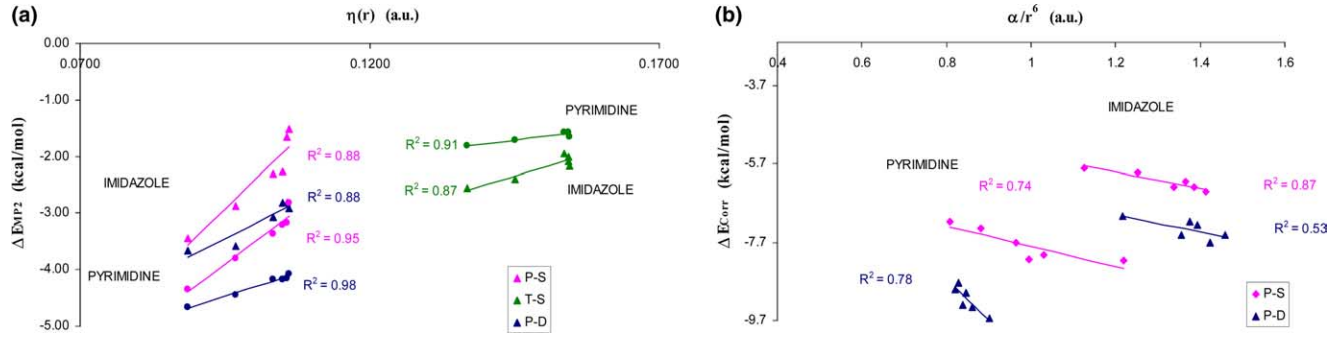

Fig. 3. (a) Interaction energy (ΔE) between pyrimidine or imidazole and the substituted benzenes (kcal/mol) vs. the local hardness $\eta_1(\underline{r})$ (Parallel-Displaced: P-D and Parallel-Sandwich: P-S conformations) or $\eta_2(\underline{r})$ (T-shaped: T-S arrangements). (b) Correlation interaction energy between pyrimidine or imidazole and the substituted benzenes (kcal/mol) vs. the polarizability over R^6 (a.u.) for parallel-displaced and parallel-sandwich arrangements.

component of the interaction energy. We propose the local hardness $\eta(\underline{r})$ and the polarizability α as suitable descriptors for the prediction of the total interaction energy and correlation interaction energy, respectively.

As stated in the introduction, the MEP as a descriptor of hard–hard interactions has been widely used for the estimation of hydrogen bond strengths. The MEP minima computed around the nitrogen atoms of the isolated pyrimidine and imidazole molecules amount to −0.0880 and −0.1246 a.u., respectively. In our previous study on pyridine stacked in a parallel-displaced conformation with substituted benzenes, the MEP is more negative upon stacking only when an electron flow to pyridine was observed (i.e., $\Delta q < 0$). Here, we find that the change in the MEP upon stacking depends on the stacking conformation, the stacked hetero-cycle (pyrimidine or imidazole, Tables 1 and 2) and the benzene substituent. Parallel stacking (both parallel-sandwich and parallel-displaced) leads to more negative values of the MEP for pyrimidine, regardless of the benzene substituent. However, for imidazole, an increased hydrogen bonding ability is observed only for electron-donating groups on the benzene. T-shaped stacking leads to more negative values of the MEP for pyrimidine upon stacking, only for complexes comprising electron-donating substituents, whereas for imidazole the MEP is less negative upon stacking, regardless of the substituent. The susceptibility to increased hydrogen bonding ability upon stacking is larger for pyrimidine than for imidazole. Accordingly, we observe a larger charge transfer to pyrimidine than to imidazole, concomitant with a larger electron affinity for pyrimidine than imidazole (electron affinities approximated by the energy of the LUMO using Koopman's theorem are 0.12001 and 0.19461 a.u.

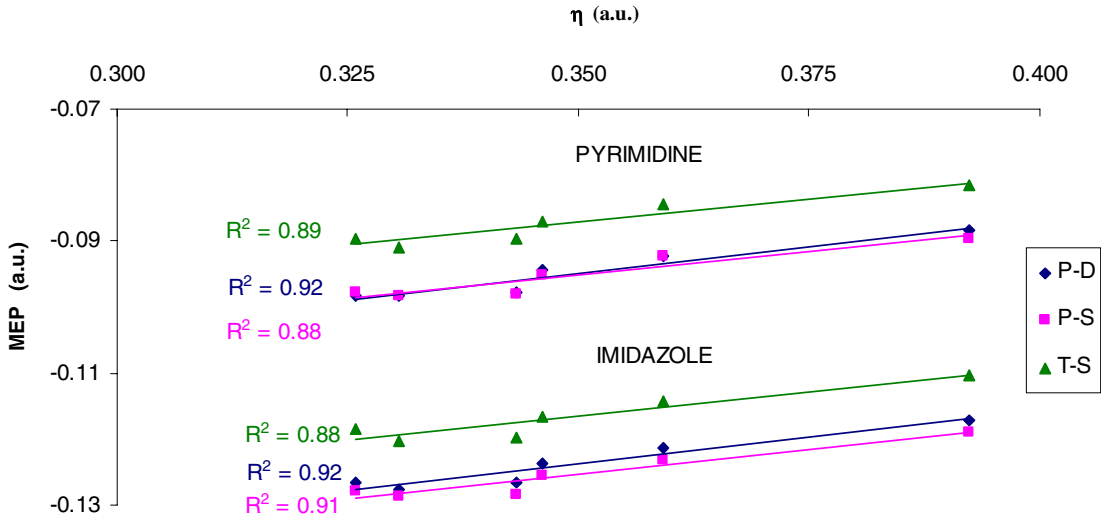

Fig. 4. Molecular electrostatic potential minimum (MEP min) around the nitrogen of the stacked pyrimidine and imidazole (a.u.) vs. global hardness (η) of the isolated substituted benzenes (a.u.).

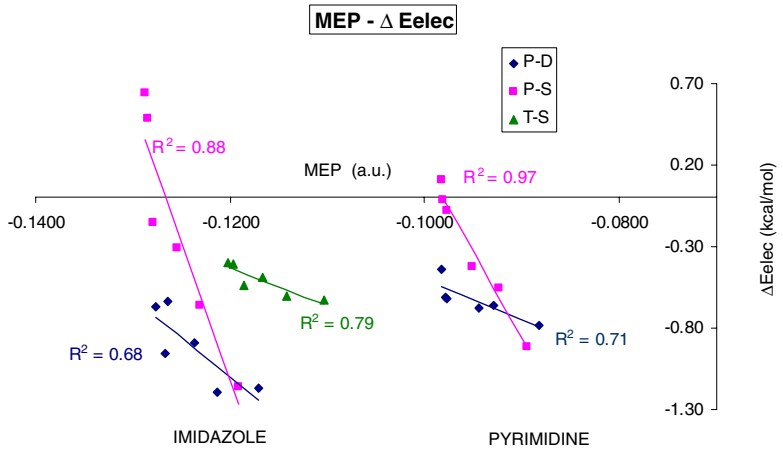

Fig. 5. Electrostatic component of the interaction energy between pyrimidine or imidazole and substituted benzene (ΔE_{elec} in kcal/mol) vs. molecular electrostatic potential minimum (MEP min) around the nitrogen atom (a.u.).

for pyrimidine and imidazole, respectively; low LUMO energies correspond to high electron affinities).

Substituent effects can be traced back to the global hardness of the substituted benzene. For parallel stacking, increasing electron transfer to pyrimidine or imidazole occurs for decreasing global hardness of the substituted benzene. For T-shaped stacking, the electron flow is inverted; electrons are pulled away from imidazole or pyrimidine. Nevertheless, the larger the charge transfer from benzene in parallel stacking or the lower the charge transfer to benzene in T-shaped stacking, the deeper the MEP, and thus the larger the hydrogen bonding ability of the stacked imidazole/pyrimidine will be (Fig. 4).

Furthermore, the H-bonding ability turns out to be inversely related to the electrostatic part of the interaction between the rings (Fig. 5). Although the relation between the hardness of the substituted benzenes, the charge transfer and the MEP can be intuitively appreciated, the role of electrostatics in the hydrogen bonding ability is quite remarkable. For parallel stacking, one observes that for increasing local hardness values (indicating increasing negative charge built up above the aromatic ring) the electrostatic interaction becomes more repulsive (π–π repulsion), in line with previous results (see [7], the correlation coefficient between ΔE_{elec} and $\eta(\underline{r})$ was $R^2 = 0.86$). Concomitantly, when the charge transfer to the aromatic nitrogen base increases, the MEP gets deeper. Thus, higher π–π repulsion, associated with less stabilizing ΔE_{elec} (i.e., more positive or less negative values), leads to stronger hydrogen bonding, resulting in an inverse correlation between ΔE_{elec} and H-bonding capability.

4. Conclusions

In all studied complexes of pyrimidine or imidazole stacked with a series of substituted benzenes in parallel-sandwich, parallel-displaced and T-shaped conformations, the dispersion interaction appears to be the major source of stabilization. Larger stabilization is observed for pyrimidine than for imidazole in parallel stacking, while the inverse is observed for the T-shaped arrangements. For parallel stacking, substituted benzenes bind stronger than unsubstituted benzene. Moreover the π electron density reaches a maximum for unsubstituted benzene, which cannot be increased by electron donating substituents. The hydrogen bonding ability of pyrimidine and imidazole increases upon parallel stacking, and more so for electron donating benzene substituents. All in all, both parallel and T-shaped complexes are stabilized by dispersion forces rather than by electrostatics, yet the latter accounts for modulation of the hydrogen bonding ability of the stacked nitrogen base.

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