

On the Nature of σ – σ , σ – π , and π – π Stacking in Extended Systems

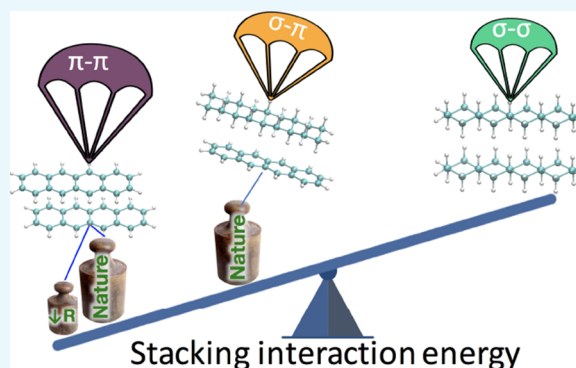
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S Supporting Information

ABSTRACT: Stacking interactions have been evaluated, employing computational methods, in dimers formed by analogous aliphatic and aromatic species of increasing size. Changes in stability as the systems become larger are mostly controlled by the balance of increasing repulsion and dispersion contributions, while electrostatics plays a secondary but relevant role. The interaction energy increases as the size of the system grows, but it does much faster in π – π dimers than in σ – π complexes and more remarkably than in σ – σ dimers. The main factor behind the larger stability of aromatic dimers compared to complexes containing aliphatic molecules is related to changes in the properties of the aromatic systems due to electron delocalization leading to larger dispersion contributions. Besides, an extra stabilization in π – π complexes is due to the softening of the repulsive wall in aromatic species that allows the molecules to come closer.



INTRODUCTION

Noncovalent interactions involving π systems are crucial in a wide variety of chemical, physical, and biological processes.^{1,2} The role of aromatic π interactions is evident in the case of proteins, considering that there are several amino acids bearing an aromatic ring in their side chains. These aromatic side chains can be involved in specific interactions affecting the protein structure and function, acting in a different way compared to aliphatic amino acids.^{3–6} Aromatic interactions also play a significant role in materials science and, more specifically, in extended π systems of evident interest as carbon nanotubes, fullerenes, graphene, and their derivatives that mostly interact by means of π interactions.^{1,7,8}

In most cases, when an aromatic unit interacts with another species, the interaction corresponds to one of the three following motifs: π – π stacking, $\text{XH}\cdots\pi$ contact, and $\text{ion}\cdots\pi$ interaction.^{5,9} Cation– π interactions are a well-established interaction pattern in proteins, and different studies indicate that their main stabilizing factor is electrostatics but with significant contributions from induction or even dispersion in the case of larger organic cations.^{6,10–16} A similar behavior has been observed for the more novel anion– π interactions, though in this case, the role of dispersion is usually larger.^{17–21} The $\text{XH}\cdots\pi$ interactions are usually weaker than the $\text{ion}\cdots\pi$ ones, and resemble a hydrogen bond with the aromatic cloud acting as an acceptor. Though weaker than $\text{ion}\cdots\pi$ interactions, the combination of several $\text{XH}\cdots\pi$ interactions can deeply affect the characteristics of the systems.^{22,23}

The stacking interaction between aromatic rings has been recognized for a long time as one of the key interacting motifs contributing to the stability of systems containing aromatic substituents.^{3,5,24} This kind of interaction has been widely studied, especially for the prototypical benzene dimer.^{25–29} For some time, it has been commonplace to consider that π stacking interactions were a sort of interaction type with some special characteristics compared to aliphatic structures. However, this view has changed in recent years, and the term stacking has been put into question as π systems do not tend to stack because of repulsion between the π electron clouds.^{30,31} In consequence, caution is required to describe the effect of π -systems in chemical or biological systems.

The main stabilizing factor in stacked π – π structures is dispersion.^{12,32,33} Because the dispersion contribution is present in any system, favorable stacking interactions are also possible among aliphatic species. In fact, it has been shown that the interaction in the cyclohexane dimer is similar in magnitude to that of the benzene dimer, and the cyclohexane–benzene dimer is more tightly bound than benzene or cyclohexane homodimers.^{32,34,35} The stacked dimers formed by benzene and cyclohexane have quite similar stabilities, as a result of a balance between different contributions: homodimers show a more important role of dispersion, while electrostatics is slightly larger in the heterodimer.^{32,36}

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Therefore, if π - π , σ - π , and σ - σ interactions can provide similar stability, all should be considered for understanding the behavior of multitude of systems, as well as for engineering new supramolecular receptors or functional molecules. However, the behavior observed for small dimers not necessarily has to be the same in extended systems. It has been recently shown that layers of graphene and graphane have similar stabilities, though the values for graphane are significantly smaller, indicating that as the system grows, aromatic stacking interactions somehow strengthen relative to aliphatic ones.³⁷

Different studies have been carried out in order to determine how aromatic and aliphatic stacking interactions behave as the size of the system grows.^{31,38–42} In a pioneering work, Grimme et al. studied the stacking interactions in homodimers of linear acenes up to tetracene in stacked and T-shaped arrangements, and compared the results to those obtained for their stacked aliphatic counterparts.³¹ The authors indicate that the interaction energy grows faster in aromatic dimers than in aliphatic ones, suggesting that the effect is due to intermolecular distance shortening in aromatic dimers as well as to some kind of cooperative effect, absent in aliphatic dimers, and mainly associated with dispersion. These results were further refined and the main conclusions remained the same, though the use of a different model for dispersion greatly improves the description of aliphatic stacked structures.³⁸ Janowski and Pulay carried out high-level calculations on dimers of naphthalene and coronene as well as their hydrogenated counterparts, concluding again that σ -stacking energies are substantial though significantly weaker than π -stacking interactions.³⁹

Alonso et al. employed the noncovalent interaction index in order to assess the characteristics of the interaction in benzene, naphthalene, and anthracene dimers and their perhydrogenated counterparts.⁴⁰ The authors found that dispersion interactions involving hydrogen atoms are the reason behind the stabilization in aliphatic dimers. Also, while aliphatic interactions are inherently localized, the delocalized character of π - π interactions gives rise to the extra stabilization observed in aromatic dimers as the system grows. Yuan et al. have shown that the interaction in mixed graphene/graphane systems is roughly additive in the number of $\text{CH}\cdots\pi$ contacts,⁴³ while the same conclusion has been reached by Wang et al. in graphane dimers.³⁷ Guijarro et al. have also shown that sublimation energies of acenes behave linearly with the number of atoms and can be traced back to the presence of dispersion-dominated $\text{C-H}\cdots\pi$ interactions.⁴⁴

A more detailed analysis of the nature of the interaction can be obtained by means of symmetry-adapted perturbation theory (SAPT) methods that allow computing different contributions to the stability associated with well-defined physical terms.^{45,46} In this respect, it is worth mentioning the work of Podeszwa et al. on several aromatic complexes including the coronene dimer.^{47,48} The results confirm that dispersion is clearly dominant. A similar conclusion has been reached by Hohenstein et al. for linear acene dimers, showing that dispersion grows faster in aromatic systems than in aliphatic ones.⁴² A thorough exploration of the potential energy surface of linear acene dimers by Ryno et al. unveils the role of electrostatic penetration effects on the stability of these systems, accounting for up to 50% of the total interaction energy.⁴¹ The results obtained by Gryn'ova et al. also highlight the relevance of penetration effects on hydrocarbon dimers.⁴⁹

However, it has to be indicated that these results have been obtained using a moderate set of systems, or employing the SAPT0 level. SAPT0 uses HF wavefunctions and though it has been shown to be capable of providing reasonable values for a variety of systems, it relies on large error compensation.⁵⁰ Also, in most of the works commented above, σ - π dimers correspond to linear acene homodimers in T-shaped orientation, but no studies are performed for mixed aliphatic-aromatic dimers.

Figure 1 summarizes the systems considered in this work: linear acenes from benzene to hexacene, as well as nonlinear

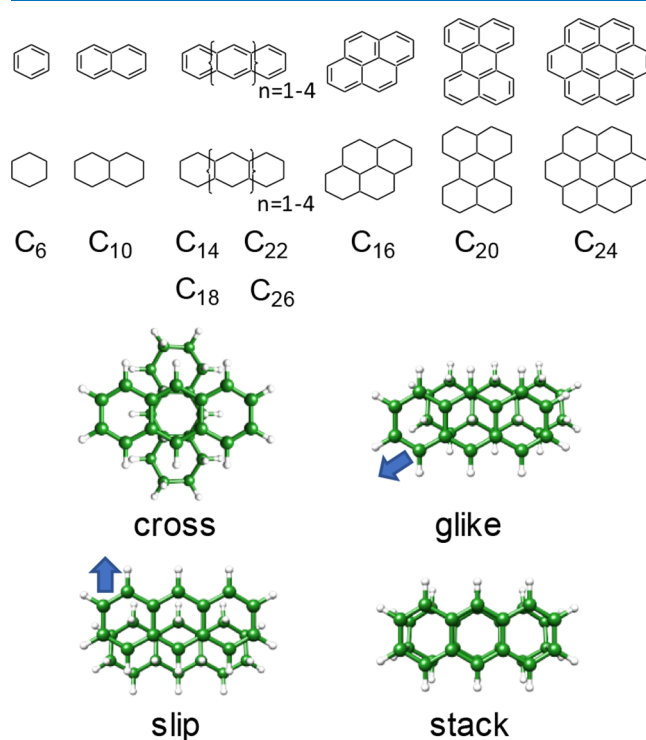


Figure 1. Molecules considered in this work (top) and the relative orientations (bottom) considered for the dimers studied. A σ - π case is shown for a dimer formed by anthracene with its perhydrogenated derivative. In glike and slip orientations, the molecules are displaced by 1.45 Å as indicated by the arrows (see text).

polycyclic aromatic hydrocarbons (PAHs) as pyrene, perylene, and coronene; besides these π species, their perhydrogenated counterparts are also considered (cyclohexane, decalin, etc.). Homodimers formed by the different aromatic species are employed to study the characteristics of the π - π stacking interactions, while homodimers formed by the perhydrogenated molecules are used to study σ - σ stacking interactions. Finally, heterodimers comprising one of the PAHs and its perhydrogenated counterpart are used to study σ - π interactions. Following Podeszwa,⁴⁷ for each of these dimers, four different orientations have been considered as also shown in Figure 1. These orientations correspond to a dimer with the units just stacked above each other (**stack**), a stacked structure where one of the units is rotated by 90° (**cross**), and two stacked structures (**slip** and **glike**) where one molecule is displaced. **glike** corresponds to an arrangement similar to that observed in graphite.

Comparing the results obtained for the total interaction energies as well as for their components could reveal the intrinsic differences of the interaction in σ - σ , σ - π , and π - π

complexes, helping to understand why π interactions are favored over σ ones as the system grows.

RESULTS AND DISCUSSION

Potential energy curves are obtained for the dimers studied, considering the relative orientations shown in Figure 1, and the minimum of each curve is obtained by interpolation (at the TPSS-D3BJ/def2-TZVPP level, see Computational Methods; the full set of results is shown in Figure S1 and Tables S2 and S3, Supporting Information). Employing these minima, the interaction energies are obtained with a more robust method (MP2.X, see Table S4, Supporting Information), and these are the values used for discussion as summarized in Figure 2. The

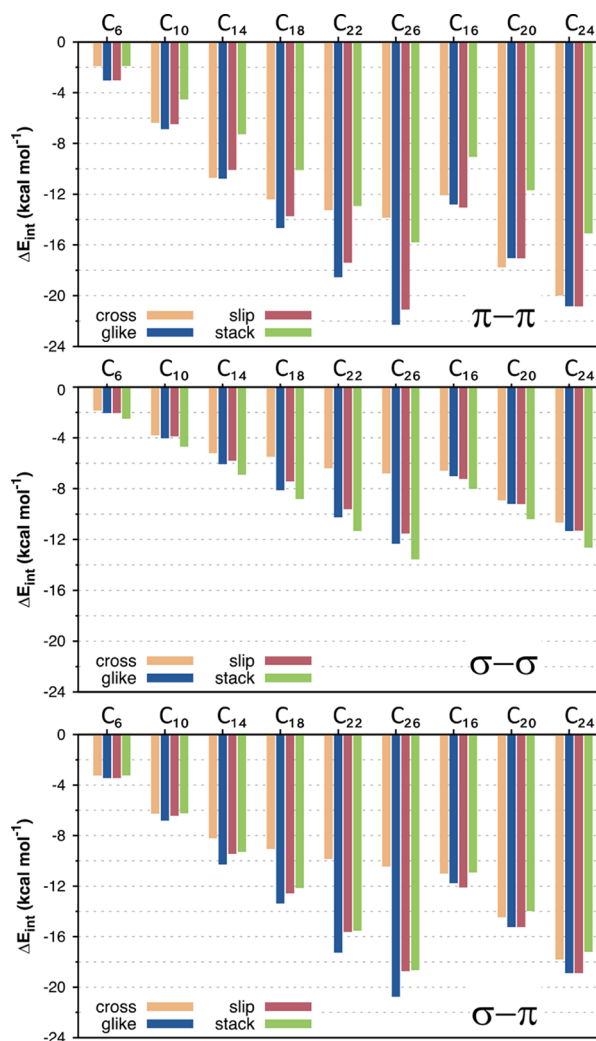


Figure 2. Interaction energies obtained at the MP2.X level for the different kind of interactions considered. C_n and orientations as defined in Figure 1.

plot on the top corresponds to systems showing π - π interactions; that is, homodimers formed by the linear acenes up to hexacene and also dimers of pyrene, perylene, and coronene. As observed in Figure 2 (top) and in accordance with previous work,^{27,28,32} the most stable benzene dimer corresponds to the **glike** or **slip** orientations, that in this case correspond to the same structure. Other relative orientations such as the **stack** and the **cross** ones are significantly less stable (see Figure 1 for a representation of these orientations). It has

to be remembered here that only parallel stacked structures are considered, so no T-shaped minima have been taken into account. The interaction energy amounts to around -3.0 kcal mol⁻¹ in **glike**/**slip**, while it only reaches -1.9 kcal mol⁻¹ for the other structures.

In the case of the naphthalene dimer, the most stable minimum is again the **glike** structure, while the **slip** and **cross** ones are less stable by around 0.5 kcal mol⁻¹. On the other hand, the **stack** structure is the least stable one, as it will be the case with the rest of unsaturated species studied. The results are also in agreement with the values found in literature, with slight differences depending on the level of calculation employed in each case.^{39,47} In the naphthalene dimer, the **cross** structure is more favored than in the benzene dimer because it allows closer proximity between carbon atoms facilitating dispersion interactions. The anthracene dimer shows a similar behavior, with the **glike** structure being the most stable, though in this case, the **cross** structure is almost as stable and about 0.5 kcal mol⁻¹ more favorable than the **slip** one. These results are also in line with previous results in the literature;⁴⁷ in the crossed anthracene dimer, all rings have another ring close by, so dispersion and stability are enhanced. In larger linear acene dimers, **glike** structures are the most stable followed by the **slip** ones. As the size of the acene grows, the **glike** structure more clearly becomes the preferred orientation, while **cross** and **stack** minima become relatively more and more unstable (though the interaction energy increases with system size, **cross** structures put atoms on the edges of the molecules too far away). Only the **slip** structures show stabilities comparable to the **glike** ones, though around 1 kcal mol⁻¹ less stable. Figure 2 also shows the values obtained for dimers of the nonlinear acenes: pyrene, perylene, and coronene. In these cases, the dependence on the orientation is less clear: in the pyrene dimer, the **slip** structure is slightly favored over **glike**, while in the perylene dimer, the **cross** minimum is the most favorable. Coronene favors **glike**/**slip** minima (they are the same structure); **stack** structures are by far less stable.

The middle section of Figure 2 shows the results obtained for homodimers of the perhydrogenated derivatives of the molecules considered above. Quite recently, the importance of aliphatic stacking interactions has been recognized, with evidences supporting their important role on the stability, with contributions of similar magnitude as the aromatic stacking. These stacking interactions between aliphatic systems are usually weaker than those observed between aromatic species but still noticeable, as already indicated in the case of the perhydrocoronene dimer.³⁹ Focusing on the results shown in Figure 2, and contrary to the results observed in aromatic systems, the most favorable orientation in dimers formed by hydrogenated species is the fully stacked one, with the molecules just lying one on top of another. With this orientation, all axial C-H groups are distributed in an alternated way, thus avoiding steric clashes and facilitating C-H \cdots C interactions, as already suggested by Alonso et al.⁴⁰ **glike** structures are the second most stable ones by around 1 kcal mol⁻¹.

Finally, the bottom section of Figure 2 shows the results obtained for heterodimers formed by one aromatic species and its perhydrogenated counterpart. Recently, it has been shown that the interaction in these mixed dimers can be stronger than both σ - σ and π - π structures.^{32,35} The stabilization can be associated to the presence of CH \cdots π interactions, though in

previous work it has been shown that the main contribution is still dispersion.³² As in π - π complexes, the most favorable orientation of the dimers is the **glike** one, allowing the formation of CH $\cdots\pi$ interactions. However, both the **slip** and **stack** structures are slightly weaker but with very similar stabilities, so it becomes clear that when talking about CH $\cdots\pi$ interactions, the directionality is not very relevant.

For all kinds of dimers considered, there is an increase in interaction energies as the size of the system grows as a consequence of the larger number of favorable contacts established between both molecules (there is an increase in the contact surface). This is clearly the case for linear acenes, with the only exception of **cross** structures. In this case, the interaction reaches a plateau for the anthracene dimer and increases to a less extent in larger systems. While the interaction energies increase with the number of carbon atoms, it does so to a different degree depending on the type of the complex considered. While π - π and σ - π complexes show interaction energies growing in a similar fashion, σ - σ complexes increase their energy at a slower rate, in agreement with previous results indicating that π - π complexes benefit from some kind of cooperativity as compared to aliphatic contacts.^{31,38,40,42} In any case, for the three types of complexes considered, a pretty good linear relationship is observed with the number of atoms (see Figure S2, Supporting Information). This linear relationship is especially good, considering the behavior of linear acenes, with the exception of **cross** structures, as expected. For the other structures considered, a good linear fit is obtained even when the nonlinear acene dimers are included, with linear regressions showing $R^2 > 0.99$ in all cases. The slopes of these linear fits already indicate how the interaction energies increase faster for π - π dimers; in σ - π complexes, the rate is slightly smaller, and clearly smaller in σ - σ complexes.

Table 1 summarizes how the interaction energy changes for the most stable structures found for the complexes studied

Table 1. Interaction Energies (kcal mol⁻¹) for the Most Stable Minima of the Complexes with Different Relative Orientations as Obtained at the MP2.X Level^a

	π - π	σ - π	σ - σ
C ₆	-3.03	-3.44	-2.50
C ₁₀	-6.86	-6.81	-4.70
C ₁₄	-10.77	-10.29	-6.90
C ₁₈	-14.67	-13.36	-8.82
C ₂₂	-18.53	-17.27	-11.33
C ₂₆	-22.27	-20.76	-13.56
C ₁₆	-13.05	-12.11	-8.02
C ₂₀	-17.76	-15.24	-10.39
C ₂₄	-20.81	-18.89	-12.63

^aC_n as in Figure 1.

(remember that this corresponds in most cases to **glike** in σ - π and π - π complexes, and to **stack** in σ - σ ones). As already found in previous work, the cyclohexane dimer is slightly less stable than the benzene dimer, which in turn is less stable than the cyclohexane \cdots benzene dimer. This has been attributed to dispersion contributions of similar magnitude but larger electrostatic terms in the σ - π complex, associated to the CH $\cdots\pi$ interactions.³² It becomes clear from Table 1 and Figure S3 that as the size of the system grows the stability

increases at different rates for the aliphatic and aromatic dimers.

Already naphthalene dimer is as stable as its mixed aliphatic-aromatic counterpart and for larger systems, the stability of the aromatic dimers is always larger than for the mixed ones, though the differences are not especially large. In aromatic dimers, the interaction energies increase from -3.0 kcal mol⁻¹ of the benzene dimer to -20.8 kcal mol⁻¹ of the coronene dimer, while in mixed dimers, the energy changes from -3.4 to -18.9 kcal mol⁻¹. Even though the interaction energy increases as we move from the cyclohexane dimer to the perhydrocoronene dimer, passing from -2.5 to -12.6 kcal mol⁻¹, the increment is larger for mixed and aromatic dimers. These results are similar to others in the literature employing a smaller subset of species, and have been interpreted considering that in the case of π - π interactions, there is some kind of a cooperative effect that makes dimers of larger systems more stable.^{31,38,42}

However, if the incremental interaction energies are considered as one more ring is fused to a linear acene, the differences between the complexes are not large. Because the interaction energies change linearly with the number of carbon atoms, the incremental stability when fusing a new ring in linear acenes is constant, amounting to -3.9 kcal mol⁻¹. The energy change is slightly smaller in σ - π complexes, amounting to -3.5 kcal mol⁻¹, while it is even less negative in σ - σ dimers (-2.2 kcal mol⁻¹). Therefore, not only the cyclohexane dimer is slightly less stable than the benzene dimer but also the aliphatic complexes become less stabilized as the systems grow, leading to significantly less stable complexes than their aromatic counterparts. This effect is not cooperative in the sense of being reinforced as the size grows, but a constant difference due to the different nature of the interactions. Therefore, there is a size effect in the sense that as the size of the system grows, the stability becomes larger for all complexes, but increases more quickly for π - π complexes than for σ - π ones, and even faster than for σ - σ ones. There is not a cooperative effect leading to a reinforced stability as the system grows, in agreement with the linear changes in interaction energies with the number of carbon atoms. The observed stability gain going from the benzene dimer to the anthracene dimer is similar to that obtained going from anthracene to pentacene dimers, and the same happens for mixed and aliphatic dimers.

SAPT(DFT) allows obtaining the interaction energy as a sum of different terms with a clear physical nature. Also, it can provide with accurate values for the interaction energies as already shown in the literature.⁵¹⁻⁵³ Figure 3 compares the values obtained with SAPT(DFT) with those at the MP2.X level (the full set of values is listed in Tables S4 and S5) for the most stable dimers. As observed in Figure 3, the values obtained for the interaction energies at the SAPT(DFT) level closely reproduce the results obtained with MP2.X. There are of course some deviations, most noticeably in the case of mixed dimers, but overall, it can be concluded that SAPT(DFT) is capable of reproducing the results obtained with MP2.X. Therefore, it can be considered that the representation of the interaction obtained from SAPT(DFT) is a sound one.

Figure 4 shows the results obtained for the different contributions to the interaction energy for the most stable dimers found for each type of complex considered in this work (the values are listed in Table S7 and a different view is shown in Figure S4). Beginning with π - π complexes, the results

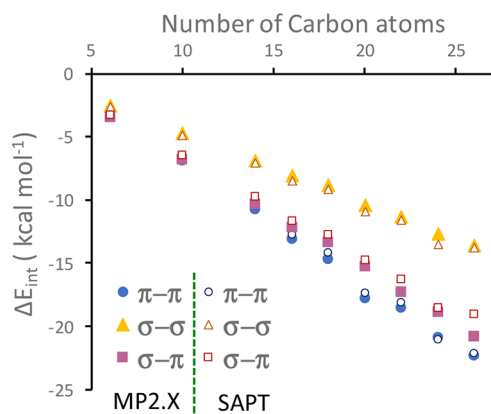


Figure 3. Comparison of SAPT(DFT) (open symbols) and MP2.X (filled symbols) interaction energies as the size of the system grows. Only the most stable orientation of each dimer is included.

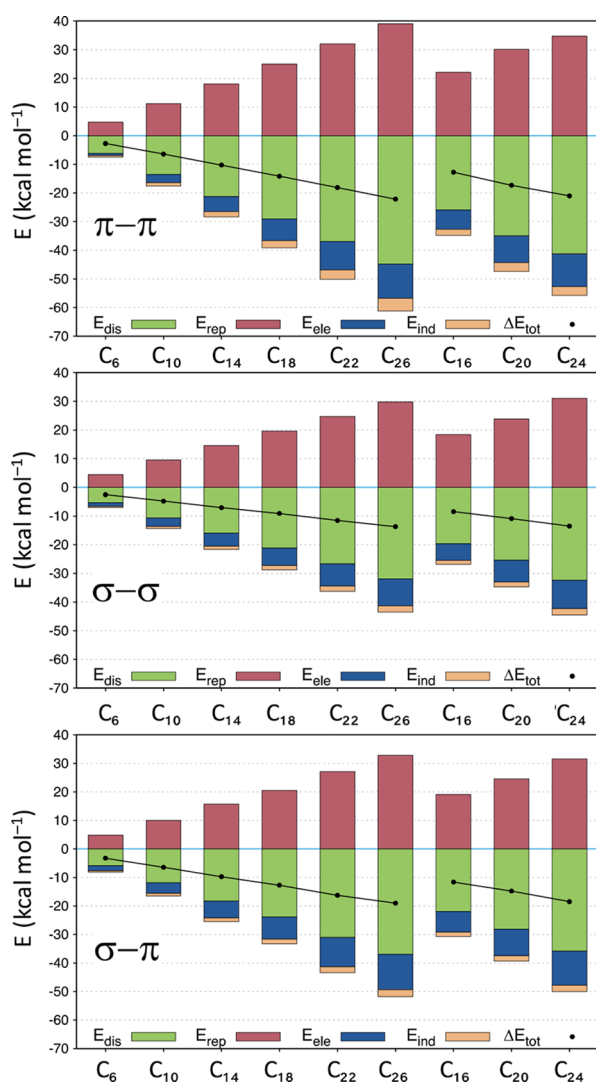


Figure 4. Variation of the SAPT(DFT) components of the interaction energy for the most stable structure of the dimers studied. C_n as in Figure 1.

indicate, as it is already known, that the benzene dimer is mainly bound by dispersion, with small contributions from electrostatics and tiny induction. The most remarkable changes

when going from the benzene dimer to the naphthalene dimer correspond to the largest contributions, namely dispersion and repulsion. These two contributions roughly double their values, as it is the case with the tiny induction term. On the other hand, electrostatics increases by a factor of three, though this is probably due to its small value in the benzene dimer as compared to other dimers. Considering the anthracene dimer, there is a neat increase in repulsion and dispersion, which are the leading contributions to the interaction energy. Again, the relative increment in electrostatics is slightly larger than for any of the other contributions. A similar behavior is observed in larger systems. When considering nonlinear acenes as in pyrene, perylene, and coronene dimers, the results are also in line with those observed for linear acenes and roughly lie where expected, considering the number of carbon atoms of the systems.

The behavior is similar in dimers formed by aliphatic molecules, though the global quantities differ significantly from the values obtained in aromatic dimers. As in the benzene dimer, the cyclohexane dimer is mainly bound by dispersion, though in cyclohexane, the electrostatic component is more favorable, while induction is negligible (see previous work).³² All terms roughly double when passing from the cyclohexane dimer to the decalin dimer and increasing the size of the systems leads to similar increments in all terms. In the case of mixed dimers, an intermediate behavior is observed. The cyclohexane–benzene dimer is also bound by dispersion, though it displays a slightly larger electrostatic character. The ratios of change as the system grows are between those observed in aliphatic and aromatic dimers, so dispersion and repulsion increase more slowly than in aromatic dimers.

The general trend (see also Figure S4) shows that all contributions change faster with the number of carbon atoms in π – π dimers. While repulsion and dispersion are quite similar in the case of the smallest complexes of each kind, the values quickly depart from each other as the size of the system grows. As a consequence, π – π dimers show larger dispersion and repulsion components as the system grows, and the same trend is observed for total interaction energies. Repulsion grows more slowly in mixed and aliphatic dimers than in aromatic ones, though this is clearly compensated in aromatic dimers by the larger increment in dispersion. In the case of σ – π complexes, dispersion grows quicker than in aliphatic ones, and the same is observed for repulsion. Though changes in electrostatics and induction are much smaller, and occur at a much smaller scale than changes in repulsion and dispersion, the electrostatic term also grows faster in aromatic complexes, so for both σ – π and π – π complexes, it reaches -12 kcal mol⁻¹, compared to barely -10 kcal mol⁻¹ in aliphatic dimers. Thus, even though the cyclohexane–benzene dimer has a larger electrostatic component than the benzene dimer, already in pentacene dimers the contributions are similar, so the electrostatic contribution also grows faster in aromatic dimers. The same is observed for induction, which only in the case of π – π complexes is relevant, reaching almost -5 kcal mol⁻¹. Therefore, all contributions to the stability seem to grow faster in aromatic complexes than in both σ – π and σ – σ complexes, so the former ones are favored as the system grows.

Overall, it can be considered that the stability of these complexes mainly comes from a balance of the opposing effects of dispersion trying to bring the molecules closer and the repulsion term avoiding it. The final stability is then tuned with the smaller electrostatic and induction contributions. An

interesting aspect of the results in Figure 4 is that the main changes affect dispersion and repulsion, occurring on a different scale than changes in electrostatic or induction, which are much smaller contributions. It can be observed, however, that the variations in dispersion and repulsion nearly cancel each other, so the final changes in energy are more dependent on the smaller electrostatic and induction terms. In a very simple description of the interaction both dispersion and repulsion depend on the number of atoms at close distance, as it would be the case in a Lennard-Jones model. If dispersion and repulsion are combined (Figure 5), the energy change

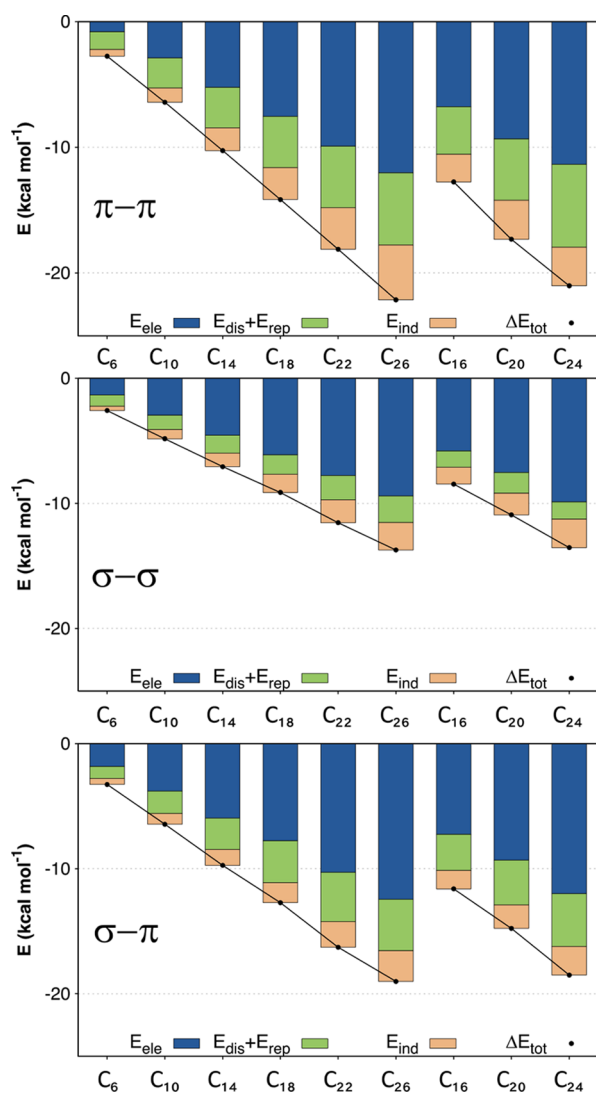


Figure 5. SAPT(DFT) decomposition for the most stable structure of the dimers studied. Repulsion and dispersion are grouped together. C_n as in Figure 1.

from benzene to pentacene amounts to -3 kcal mol^{-1} in π - π complexes and to only $-1.2 \text{ kcal mol}^{-1}$ in σ - σ ones. Thus, dispersion and repulsion quench each other almost totally, so the final stability is more controlled by electrostatics. In Figure 5, it can be observed that the contributions from induction and electrostatics, and the combination of dispersion and repulsion are of similar magnitude. Considering aromatic dimers, it can be observed that the combination of dispersion and repulsion is always favorable, and increases as the size of the system

grows. Thus, both terms contribute a net $-1.4 \text{ kcal mol}^{-1}$ in the benzene dimer, increasing to $-4.4 \text{ kcal mol}^{-1}$ in the pentacene dimer or $-5.9 \text{ kcal mol}^{-1}$ in the coronene dimer. However, induction, which contributes with just $-0.5 \text{ kcal mol}^{-1}$ in the benzene dimer, amounts to $-3.4 \text{ kcal mol}^{-1}$ in the pentacene dimer and $-3.2 \text{ kcal mol}^{-1}$ in the coronene dimer. Thus, the stability of the complexes increases by quite similar amounts because of the combined effect of repulsion + dispersion and induction. Finally, a look at electrostatics reveals a totally different behavior. While electrostatics is small in the benzene dimer amounting to $-0.8 \text{ kcal mol}^{-1}$, it grows quickly, reaching $-10 \text{ kcal mol}^{-1}$ in the pentacene dimer and $-12 \text{ kcal mol}^{-1}$ in the coronene dimer. Therefore, the increase in stability of the complexes could be also associated with the increment on electrostatic contribution as the size grows. This increase in electrostatic energy could be related, at least partially, to penetration effects that become larger as the distance between monomers decrease and that would explain the growth in this contribution.^{41,49} While the combination of repulsion + dispersion or induction changes by -4 kcal mol^{-1} , electrostatics varies by -9 kcal mol^{-1} , so being mainly responsible for stability changes.

In aliphatic dimers, all contributions are smaller. The combination of repulsion + dispersion is favorable and increases by just $-1.5 \text{ kcal mol}^{-1}$ on going from the cyclohexane dimer to the perhydropentacene dimer. On the other hand, even though the electrostatic term changes noticeably when increasing the system size (from -1.34 in the cyclohexane dimer to $-9.9 \text{ kcal mol}^{-1}$ in the perhydropentacene dimer), its contribution is always smaller than that observed for aromatic dimers, as it is also the case of induction.

In the case of the heterodimers, the behavior is very similar to the one observed in aromatic dimers. While the electrostatic term is similar to that observed in aromatic dimers (even slightly favoring mixed dimers), the combined dispersion + repulsion term grows to a less extent than in aromatic dimers. This, combined with a less favorable induction contribution makes σ - π complexes less stable than π - π ones. Thus, aromatic dimers are more stable than aliphatic ones because of the combined effect of all stabilizing contributions, with electrostatics playing a significant role, while energy differences with mixed dimers are not related with electrostatics but with rather small favorable induction and dispersion + repulsion contributions.

The question now is why this kind of behavior is observed. As already suggested by Grimme,³¹ there seems to be two possible factors contributing to the enhanced stability of π - π complexes: some kind of cooperative effect associated with electron delocalization in these extended π systems, as also suggested by Alonso et al.,⁴⁰ and a softening of the repulsive wall leading to smaller repulsion terms, allowing the molecules to come closer and therefore increase dispersion. In order to check these aspects of the interaction in the studied systems, the interaction energies for all dimers have been obtained using an intermolecular distance corresponding to the minima of the smallest dimer of each kind.

It can be observed in Table S2 that there is in fact a shortening of intermolecular distances at the minima as the size of the system grows. This effect is observed for all kinds of complexes, and it can be related with the larger interaction energies that hold the molecules closer against the repulsive wall. However, the extension of these changes in equilibrium

distances is quite different depending on the type of complex considered. A shortening of 0.18 Å is observed when passing from the benzene dimer to the pentacene dimer, while in the corresponding σ - σ complexes, it amounts to just 0.06 Å, and in σ - π complexes, it is slightly larger (0.08 Å) but still significantly smaller than in π - π dimers. The results suggest that as the size of the aromatic system extends, there is a softening of the repulsive wall because of electron delocalization, allowing the molecules to come closer. On complexes containing aliphatic species, though, there is almost no change on the characteristics of the repulsive wall, so the minima are mostly at the same position. Then, it can be deduced that the stability of the different dimers diverges as the size of the system grows because the changes on distance observed in π systems allow for a reinforcement of the attractive contributions overwhelming the increase in repulsion. Thus, there is a larger energy increase in π - π systems because the distance shortening is more accused, followed by mixed dimers, while in aliphatic dimers, the distance barely changes and therefore the stability is enhanced to a less extent.

Table 2 lists the energy changes on the interaction energy and its contributions when the dimers are moved to their

Table 2. Changes in the Different Contributions to the Interaction Energy (kcal mol⁻¹) when Changing the Intermolecular Distance of a Given Complex to Its Equilibrium Distance from a Position Corresponding to the Equilibrium Distance of the Smallest Dimer of Each Kind

π - π	ΔR (Å)	E_{ele}	E_{rep}	E_{ind}	E_{dis}	E_{tot}
C ₁₄	-0.14	-2.37	6.21	-0.57	-3.86	-0.59
C ₂₂	-0.18	-4.91	12.77	-1.26	-7.85	-1.26
C ₂₄	-0.19	-5.85	15.09	-1.25	-9.54	-1.55
σ - σ	ΔR (Å)	E_{ele}	E_{rep}	E_{ind}	E_{dis}	E_{tot}
C ₁₄	-0.05	-0.58	1.75	-0.13	-1.08	-0.05
C ₂₂	-0.06	-1.14	3.45	-0.26	-2.11	-0.07
C ₂₄	-0.08	-1.80	5.37	-0.42	-3.19	-0.03
σ - π	ΔR (Å)	E_{ele}	E_{rep}	E_{ind}	E_{dis}	E_{tot}
C ₁₄	-0.06	-0.92	2.48	-0.18	-1.51	-0.14
C ₂₂	-0.08	-1.99	5.30	-0.37	-3.19	-0.26
C ₂₄	-0.08	-2.30	6.08	-0.41	-3.59	-0.21

equilibrium distance from a position corresponding to the equilibrium distance of the smallest dimers (see the full set of values in Table S8). In π - π systems, there is a clear shortening in the intermolecular distance, responsible of a change of -1.3 kcal mol⁻¹ in the interaction energy of the pentacene dimer. This increment is mainly due to an increase in dispersion but also electrostatics, and it is counterbalanced by the increase in repulsion. It is worth noting that the increase in electrostatics is probably due to penetration effects because the distance shortening facilitates charge overlap. In aliphatic dimers, there is no significant shortening and therefore the changes in the contributions are tiny. Mixed complexes show an intermediate behavior, with slightly larger shortening reflected in moderate increases in dispersion and electrostatics.

Therefore, it seems clear that a different behavior associated with the intermolecular distance shortening takes place in π - π complexes. However, it can be observed in Table 2 that the effect of this shortening, though large in several of the contributions as repulsion or dispersion, has a limited effect on the total stability of the complexes. For complexes containing pentacene and perhydropentacene, the stability gain due to

distance shortening amounts to just -1.3 kcal mol⁻¹ in π - π complexes, being much smaller in mixed or aliphatic ones. However, when comparing the stability of the different complexes, the pentacene dimer is more stable by almost -2 kcal mol⁻¹ compared to the σ - π complex and more than -6 kcal mol⁻¹ compared to the σ - σ analogue. Thus, the shortening on intermolecular distances is capable of explaining a large fraction of the energy differences between π - π and σ - π complexes (more than 50%), but only recovers a small fraction of the stability differences when comparing π - π and σ - σ complexes.

Figure 6 summarizes this behavior. It can be observed that the values obtained at the minima or employing a constant

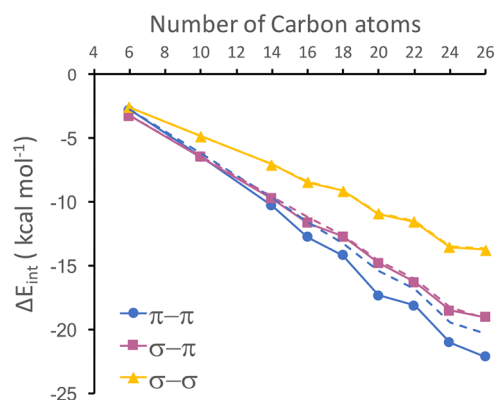


Figure 6. SAPT(DFT) interaction energies for the most stable structure of the dimers as the system grows. Solid lines correspond to values obtained at the equilibrium distance of each dimer; dotted lines show values obtained fixing the distance at the value obtained for the smallest dimer of each kind.

intermolecular distance only differ significantly in the case of π - π dimers. The steepest energy gain in π - π complexes can be clearly seen while aliphatic ones increase their stability much slowly. As indicated above, the figure suggests two different origins for this fact. On the one hand, the softer repulsive wall in π - π systems allows an extra increment in stability associated with the shortening on the intermolecular distance. On the other hand, there seems to be an effect associated to the extension of the π systems leading to larger interaction energies even at a constant distance.

It is worth noting that when the intermolecular distance is kept fixed, the rate at which the interaction grows is similar in both π - π and σ - π complexes, and the differences only appear when the intermolecular distances are allowed to change. Thus, the different behavior observed between π - π and σ - π complexes can be largely ascribed to the shortening of interplane distances observed in π - π systems. However, the differences remain in the case of σ - σ complexes even keeping fixed intermolecular distances, so there must be another effect associated with the nature of the interacting systems. There seems that the properties of the π molecules change as the system grows leading to larger interaction energies.

In fact, comparing how the different contributions to the interaction energy increase at a constant intermolecular distance (Figure 7), it can be observed that the electrostatic contribution favors mixed complexes over π - π ones (compare with Figures 4 and S4), leading to a stability gain of more than 2 kcal mol⁻¹ in pentacene complexes. Also, repulsion is larger in mixed complexes, while dispersion slightly favors π - π ones.

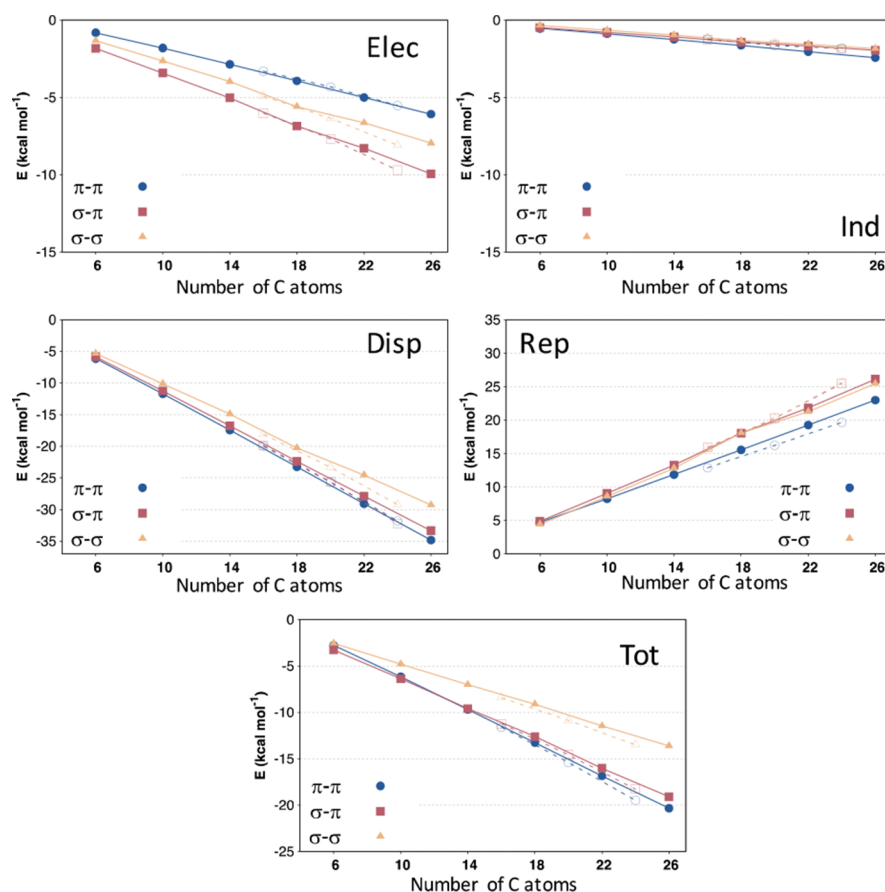


Figure 7. Changes on the contributions to the interaction energy keeping the intermolecular distance fixed at the value obtained for the smallest dimers of each kind.

At a constant intermolecular distance, the energy differences between π - π and σ - π remain tiny as the size grows. The picture is different in aliphatic complexes; the electrostatic term still favors σ - σ complexes but the stability difference comes from dispersion, which changes more quickly in π - π complexes. Therefore, aromatic complexes are favored over aliphatic ones because dispersion grows more quickly while repulsion does it more slowly. The stability gain over aliphatic systems comes from both a decrease on repulsion and from an increase in dispersion due to changes in the electronic distribution. Also, the decrease in repulsion allows for the molecules to become closer, favoring even more stabilizing contributions, especially dispersion.

For all the abovementioned reasons, the main factors affecting the stability gain of π - π complexes relative to aliphatic ones are changes on molecular properties allowing a stronger interaction. As an example, the behavior of the isotropic polarizability was monitored for aromatic and aliphatic molecules. It can be observed that as the size of the system grows, the polarizability increases much faster in aromatic molecules than in aliphatic ones. Considering that polarizabilities are related with induction but also with dispersion contribution (recall that in the simple London expression, dispersion coefficients are proportional to polarizabilities: $C_{6,ab} \approx IP_a IP_b / (IP_a + IP_b) \alpha_a \alpha_b$; IP s are ionization potentials and α represents polarizabilities), these changes in polarizability could mimic the trends observed in interaction energies. Thus, while cyclohexane polarizability amounts to 70 a.u., for benzene it is slightly smaller (66 a.u.). Already in

anthracene, the polarizability (177 a.u.) is larger than in its perhydrogenated counterpart (158 a.u.), and the difference is even larger in pentacenes (334 a.u. vs 249 a.u. in the hydrogenated derivative).

In summary, the changes observed fixing intermolecular distances are related to the intrinsic properties of the interacting systems, and indicate that π - π stacking interactions have some special characteristics when compared to similar aliphatic stacking interactions. This particular behavior, probably related to electron delocalization, is only evident in extended systems, in agreement with previous findings.^{31,40} The interaction energies grow faster in complexes containing aromatic molecules as a consequence of a larger increase in dispersion. Simultaneously, repulsion increases in π - π complexes at a slower rate than in σ - π or σ - σ complexes, so the combined result of these two effects clearly favors π - π dimers. This accounts for around 80% of the energy differences observed relative to σ - σ dimers and 40% relative to σ - π ones. Besides, because of the shortening of intermolecular distances, π - π complexes display an extra stabilization mostly related to increasing electrostatics and dispersion contributions, though the same happens to repulsion so the final effect is not large (but still responsible of more than 50% of the energy differences between π - π and σ - π dimers).

CONCLUSIONS

A computational study has been carried out to determine the characteristics of the interaction in stacked systems. In order to unveil their inherent differences and similarities, systems were

studied comprising aromatic–aromatic, aliphatic–aliphatic, and aromatic–aliphatic stacked dimers. The systems considered include linear acenes up to hexacene and nonlinear ones as pyrene, perylene, and coronene; as aliphatic molecules, their perhydrogenated derivatives were employed. Stacked homodimers of each of these molecules, as well as heterodimers formed by an aromatic species and its perhydrogenated derivative were studied employing a set of different relative orientations.

For π – π complexes, the most favorable relative orientation is a displaced stacked geometry resembling the arrangement of the different layers in graphite. The same arrangement is the most favorable one in σ – π dimers, while in the case of aliphatic σ – σ dimers, the most favorable geometry is the fully stacked one, with one molecule just on top of the other one. Several exceptions have been observed in nonlinear systems, favoring in some cases another structure, though this usually happens by a narrow energy margin.

The results show that the interaction energies increase as the size of the system grows following a linear relationship with the number of carbon atoms in the system. However, the interaction energy increases much faster in π – π complexes than in σ – σ ones. For σ – π complexes, an intermediate behavior is observed, though the energies lie closer to the π – π values. The main reason behind these changes on the interaction energies as the size of the system grows is dispersion, which is larger in π – π complexes and also increases at a higher rate. However, the results indicate that repulsion also increases in a similar way as dispersion, so the effects of both contributions to the interaction energy cancel each other to a large extent and the net effect is not especially large, though favorable.

The main factor favoring the stability of aromatic dimers over aliphatic ones as the size of the system increases is related to the nature of the aromatic systems. Changes in molecular properties due to larger electron delocalization as the aromatic system grows lead to an increase in the dispersion contribution to the stability, absent in aliphatic dimers. Besides, an extra stabilization is observed in π – π dimers related to the softening of the repulsive wall that allows shorter intermolecular distances. The combination of these two effects makes π – π dimers to become more and more stable relative to complexes containing aliphatic species as the size of the system grows.

COMPUTATIONAL METHODS

In order to obtain interaction energy curves for each of the dimers, the intermolecular distance between molecules is changed along a series of values, while keeping the monomer geometries frozen at the values obtained for the isolated molecules. Calculations are performed using the dispersion-corrected TPSS-D3BJ method^{54,55} together with the def2-TZVPP basis set.⁵⁶ Ehrlich et al. showed that this method gives a proper description of the interaction in this kind of systems.³⁸ Also, it has been shown recently that TPSS-D3BJ is capable of reproducing the values obtained for the interaction energies in bowl-shaped dimers.⁵¹ At each intermolecular distance, the interaction energy is computed at this level of calculation applying the counterpoise correction avoid basis set superposition error.^{57,58} The resolution of the identity approach is used in these calculations employing the def2-TZVPP auxiliary basis set.⁵⁹ These calculations were performed with Turbomole 6.3.⁶⁰ Once the potential curves for the dimers are available, the positions of the minima are obtained by interpolation.

Interaction energies at the minima of the TPSS-D3BJ curves have also been obtained with the MP2.X method proposed by Riley et al.^{61–63} In the MP2.X method, the energy is extrapolated to the complete basis set limit at the MP2 level using the two-point extrapolation procedure of Helgaker with the cc-pVTZ and cc-pVQZ basis sets.^{64,65} In order to save computation time, the polarization function with highest angular momentum has been deleted in both basis sets, and RI and RIJCOSX approaches were employed.^{66,67}

$$\Delta E_{\text{corr,MP2}}^{\text{CBS}} = \frac{X^3}{X^3 - Y^3} \Delta E_{\text{corr,MP2}}^{\text{VQZ}} - \frac{Y^3}{X^3 - Y^3} \Delta E_{\text{corr,MP2}}^{\text{VTZ}}; X = 4, Y = 3 \quad (1)$$

and

$$\Delta E_{\text{MP2}}^{\text{CBS}} = \Delta E_{\text{HF}}^{\text{VQZ}} + \Delta E_{\text{corr,MP2}}^{\text{CBS}} \quad (2)$$

The effects of higher-order terms on the correlation energy are estimated by means of a properly scaled MP3 calculation employing the 6-31G(0.25) basis set (scale factor $C = 0.62$). The final interaction energy at the MP2.X level is the combination of the MP2 energy extrapolated to basis limit plus the third-order contribution scaled by 0.62.⁶¹ MP2.X calculations have been carried out using the ORCA program.⁶⁸

$$\Delta E_{\text{MP2.X}} = \Delta E_{\text{MP2}}^{\text{CBS}} + 0.62 (\Delta E_{\text{MP3}}^{6-31\text{G}(0.25)} - \Delta E_{\text{MP2}}^{6-31\text{G}(0.25)}) \quad (3)$$

The interaction energies have also been obtained by applying SAPT with intramonomer correlation effects described at the DFT level [SAPT(DFT)]^{45,69–71} using Molpro 2015.⁷² These calculations have been performed with the PBE0 functional and the cc-pVTZ basis set, employing as auxiliary basis sets cc-pVTZ/JKFIT for Hartree–Fock and cc-pVTZ/MP2FIT for the second-order dispersion terms, and with the nonlocal part of the exact exchange in PBE0 being replaced by a local approach.^{69,73} The adiabatic local density approximation has been used to compute the frequency-dependent response functions involved in the calculation of dispersion. To obtain proper results with SAPT(DFT), the functional must be asymptotically corrected, using a shift parameter obtained as the sum of the ionization potential and the energy of the highest occupied molecular orbital (HOMO).^{52,73} Ionization potentials and HOMO levels of the systems studied have been obtained at the PBE0/cc-pVTZ level (see values in Table S1).

The contributions obtained from SAPT are grouped into four terms, corresponding to repulsion, electrostatic, induction, and dispersion contributions. It is considered that $E_{\text{rep}} = E_{\text{exch}}^1$; $E_{\text{ele}} = E_{\text{pol}}^1$; $E_{\text{disp}} = E_{\text{disp}}^2 + E_{\text{exch-disp}}^2$; $E_{\text{ind}} = E_{\text{ind}}^2 + E_{\text{exch-ind}}^2 + \delta_{\text{HF}}$. δ_{HF} is a term representing contributions higher than second order and it is obtained from a SAPT calculation employing Hartree–Fock wavefunctions: $\delta_{\text{HF}} = \Delta E_{\text{HF}} - (E_{\text{exch}}^1 + E_{\text{pol}}^1 + E_{\text{ind}}^2 + E_{\text{exch-ind}}^2)$, with ΔE_{HF} being the counterpoise-corrected interaction energy at the HF level. The value of the coupled $E_{\text{exch-disp}}^2$ is estimated by applying a scaling factor to the uncoupled $E_{\text{exch-disp}}^2$.

While most contributions to the interaction energy already reach values close to the basis set limit with a basis set of triple-zeta quality, dispersion contribution converges very slowly with the basis set size. Therefore, dispersion values are extrapolated to the basis set limit assuming a cubic dependence as suggested by Helgaker employing cc-pVDZ and cc-pVTZ basis sets.^{64,65} Thus, the final values are a combination of the cc-pVTZ

electrostatic, repulsion, and induction contributions, plus the dispersion contribution extrapolated to basis limit.^{51,52,74} This strategy has been successfully followed by Heßelmann and Korona in their study of the interaction in large complexes.⁵²

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01339.

Potential energy curves for all the dimers studied at the TPSS-D3BJ/def2-TZVPP level, interpolated equilibrium distances, interaction energies for the dimers at the different levels of calculation employed, linear fits of the MP2.X interaction energies, HOMO energies and ionization potentials employed in SAPT(DFT) calculations, SAPT(DFT) contributions to the interaction energies, and Cartesian coordinates and polarizabilities for the isolated molecules (PDF)

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Notes

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