# Supplementary Information

## Aliphatic-aromatic stacking interactions in cyclohexane–benzene are stronger than aromatic-aromatic interaction in benzene dimer

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**I Area correction**

The area correction assumes that the frequency distribution of interactions must be corrected for the fact that the acceptor, being of a multiatom type, has a finite area. The number of interactions with offset r is proportional to $2\pi r$. If N is the number of interactions in the range r and $r+\Delta r$, the area correction assumes the use of N/r in histograms instead of N.[S1]

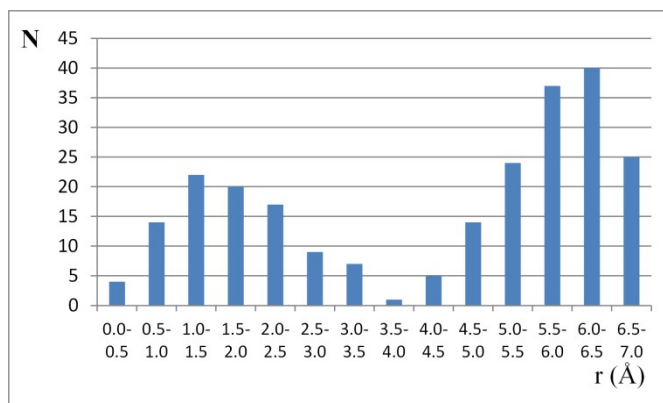The non-corrected distribution of the offset values r for cyclohexyl–phenyl interactions is shown in Fig S1.



**Fig. S1** The non-corrected distribution of the offset values r for cyclohexyl–phenyl interactions. N is number of the cyclohexyl–phenyl interactions.

**II The optimized geometries of cyclohexane and benzene molecules**

After optimization, the cyclohexane molecule was in the chair conformation with all C–C bond lengths equivalent. There were small differences between bond lengths and angles for equatorial hydrogen ($H_e$) and axial hydrogen atoms ($H_a$). The optimized cyclohexane bond lengths were C–C 1.528 Å, C–$H_e$ 1.092 Å and C–$H_a$ 1.095 Å, while the bond angle values were ∠CCC 111.15°, ∠CC$H_e$ 110.33° and ∠CC$H_a$ 109.01°. The optimized geometry of benzene molecule was a planar regular hexagonal ring, with a C–C bond length of 1.392 Å and a C–H bond length of 1.082 Å.

**III The comparison of calculated energies for cyclohexane–benzene interactions with CCSD(T) and MP2 methods**

Table S1. The calculated normal distances ($R$) and interaction energies ($\Delta E$) at different offset values *(r)* for cyclohexane–benzene dimer

| r [Å] | R [Å] | ΔE(CCSD(T)/CBS) [kcal/mol] | MP2/def2-TZVP [kcal/mol] |
|---|---|---|---|
| 0.0 (orientation **B**) | 4.2 | -3.05 | -3.17 |
| 1.5 (orientation **A**) | 3.9 | -3.27 | -3.34 |
| 4.0 (orientation **A**) | 4.0 | -1.19 | -1.19 |

## IV The calculated normal distances *(R)* vs. horizontal displacement *(r)* for cyclohexane–benzene dimer

For the positive offset values, the normal distances R for orientations A and B decrease in the proximity of the minimum at the offset values between 1.5 and 2.0 Å. In both orientations, one axial hydrogen atom is situated above the center of the benzene ring forming CH/π interaction, while the other two axial hydrogens are positioned almost beyond benzene ring. Moving to larger offset values, when the first axial hydrogen atom passes the center of the benzene ring the normal distances increase. For B orientation, when axial hydrogen passes the C–C bond (r = 4.5 Å) normal distances are getting lower in comparison to Acb where the same hydrogen atom is moving along the C–H bond.

For the negative offset values, the normal distances R for all three orientations are similar in the offset range from 0.0 Å to –3.0 Å. At the offset values between –3.0 and –4.5 Å, the normal distances are the shortest for A orientation due to attractive interaction of equatorial hydrogen atom with π–system and smaller steric interactions of hydrogen atoms in comparison to the other two orientations (Fig. S2). At the other hand, for orientation B at the same negative offset range there are steric interactions of hydrogen atoms. For orientation C, the normal distances are longer than for the other two orientations at the offset values from –3.0 Å to –5.5 Å because of the one axial hydrogen atom situated almost above the C–H bond and two equatorial hydrogen atoms too far from π–system. At larger offset values (more negative than –5.0 Å) the same axial hydrogen atom is far from benzene C–H bond what allows shorter normal distances.
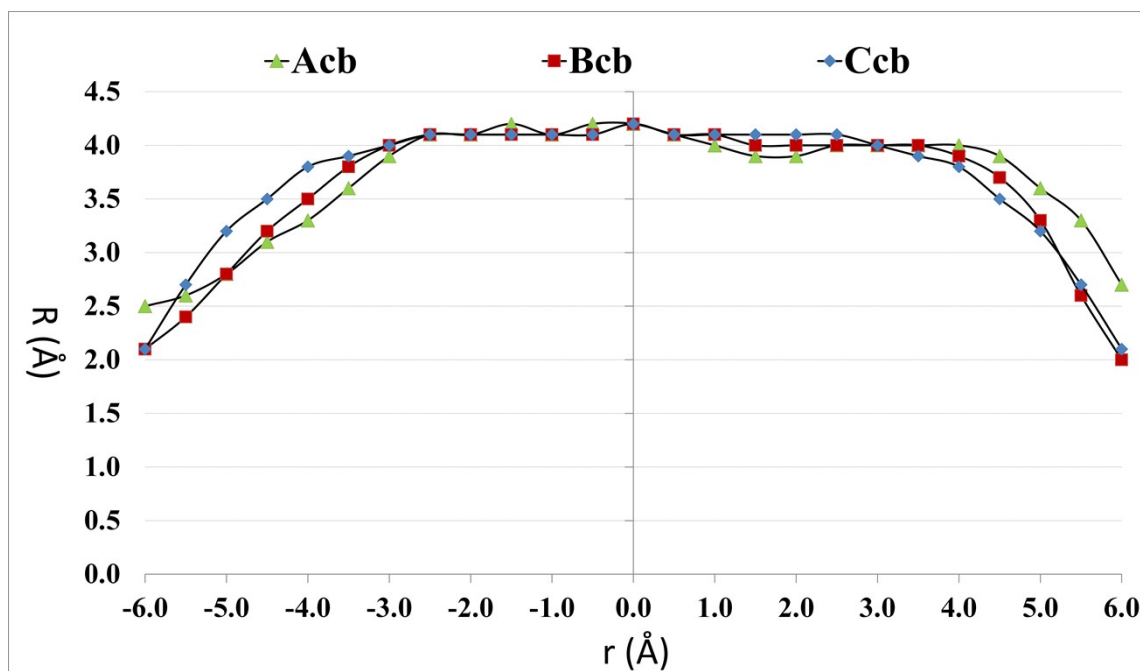


**Fig. S2** Normal distances (R) that correspond to energy minimums from Fig 4 for three different orientations of cyclohexane–benzene dimer plotted as a function of the offset value r. The interactions energies for each offset value r were calculated (using MP2/def2–TZVP method) by varying the normal distance (R) between two molecules in a series of single point calculations. The normal distances (R) for strongest calculated energy for each offset value is presented. The A, B, and C orientations are presented in Fig. 3.

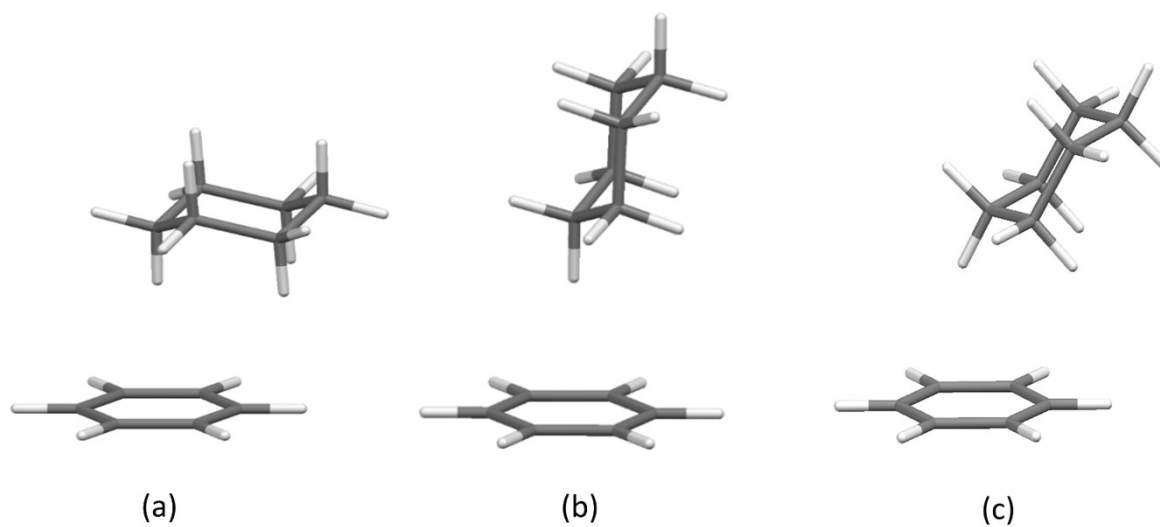**V Optimal CH/π interactions of cyclohexane's equatorial, and axial H atoms with benzene**



(a)                              (b)                              (c)

**Fig. S3** Geometries for calculated optimal CH/π interactions with cyclohexane's axial (a) equatorial (b) and optimized equatorial (c) H atoms. Energy for the optimal axial CH/π interaction, with distance between the center of the benzene and the axial H atom of 2.6 Å, is -3.26 kcal/mol. Energy for the optimal equatorial CH/π interaction, with distance between the center of the benzene and the equatorial H atom of 2.5 Å, is -2.55 kcal/mol. Energy for the counterpoise optimized interaction starting from optimal equatorial CH/π interaction, with geometry that mimics tilted T-shape interaction of benzene, is 3.11 kcal/mol. All the calculations are done using MP2/def2–TZVP method.

## VI Electrostatic potential maps

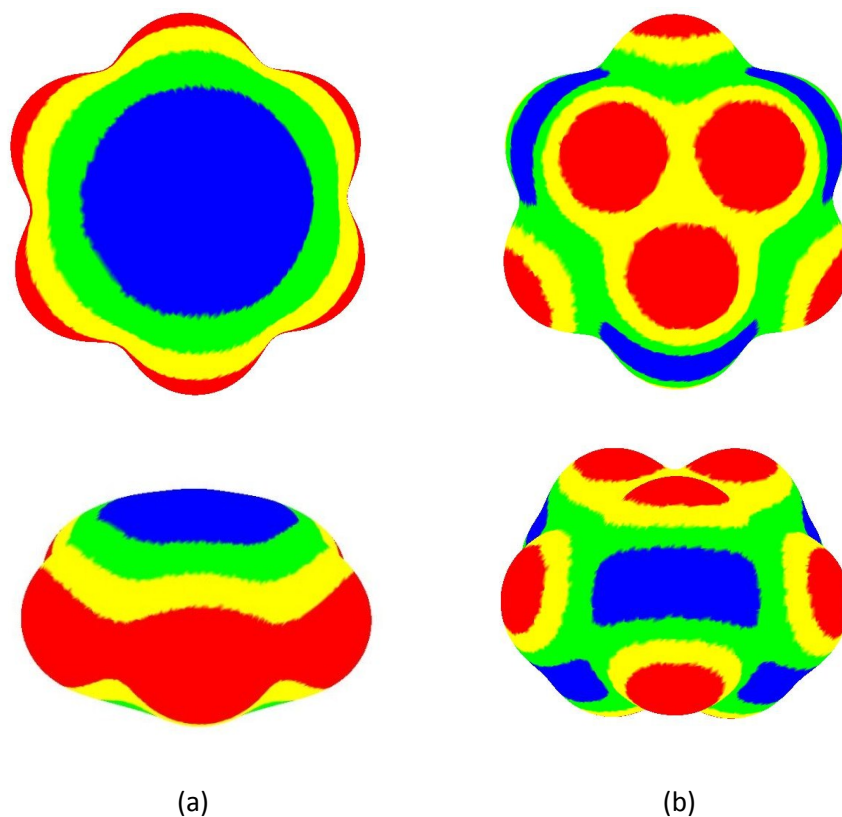

|  |  |
|---|---|
| (a) | (b) |

**Fig. S4** Two views of electrostatic potential maps of a) benzene and b) cyclohexane. Electrostatic potential scale for benzene: red (0.53 to 0.24 kcal/mol), yellow (0.24 to -0.04 kcal/mol), green (-0.04 to -0.33 kcal/mol), blue (-0.33 to -0.61 kcal/mol ) . Electrostatic potential scale for cyclohexane: red (0.23 to 0.15 kcal/mol), yellow (0.06 to -0.02 kcal/mol), green (-0.02 to -0.11 kcal/mol), blue (-0.33 to -0.61 kcal/mol).

[S1] Z. Ciunik and G. R. Desiraju, Chem. Commun., 2001, 703-704