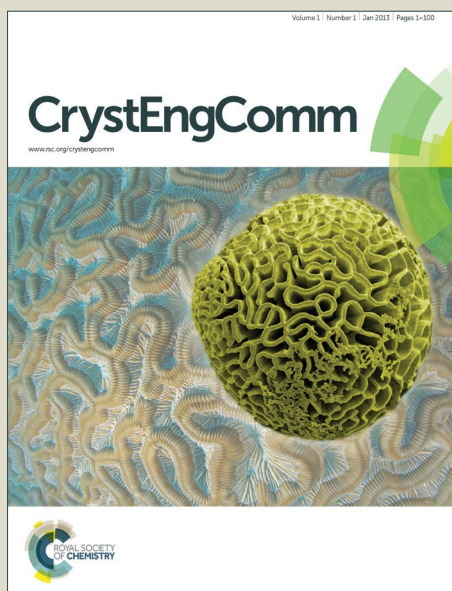


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Stacking interactions between hydrogen-bridged and aromatic rings. Study of crystal structures and quantum chemical calculations.

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Geometric analysis of data from Cambridge Structural Database (CSD) reveals that contacts between planar hydrogen-bridged rings and C₆-aromatic rings are mostly parallel stacked geometries. High level quantum chemical calculations show that interaction energies are comparable with interactions between two hydrogen-bridged rings. Namely, the interaction energy, at CCSD(T)/CBS level, of the most stable geometry is -4.38 kcal/mol, which is comparable with interaction between two hydrogen-bridged rings (-4.89 kcal/mol), and significantly stronger than stacking between two benzene rings (-2.73 kcal/mol).

Introduction

Although stacking (parallel) interactions have been considered typical for aromatic ring and studied extensively on model systems with aromatic rings, evidence of parallel interactions of other planar molecules and fragments has been reported.¹⁻¹⁴

It has been discovered that the monomer aromaticity can even hinder stacking interactions in some cases. By analysing stacking energies calculated for a wide range of π -stacking systems, it has been concluded that stacking interactions involving non-aromatic polyenes are as favourable as, if not more favourable, than interactions among equivalent aromatic species.^{15,16}

Cyclohexane and benzene dimers have similar interaction energies, but the energy differences are dependent on the functional and basis set used. Electrostatic component is the largest contributor to the observed differences.¹⁷ When the number of condensed rings becomes larger, aromatic rings begin to exhibit distinct behaviour from their aliphatic analogues. Thus, calculated stacking interaction of tetracene is 5-7 kcal/mol more stable than stacking of octadecahydrotetracene, depending on the method used.¹⁸ This additional effect, called π - π stacking effect, is a special nonlocal electron correlation between π -electrons in the two fragments and it is not pronounced in small stacked systems.

Some recent studies reveal that aromatic interactions in amyloid formation are not as important as previously postulated, since aliphatic peptides show similar self-assembly, justifying the use of aliphatic ultrasmall peptides as a simplified model-system to study amyloidosis.¹⁹ Theoretical investigation of the nonintercalative binding of an aliphatic and an aromatic bisguanilylhydrazone (BGH) to the minor groove of double-stranded (dA-dT)_n oligomers shows that the binding energy is larger with the aliphatic BGH than the aromatic one. Interactions with water are also larger with the aliphatic BGH than with the aromatic BGH. Dehydration energy is what makes the energy balance more favourable for the interaction of the aromatic than of the aliphatic BGH with the polynucleotide.²⁰

Rings containing metals or hydrogen bonds can also form stacking interactions.^{3,4,6,11-14,21} Thus, planar metal-chelates with delocalized π -bonds can stack with aromatic species and with other metal-chelate rings, exhibiting large interaction energies.^{3,4,6,11} Quasi-rings, formed by resonance-assisted hydrogen bonding,^{12,21} can form π -stacking interactions. Moreover, hydrogen-bridged rings with only single bonds in the ring form stacking interactions much stronger than stacking of two benzene molecules.^{13,14} Namely, saturated hydrogen-bridged rings in crystal phase are mostly antiparallel with normal distances typical for stacking (3.0-4.0 Å). High level *ab initio* calculations of interaction energies of dimers showed that energies can be much higher than stacking in benzene dimer. Stacking energy of 2-methylidenehydrazinecarbothioamide dimer, by far the most common saturated hydrogen-bridged species found in CSD, is -4.89 kcal/mol at CCSD(T)/CBS level,¹³ while stacking between two benzene molecules is much weaker, -2.73 kcal/mol²² calculated at the same level of theory.

Studying interactions between hydrogen-bridged and aromatic rings is important for understanding supramolecular systems.

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For example, small angle neutron scattering (SANS) and molecular dynamics (MD) simulations were used to characterize hydrophobic clusters of isopropanol and pyridine in aqueous solutions, which serve as highly soluble analogues of the nonpolar aliphatic and aromatic side chains of proteins, respectively. Addition of guanidinium-chloride reduced the aggregation of pyridine molecules, but had no effect on isopropanol aggregation, which indicates denaturant activity of guanidinium-chloride in proteins involving aromatic amino acid side chains.²³ Guanidinium cation is among the most frequent hydrogen-bridged species found in the Cambridge Structural Database (CSD).¹⁴

In this work we studied stacking between aromatic and hydrogen-bridged rings, by inspecting their mutual contacts in CSD and by calculating the interaction energies at high quantum mechanical level.

Methodology

Contacts between hydrogen-bridged rings, having only single bonds, which are all parts of the acyclic systems, and C₆-aromatic groups are studied in this work. A CSD search (CSD version 5.36 and updates-February 2015) is performed by using ConQuest 1.17. Constraints applied in search were: 1) distances between donor (D) and acceptor (A) atoms within hydrogen-bridged ring less than 4.0 Å; 2) angles between donor (D), hydrogen, and acceptor (A) atoms within the ring from 90° to 180°; 3) absolute torsions AX₁YD and XYDH (Fig. 1a) from 0 to 10°; 4) donor (D) and acceptor (A) atoms include N, O, Cl, S and F atoms, due to their considerable electronegativities; 5) all covalent bonds within the hydrogen-bridged ring are set to be single acyclic; 6) all atoms in the hydrogen-bridged ring were planar (rings with nonplanar atoms; tetrahedral nitrogen, oxygen or carbon atoms, polyvalent sulphur or metal atoms were excluded); 7) intermolecular contacts having distances between two centroids 4.5 Å or less (Fig. 1a) are considered as contacts

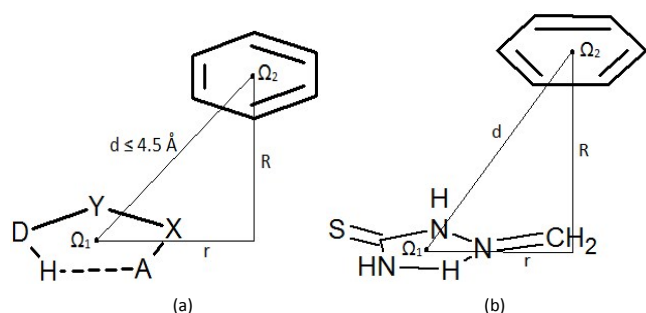


Fig. 1. (a) Geometric parameters and atom labelling scheme used for the description of intermolecular interactions between hydrogen-bridged and aromatic rings, studied in this work; Ω_1 and Ω_2 mark the ring centroids, X and Y letters stand for any atoms adjacent to acceptor (A) and donor (D) atoms, respectively, R and r mark normal distance and offset value, respectively; (b) Model system which was used for the estimation of the interaction strength, by varying parameters R and r.

between rings. The criterion 6), for planar atoms in the ring was set in order to avoid side interactions or steric hindrances coming from atoms or groups which are situated in the region between the rings. The crystallographic R factor is set to be less than 10%, disordered structures are excluded, coordinates are error-free, according to the criteria used in the CSD, the H-atom positions were normalized using the CSD default X-H bond lengths (O-H = 0.983 Å; C-H = 1.083 Å and N-H = 1.009 Å), no polymer structures and no powder structures were included.

Molecules of benzene and 2-methylidenehydrazine-carbothioamide (Fig. 1b) were chosen for the estimation of stacking energies among hydrogen-bridged and aromatic molecules. Results from our previous work,¹³ where stacking between two 2-methylidenehydrazinecarbothioamide molecules is calculated, could be useful for comparison. Optimizations of monomers are done at MP2/cc-pVTZ level. Stacking interaction energies between two rings at certain mutual positions were calculated at CCSD(T)/CBS level, while potential curves are obtained by methods that are in good agreement with CCSD(T)/CBS (ESI). Single-point interaction energy was determined as a difference of the dimer energy and the sum of energies of monomers, having included correction of basis set superposition error (BSSE).²⁴ All calculations are done by using Gaussian09 series of programs.²⁵

Energy decomposition analysis was done using perturbation method SAPT.²⁶ In SAPT approach, calculated interaction energies can be decomposed into four components: electrostatic, exchange, induction and dispersion energy. High-order SAPT 2+3 computations with density-fitting approximation and aug-cc-PVDZ basis set were performed using PSI4 program.^{27, 28}

Results and discussion

Interactions in crystal structures from the CSD

The number of structures with both planar hydrogen bridged rings, with only single bonds in the ring, (satisfying constraints 1-6 from Methodology section) and C₆-aromatic ring, was 1985. The number of rings (only constraints 1-6) was 1053. It was considered that an interaction between hydrogen bridged and aromatic ring exists if distance between centers of the rings is 4.5 Å or less (Fig. 1a). In that way we found 493 contacts (47% of 1053 rings found). Somewhat larger fraction of hydrogen bridged rings in the CSD forms interactions between two hydrogen bridged rings, 31%.¹³

Fig 2. shows interplanar angle distribution which indicates that contacts between hydrogen bridged and aromatic rings are mostly parallel, namely 221 contacts (44.8%) have interplanar angle smaller than 10°. Similar number of parallel contacts between hydrogen-bridged rings is found, namely 264 contacts.¹³

The typical normal distances of parallel contacts (with interplanar angle π smaller than 10°) found in CSD are

common for stacking interactions,^{3,11-14,29,30} since most of them are between 3.0 Å and 4.0 Å. Normal distance dependence on offset values is given in Fig. 3.

It is noticed by visual inspection that most of obtained contacts are between molecules that contain both C₆-aromatic and a hydrogen-bridged ring. Some structural motifs are particularly frequent. The most frequent is structural motif presented in

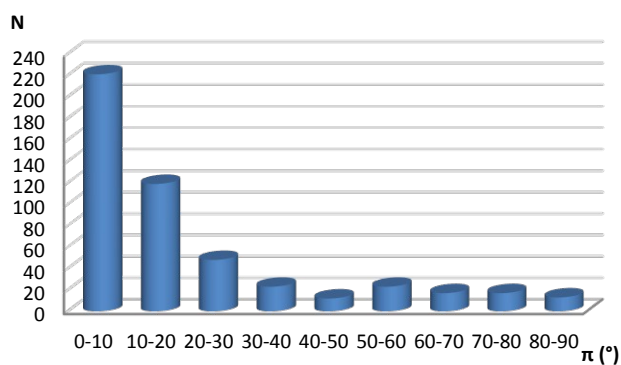


Fig. 2. Interplanar angle (π) distribution of contacts between planar hydrogen-bridged rings and aromatic rings

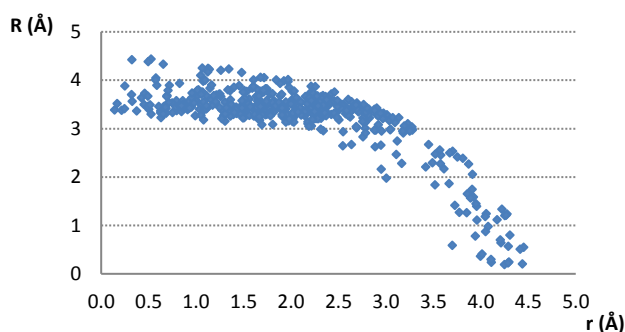


Fig. 3. Normal distance dependence on offset values for parallel contacts between planar hydrogen-bridged rings and aromatic rings

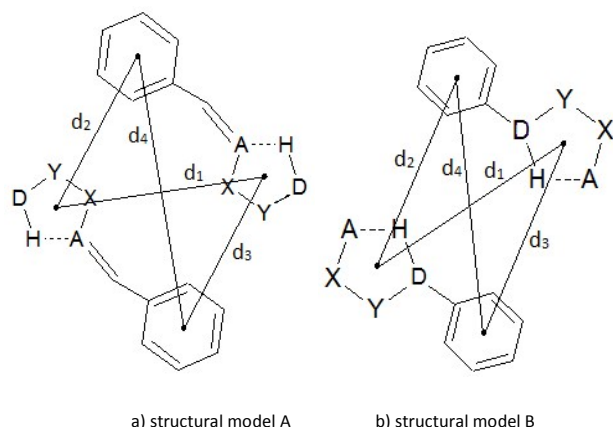


Fig. 4. Some of the most common structural motifs observed in the CSD with the distances between centers of the rings.

Figure 4a. It was found in 129 intermolecular parallel interactions (58% of 221 parallel contacts). In this structural motif C₆-aromatic group is attached to the acceptor atom by a

linker consisted of one planar carbon atom. Structures presented in Fig. 4b, where C₆-aromatic group is directly attached to the donor atom are less numerous (21 contacts, 9.5%).

Interactions between two molecules with structural motif A were inspected more closely. The number of motifs A found in the CSD and the number of contacts between particular rings are shown in Table 1. Contacts between hydrogen-bridged and

Table 1. Number of parallel interactions of a structural motif A (Fig.4a) in crystal structures from the CSD

number of monomers	parallel HRB/HRB ^a contacts ($d_1 \leq 4.5$ Å)	parallel HBR ^a /aromatic contacts (d_2 or $d_3 \leq 4.5$ Å)	parallel aromatic/aromatic contacts ($d_4 \leq 4.5$ Å)
538	46 (9%)	129 (24%)	40 (7%)

aromatic rings are roughly three times as frequent as contacts between two hydrogen-bridged or two aromatic rings, which are approximately equally frequent. The prevalence of hydrogen-bridged/aromatic contacts is probably a consequence of the possibility for the existence of two simultaneous HRB/aromatic interactions between two molecules (Fig. 5). Results from Table 2 support this conclusion, since two simultaneous hydrogen bridged/aromatic interactions are present in most cases (80 contacts, which is 62% of totally 129 HBR/aromatic contacts).

Quantum-chemical calculations on interactions

In order to evaluate energies of parallel interactions between hydrogen bridged and aromatic rings we performed quantum chemical calculations. Estimation of the best method for calculating stacking energies is based on good agreement with CCSD(T)/CBS energies.³¹ Potential surfaces are calculated on MP2/cc-pVTZ level, since the energies are very similar to the CCSD(T)/CBS limit for all five orientations (Tables S1). The model system used for calculations is presented in Fig. 7.

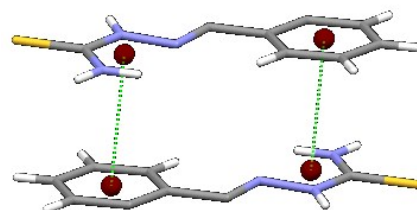


Fig. 5. One of the possible structural fragments found in CSD illustrating the typical orientation of the interacting rings with two simultaneous hydrogen bridged/aromatic interactions

Potential surface was calculated by varying offset values in Ω_1 -C direction and in the orthogonal direction in steps of 0.5 Å, while normal distances were examined for every particular offset value in order to obtain the strongest energy. The potential curves, showing the strongest energy for given offset value, are given in Fig. 6. Corresponding normal distance dependences on offset values are shown in Fig. S5.

Table 2. Number of two simultaneous parallel interactions between particular rings of motif A (Fig. 4a) in crystal structures from the CSD

Type of contacts	Number of contacts
HBR/HBR ^a and HRB ^a /aromatic contacts	4(0.01%)
HBR/HBR ^a and aromatic/aromatic contacts	8(0.01%)
Double HRB ^a /aromatic contacts	80 (14.87%)
HRB ^a /aromatic and aromatic/aromatic contacts	8(0.01%)

^aHBR refers to hydrogen-bridged ring

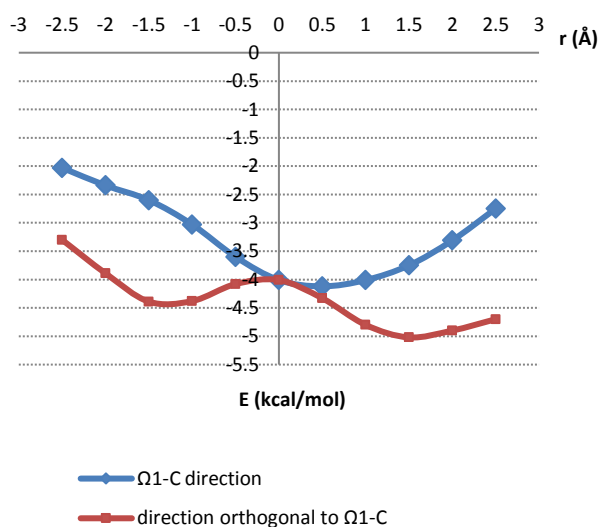


Fig. 6. Potential curves calculated on mp2/cc-pVTZ level. The strongest energy for a given offset value is shown.

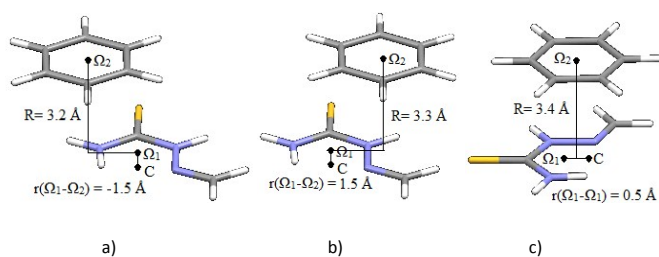


Fig. 7. Geometries of potential curves minima (Fig. 6, Table 3); a) Minimum at -1.5 Å, along the direction orthogonal to Ω1-C, corresponding to stacking interaction of the two rings; b) Minimum at 1.5 Å, along the direction orthogonal to Ω1-C, corresponding to interaction of benzene ring with doubly bonded methylidene group; c) Minimum at 0.5 Å, along Ω1-C direction, corresponding to stacking interactions of the two rings.

The potential curves in Fig. 6 show that minima occur at parallel-displaced positions, similar to benzene²² and pyridine³⁰ and hydrogen-bridged ring stacking dimers.¹³ Interaction energies in Ω1-C direction are less strong than in the orthogonal direction (Fig. 6). The strongest interaction is for direction orthogonal to Ω1-C (Fig. 6 and 7a); interaction energy at -1.5 Å minimum on the curve is -4.38 kcal/mol at CCSD(T)/CBS level (Table 3). This energy is comparable to

stacking energy in hydrogen-bridged ring dimer, -4.89 kcal/mol for the same hydrogen bridged ring (2-methylidenehydrazinecarbothioamide)¹³ (Table 3). The result is somewhat surprising because benzene molecule does not possess dipole moment.

Table 3. Interaction energies (ΔE) at CCSD(T)/CBS level, normal distances (R) and offset values (r) at potential curves minima. Model systems are given in Fig. 7; potential curves are given in Fig. 6.

2-methylidenehydrazinecarbothioamide dimer ^a			
	ΔE (kcal/mol)	r (Å)	R (Å)
Along Ω - Ω' direction	-4.84	0.0	3.3
Orthogonal to Ω - Ω' direction	-4.89	-1.0	3.0
2-methylidenehydrazinecarbothioamide/benzene			
	ΔE (kcal/mol)	r (Å)	R (Å)
Along Ω - Ω' direction	-4.04	0.5	3.4
Orthogonal to Ω - Ω' direction	-4.38	1.5	3.2

(a) Data from reference 13

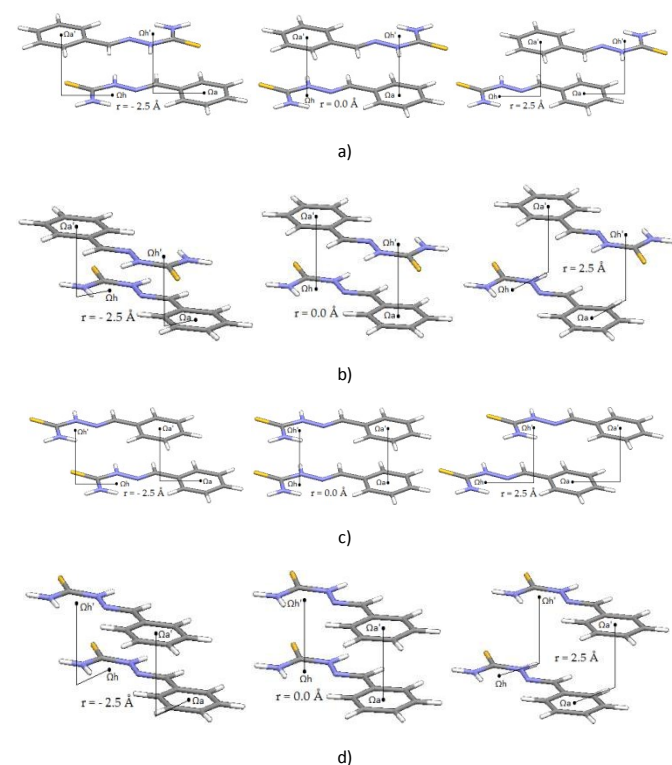


Fig. 8. Geometries of *E*-benzylidenehydrazinecarbothioamide dimers at different mutual positions; a) antiparallel with offset changing in Ω_h - Ω_a direction; b) antiparallel with offset changing in direction orthogonal to Ω_h - Ω_a ; c) parallel with offset changing in Ω_h - Ω_a direction; d) parallel with offset changing in direction orthogonal to Ω_h - Ω_a

The other minimum at positive offset of 1.5 Å, on the same curve, does not correspond to interaction between hydrogen

bridged and aromatic ring, it is consequence of side interactions with the doubly bonded methyldene group (Fig. 7b). Energy corresponding to Ω_1 -C curve minimum (Fig 6 and 7c), calculated at CCSD(T)/CBS level, is -4.04 kcal/mol (Table 3). Energies at both minima on potential curves for stacking between hydrogen-bridged and benzene are significantly stronger than stacking of two benzene molecules (-2.73 kcal/mol).²² Since the data from crystal structures showed that most of stacking interactions are between molecules that contain both C6-aromatic and a hydrogen-bridged ring (Fig. 6), we performed calculations on E-benzylidenehydrazinecarbothioamide dimers.

This molecule was chosen as an example of structural motif A (Fig. 4a). Quite strong energies were calculated for stacking dimers of E-benzylidenehydrazinecarbothioamide (Fig. 8b). The potential curve is obtained by calculations at MP2/cc-pVTZ method, since it was shown that this method is good for interaction energy calculations of 2-methylidenehydrazinecarbothioamide/benzene dimers in different mutual positions (ESI).

Two E-benzylidenehydrazinecarbothioamide molecules in antiparallel and parallel alignment are moved in Ω_h - Ω_a direction and the orthogonal direction in steps of 0.5 Å, while normal distances were varied for every particular offset value in order to obtain the most stable interaction for each offset value.

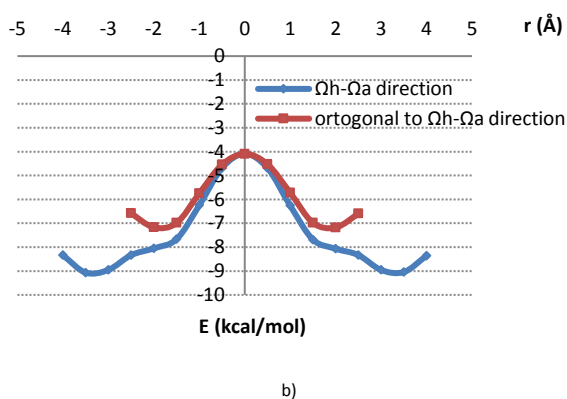
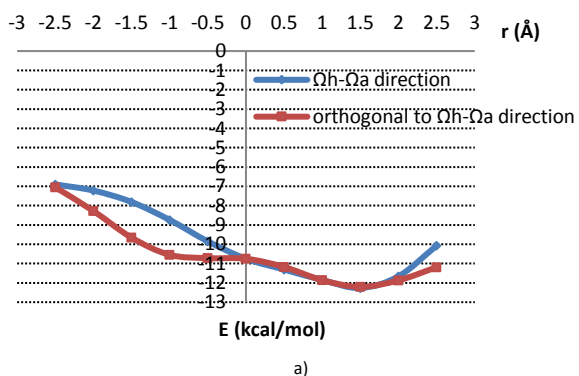


Fig. 9. Potential curves for the dimer interaction of E-benzylidenehydrazinecarbothioamide) in a) antiparallel alignment b) parallel alignment; model systems are shown in Fig. 8.

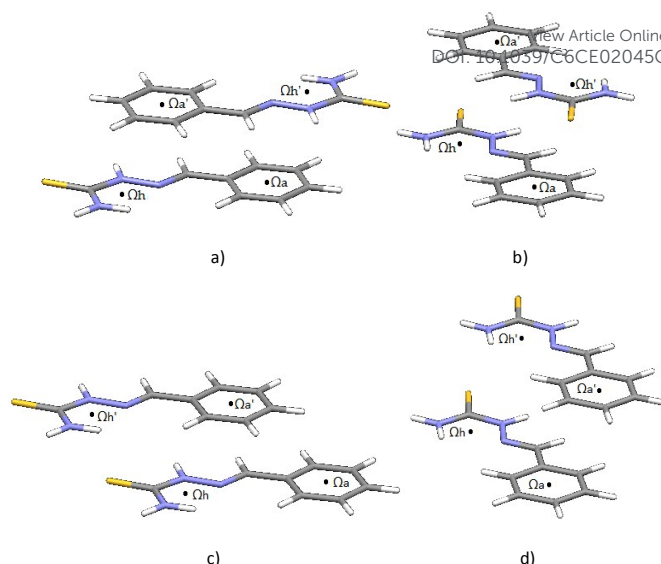


Fig. 10. Geometries at the curve minima; a) antiparallel alignment, Ω_h - Ω_a direction; b) antiparallel alignment, orthogonal to Ω_h - Ω_a direction; c) parallel alignment, Ω_h - Ω_a direction; d) parallel alignment, orthogonal to Ω_h - Ω_a direction

Potential curves are given in Fig. 9, while geometries corresponding to the minima are given in Fig. 10. For antiparallel orientation, energies at the minima for both curves (at offset of 1.5 Å in both cases and normal distance of 3.2 Å and 3.3 Å, for Ω_h - Ω_a direction and the orthogonal direction, respectively) are quite strong; -12.26 kcal/mol and -12.21 kcal/mol, for Ω_h - Ω_a direction and the orthogonal direction, respectively. In the geometries at minima there are two simultaneous stacking interactions between hydrogen bridged and aromatic rings (Fig. 10a,b). In the geometries at the curve minima the two molecules are slipped (Fig. 10a,b). Potential curves corresponding to parallel orientations (Figure 9b) are symmetric since dimer geometries at positive and negative offsets are the same (Fig. 8c and 8d).

Table 4. Horizontal displacements (r), normal distances (R) and interaction energies of E-benzylidenehydrazinecarbothioamide dimers at potential curves minima. Model systems are given in Fig. 10; potential curves are given in Fig. 9.

antiparallel alignment			
	ΔE (kcal/mol)	r (Å)	R (Å)
Ω_h - Ω_a direction	-12.26	1.5	3.2
orthogonal to Ω_h - Ω_a direction	-12.21	1.5	3.3
parallel alignment			
	ΔE (kcal/mol)	r (Å)	R (Å)
Ω_h - Ω_a direction	-9.07	± 3.5	3.3
orthogonal to Ω_h - Ω_a direction	-7.18	± 2.0	3.3

Potential curves corresponding to parallel orientations (Figure 9b) are symmetric since dimer geometries at positive and negative offsets are the same (Fig. 8c and 8d). Compared to the minima in antiparallel positions (Fig. 9, Table 4), interaction energies are less strong (-9.07 kcal/mol and -7.18 kcal/mol, Ω_h - Ω_a and the orthogonal direction, respectively) and offset values at the curves minima are larger (-3.0 Å and -2.0 Å in Ω_h - Ω_a and the orthogonal direction, respectively) (Table 4).

Strong calculated energies of stacking interactions for antiparallel orientation explain data from CSD search (Tables 1 and 2 and Fig. S3), ie. structures with two simultaneous interactions between hydrogen bridged and aromatic rings (and consequently antiparallel) are significantly more prevalent than structures with single contacts (HBR/HBR, aromatic/aromatic or HRB/aromatic) or two simultaneous interactions in parallel orientation.

SAPT decomposition

In order to better understand the nature of stacking between aromatic and hydrogen-bridged rings, SAPT decomposition analysis was applied. The SAPT calculations were performed on two minima presented in Figure 7 and Table 3, the minimum along Ω - Ω' direction and the minimum orthogonal to Ω - Ω' direction.

The results given in Table 5 show that terms for both studied minima are similar. In both systems electrostatic, induction and dispersion energies are attractive, while the strongest attractive contribution is dispersion; it is more than two times larger than electrostatic term. Exchange is repulsive in both systems. The calculated total SAPT energies (-3.94 and -4.44 kcal/mol, Table 5) are in very good agreement with CCSD(T)/CBS values (-4.04 and -4.38 kcal/mol, Table 3). The stronger interaction energy for minimum orthogonal to Ω - Ω' direction is a consequence of stronger electrostatic, induction and dispersion energies, although, the repulsive exchange term is also larger for this minimum (Table 5).

Comparison with SAPT decomposition for stacked benzene dimer³² show that electrostatic and dispersion terms are more attractive in benzene/hydrogen-bridged ring, while repulsive exchange terms are similar. It results in significantly more stable stacking in benzene/hydrogen-bridged ring in comparison to benzene.

Table 5. SAPT energy decomposition results for 2-methylidenehydrazinecarbothioamide/benzene interactions

Energy therm	Minimum along Ω - Ω' direction	Minimum orthogonal to Ω - Ω' direction
Electrostatics	-3.20	-4.29
Exchange	8.48	9.49
Induction	-0.86	-1.04
Dispersion	-8.36	-8.59
Total SAPT2+3	-3.94	-4.44

Conclusions

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In summary, contacts between planar hydrogen-bridged rings and aromatic C_6 -rings, found in the CSD, are mostly parallel displaced, with normal distances typical for stacking. In the crystal structures very often these interactions are between two molecules that possess both hydrogen-bridged and aromatic rings.

Interaction energies are calculated on model system composed of hydrogen-bridged ring (2-methylidenehydrazinecarbothioamide) and benzene molecule. The most stable orientation is parallel-displaced, in accordance with data in crystal structures, with interaction energy of -4.38 kcal/mol at CCSD(T)/CBS level. SAPT decomposition of interaction energies show that the main contribution to attraction is dispersion energy, although, attractive electrostatic energy is also significant.

The data show that interaction energy between hydrogen-bridged and benzene ring is comparable with interaction between two hydrogen-bridged rings (2-methylidenehydrazinecarbothioamide), -4.89 kcal/mol, while it is significantly stronger than stacking between two benzene rings, -2.73 kcal/mol.

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Notes and references

#Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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