π-Stack Dimers of Small Polyaromatic Hydrocarbons: A Path to the Packing of Graphenes

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MP2 calculations of the stacking energy are reported for the dimers of a set of polycyclic aromatic hydrocarbons. The interaction strengths and their dependence on the shape-dependent measures as well as the aromatic character of the monomer are studied. For small systems involving four to six rings, the noncovalent interactions seem to be independent of the shape of the monomers. The most preferred conformations for parallel stacked dimers are not aligned exactly but off-center with small shifts; however, these shifts are on the order of 1 Å, and the energy necessary to keep them aligned is less than 0.5 kcal/mol per ring. Small-angle rotations within the molecular planes also do not require much energy, and in some cases they lead to stronger interactions.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have always been an attractive area of study for chemists. They are composed of mostly planar and fused six-membered rings. They may contain heteroatoms such as nitrogen. Even though the name PAH implies an aromatic nature, all structures generated by this definition do not necessarily display aromaticity. The symmetry generated by fusing identical hexagons and/or the planarity of these molecules were strong motivations for the graph theoretical approaches to classify and to understand the chemistry of PAHs.[1]

In the graph theoretical terminology, there is a large lexicon for defining various forms used for PAHs. A hexagon is a six-membered ring, and the polyhex is the connected combination of at least two hexagons which share a bond or an atom. If the carbon skeleton of a molecule can be described by a polyhex, then it can be classified as a polyconjugated hydrocarbon. There is a small section of polyhexes which are described by outer and inner perimeters on a hexagonal lattice; that is, they exhibit at least one hole, and they are called coronoids. The smallest single coronoid can be constructed with eight hexagons. The remaining majority of graphs do not have such holes, and they are called benzenoids. (It is important to note that although such single coronoids and their corresponding benzenoid structures are described by different graphs, the corresponding PAHs are exactly identical). In benzenoids any two hexagons share one and only one edge or they are disjointed. Even though there are numerous subclassifications from these two general classes, we would resrict ourselves to benzenoids and refer the readers to the detailed classifications given by several groups.[1−3]

One of the mathematically challenging questions is the enumeration of isomers for a given number of hexagons (denoted by h). The question of "how many distinguishable polyhexes (or benzenoids, coronoids, etc.) are there for a given h" is also known as the "cell-growth" and remains as an unsolved problem. From a chemical perspective, the question was posed as early as the 1960s.[4] The computational approaches have been used extensively to obtain numerical answers, and the complete databases are published at least for small h values.[2,3] Algorithms for generating these lists start with all possible isomers of a given h, then new hexagons are added to all possible sites, and duplications are eliminated. In this manner it is possible to systematically increase the size and devise schemes to identify equivalent graphs. However, the number of isomers quickly increases with h. For example, for $h = 21$ it is estimated that there are around 10^{12} isomers.[5]

The chemically interesting question relates to the stability of these compounds. Aromaticity is probably one of the oldest concepts in organic chemistry; on the other hand, there is still not an agreed definition from a quantum chemical perspective.[6] There are various aromaticity measures which sometimes contradict the results of others.[7−11] The one commonly used graph theoretical measure is the so-called K-number of the Kekule number which is defined by the number of possible Kekule structures for a given benzenoid. Each of these structures differs by the positions of double bonds while the conjugation is kept intact. They all contribute to the total wave function equally. Higher K-numbers imply higher aromaticity as well as higher stability. All polyconjugated hydrocarbons with K-number larger or equal to 1 are called Kekulean benzenoids. They are known to be stable as they show similarities to benzene, while all structures with zero K-numbers are unstable. Therefore, the enumeration of K-numbers is an important but also computationally challenging question as they can climb up to 100 even for systems as small as $h = 9$.

Once the chemical graphs of PAHs are generated, their various properties can be calculated to obtain generalizations of their physical and chemical properties. This approach dates to the 1940s where Wiener[12] has proposed one of the first structure−property measures. Then there are numerous studies mostly in the era of 1980−2000 which classify these compounds in terms of their chemical properties, even extending to the level of their carcinogenity.

PAHs are mostly found in crude oil and in coal; some are carcinogens, and recently new methods have been developed for their efficient synthesis. As was expected from the graph theoretical approaches, their stabilities strongly depend on geometrical parameters and shapes.

For many years, the conjugated molecules are used in organic electronics; however, PAHs bring a new dimension as they could form disklike structures upon stacking in columnar forms.[13−15] It has been shown that these disklike systems, mostly based on triphenylene and hexa-perihexabenzocoronene (HBC) derivatives, can be synthesized; they form columnar structures due to the large overlaps of π-orbitals and high symmetry. These structures can provide molecular-scale electronic devices. The strong dependence of the physical properties on the molecular

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TABLE 1: MP2 Interaction Energies (kcal/mol)[a]

	3-21	6-31(d)	6-31(d,p)	6-31+(d)	6-311(d,p)	6-311++(d,p)	aug-cc-PVDZ
benzene	−0.72	−2.01	−2.27	−3.82	−2.71	−4.79	−5.28
	1.42	0.01	−0.28	−1.02	−1.25	−1.91	−2.85
naphthalene	−2.59	−5.40	−5.80	−10.59	−7.00	−12.20	−12.89
	1.65	−1.64	−2.09	−4.04	−4.26	−5.58	−7.28
anthracene	−4.88	−9.29	−9.83	−17.65	−11.93		−20.56
	1.57	−3.75	−4.35	−7.53	−7.80		−12.26
phenanthrene	−4.65	−9.05	−9.60	−17.64	−11.70		−20.77
	1.77	−3.53	−4.13	−7.34	−7.57		−12.05
pyrene	−6.81	−12.35	−12.94	−22.97			−27.88
	1.14	−5.71	−6.35	−10.42			−16.02
tetracene	−7.42	−13.56	−14.24	−25.32			−30.65
	1.63	−5.98	−6.75	−11.29			−17.72

[a] For each PAH, the first value is the energy difference between dimers and two separate monomers while the second value is the potential energy after the BSSE correction.

shape can be used advantegeously to control the size and structures of the resulting nanosystems.

In this work we will report extensive calculations on π-stacked dimers of small PAHs which could be seen as precursors of graphenes. We are interested in the extent of the interactions between two PAHs which are exactly aligned in the z-direction, find out the topological dependence of the interactions, and generate basic guidelines for larger systems. Then briefly we discuss the variations in the interaction energy if one of the molecules shifts away from the aligned position or rotates around the z-axis. These studies should then lead to a beter understanding of the stacking of PAHs.

Calculations

The term “noncovalent interactions” has recently became very popular. It is well-known that noncovalent interactions pose serious challenges for quantum chemists as well as experimentalists.[16] The formation of molecular clusters which do not involve bond-breaking or -formation can be classified as typical noncovalent interactions. Even though they are weaker than covalent interactions, they play an important role in many areas especially in H-bonded systems.[17] The relative weakness of interactions coupled with the rather longer distances between constituents require more accurate and careful calculations than the conventional ab initio or density functional theory (DFT) calculations of the organic reaction mechanisms. For example, the most commonly used DFT functionals, such as B3LYP, find the stacking interaction between two benzene molecules as repulsive. In fact, the majority of the DFT methods have serious difficulties in predicting noncovalent interactions correctly. Even though there are strong efforts in producing density functionals which are broadly applicable,[18] most of the functionals are not suitable to study such interactions due to the lack of dispersion terms. Even though it is possible to develop tailored functionals for a specific set of compounds, the dependence of results on the choice of a functional form is not a very soothing concept. Similarly ab initio calculations excluding the correlation terms seem to fail as poorly as B3LYP. For example, as in the DFT case, the dimerization of benzene in HF/6-31(d) is again purely repulsive. For the hexa-perihexabenzocoronene (HBC) which is one of the important molecules forming disklike structures, again Hartree−Fock (HF) and DFT methods using the small 3-21 basis sets give repulsive potential energy functions. On the other hand, ab initio based calculations including the correlation energy seem to be working much better; however, they are computationally demanding. Computationally the most economical method is MP2, and it was shown that it gives very good estimates of the interaction potential.[16]

Ground-state energies of monomers and dimers of the set of small PAHs are first calculated with MP2 using Gaussian03[19] and with different basis sets. Geometries of monomers are optimized with a very small basis set of 3-21g. Internal coordinates obtained from larger basis sets differ very slightly from this minimal basis set or at least the interaction energies remain largely unaffected. Each dimer is constructed by parallel stacking of monomers (sandwiched structures) and scanning the distance z without reoptimizing the internal coordinates. The potential energy of a group of smaller systems are calculated with a large basis set of aug-cc-PVDZ using Molpro.[20]

It is obvious that, in the gas phase, these molecules will reorient themselves and the global minima of these structures are not usually aligned stacks. In fact, for benzene and naphthalene there are a number of very accurate results which identifies the paralel displaced shape as the global minimum.[21−26] Most of our calculations use the sandwiched conformations as the building blocks of columnar structures.

The optimization of the intermolecular distance is carried out with 3-21g, 6-31g(d), and aug-cc-PVDZ in some cases. The interaction energy changes very slowly around the potential minimum so that we were able to scan the interlayer separation with rather large increments of 0.05 Å. Due to this slow variation, the equilibrium bond lengths depend strongly on the basis set and the counterpoise correction. However, around the minimum energy conformation, changing the distance by 0.05 Å results in energy changes of 0.012 kcal/mol for anthracene for 3-21g and 0.05 kcal/mol for 6-31g(d) and aug-cc-PVDZ basis sets. Therefore for the large systems such as $h = 4$ or 5 we simply used the 3-21g basis to locate the monomer−monomer distances.

The magnitude of the interaction energy depends on the basis set strongly. To study the basis set dependence, we calculated dimerization energies of benzene, naphthalene, anthracene, phenanthracene, pyrene, and tetracene with and without the basis set superposition error (BSSE) corrections. A variety of basis sets of 3-21g, 6-31g(d), 6-31g(d,p), 6-311g(d,p), 6-31g+(d), 6-311g++(d,p), and aug-cc-PVDZ are used. BSSE corrections are made by the counterpoise method. In Table 1, a sample of these convergence studies are presented

The results could be summarized in a few points. First of all the dimerization energy increases as the basis set increases. The largest contribution comes from the first addition of the augmented +-type functions. However, increasing the number of augmented functions does not change the results. Similarly, addition of p-functions on hydrogens seems to affect the results insignificantly. BSSE corrections are very significant and can be around 50% of the uncorrected potential. For small molecules

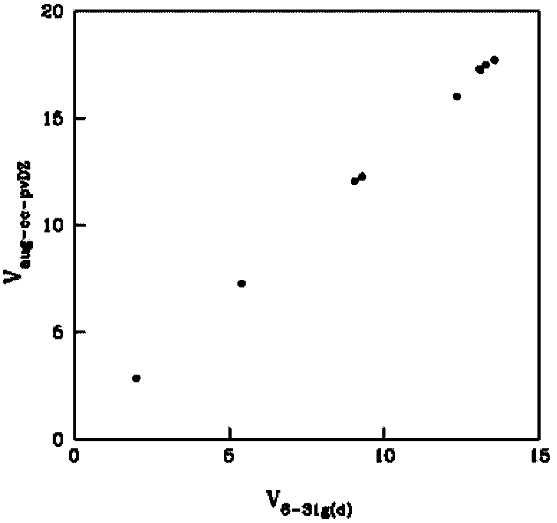


Figure 1. Correlation between dimerization energies (kcal/mol) obtained from 6 to 31 g(d) and BSSE corrected aug-cc-PVDZ basis sets.

and small basis sets, the interaction may also become repulsive upon introducing BSSE corrections.

Because our aim was to study the trends in the shape-dependent nature of the interactions rather than the actual magnitude of the interaction potentials, we have decided to proceed with the 6-31g(d) basis set. First of all, we note that the stability of dimers with large basis sets and BSSE corrections in our test cases are very close to those obtained with 6-31g(d) without BSSE corrections. Since the dimerization of small aromatic systems has always been a computationally challenging problem, there exists highly detailed calculations for benzene and naphtalene. Sherrill and co-workers have reported the complete basis set limit estimations of the interaction energies of benzene oligomers.[21,22] The minimum energy conformation for the sandwich structure is found at $R = 3.9$ Å with an interaction energy of 1.81 kcal/mol. Similarly large calculations on stacked naphthalene dimer, the interaction energy is found to be 3.78 kcal/mol at $R = 3.8$ Å.[25] Both of these results support the use of small basis set MP2 calculations to predict the shape and size dependency of larger PAHs. Of course, there is a cancelation of errors from incomplete basis sets, basis set superposition error, and MP2. In fact, this point was also noted by Sherrill who reported[21] that "... we have observed that MP2 in conjunction with small basis sets tends to exhibit a fortuitous cancelation of errors: small basis sets underestimate binding while MP2 overestimates binding". We belive that this method gives a reasonably good measure of the strength of the interaction, and we will report results with the 6-31g(d) basis. The summary of this correlation is given in Figure 1, where we plot the interaction energies from 6-31 g(d) and BSSE-corrected aug-cc-PVDZ basis. There is a strong linear dependence between two sets of calculations. In fact, there is also a very high correlation between 3-21g and 6-31g(d) calculations hinting that one can use even 3-21g for oligomers of larger PAHs as long as the absolute potential energy values are not taken too seriously. Even a very small basis set reflects the variations of the stacking energy in a qualitatively correct form.

Altogether 71 π-stacked dimers are studied. Definition of the number of isomers is not always a simple issue. For example, in the case of coronenes, graph theory differentiates structures if the center hexagon is a hole or not. On the other hand, even for simple systems such as triphenylene, one can generate different molecules depending on whether certain adjacent rings share a bond or an atom. For example if the bond represented by a dotted line in Figure 2 is broken and the carbon atoms on these positions are hydrogenated, a graph theoretically (considering only the carbon atoms) equivalent new molecule will be obtained. However, this molecule will not be planar.

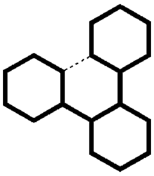


Figure 2. Triphenylene.

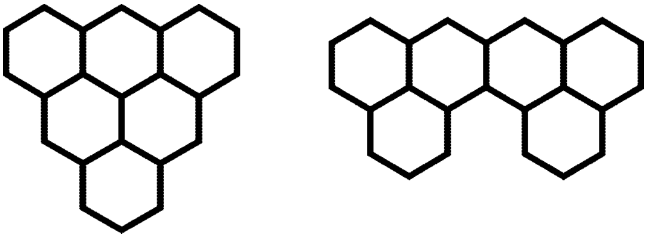


Figure 3. Two non-Kekulean six-hexagon PAHs.

In these cases we choose to select the molecules such that if two C atoms are close enough to form a bond, they will do so. Hydrogenation of these sites generating nonplanar structures are left out in out list. Because of this rather technical point, one finds a different number of isomers in certain cases. For example, in some reports the number of isomers for $C_{22}H_{14}$ is given as 12 and that of $C_{22}H_{12}$ as 2.

Results and Discussion

Parallel Aligned Stacking. The distance (R) between two parallel stacked PAHs is scanned to find the minimum energy conformations. For isomers of $C_{14}H_{10}$, R is found to be 3.70 Å. For the remaining dimers, R changes between 3.60 and 3.55 Å. There are two exceptions which are given in Figure 3.

Both of these structures are non-Kekulean; that is, it is not possible to write any Kekule-type conjugations. These systems are known to be unstable biradicals. MP2 calculations treating these molecules as closed shells result in higher ground-state energies and much higher interaction energies at shorter ($R = 3.0$ Å) distances. However, these interaction energies do not reflect the actual chemistry, and we exclude these two molecules from our list. For larger h values, there is a large number of such non-Kekulean structures.

The calculated noncovalent interactions are reported in Table 2 for each molecule with their Zagreb notation and Kekule numbers as reported by Trinajstic.[2] If they belong to a symmetry group, it is also shown.

The average interaction energy as a function of the number of rings (h) is highly linear (Table 3). With each new ring approximately 4.0 kcal/mol is added to the potential energy. The linear fit can be expressed as $V = -2.86 + 3.99h$ with the correlation coefficient of 0.9999.

Each set for h may include molecules with a different number of carbon atoms, and the dependence of V on the number of carbons is plotted in Figure 4. There is again a general trend of increasing V with the number of carbons; however, there are strong irregularities, depending on the closed formula of the PAH, and a simple formulation of V is not possible.

To see the shape dependency of the interactions, we investigated two measures. The first measure is obtained from

TABLE 2: List of PAHs Studied with Their Corresponding Dimerization Energy (kcal/mol) from BSSE Uncorrected MP2/6-31g(d)[a]

PAH	group	V	K	Zagreb
		$h = 3$		
$C_{10}H_{14}$	D_{2h}	9.29	4	3,0,1
	C_{2v}	9.05	5	3,0,2
		$h = 4$		
$C_{16}H_{10}$	D_{2h}	12.35	8	4,2,1
$C_{18}H_{12}$	D_{2h}	13.56	5	4,0,5
		13.10	7	4,0,4
	C_{2h}	13.07	8	4,0,3
	C_{2v}	13.27	8	4,0,2
	D_{3h}	12.95	9	4,0,1
		$h = 5$		
$C_{20}H_{12}$		16.66	9	5,2,3
	D_{2h}	16.40	9	5,2,1
	C_{2v}	16.32	11	5,2,2
$C_{22}H_{14}$	D_{2h}	18.08	8	5,0,12
		17.19	9	5,0,11
		17.09	11	5,0,6
	C_{2v}	17.03	10	5,0,10
		17.35	11	5,0,8
	C_{2v}	16.91	12	5,0,9
	C_{2h}	16.87	12	5,0,5
	C_{2v}	16.91	13	5,0,7
		17.15	13	5,0,3
	C_{2v}	16.92	13	5,0,4
		17.20	14	5,0,1
		$h = 6$		
$C_{22}H_{12}$	C_{2v}	19.59	14	6,4,1
	C_{2h}	20.52	10	6,4,3
	D_{3h}	93.04	0	6,4,2
$C_{24}H_{14}$		20.84	12	6,2,14
	C_{2h}	20.90	9	6,2,6
		20.38	15	6,2,5
	C_{2v}	20.35	16	6,2,10
	C_{2v}	72.33	0	6,2,13
	D_{2h}	20.22	20	6,2,1
	C_{2h}	21.01	13	6,2,8
	C_{2v}	20.71	14	6,2,12
		20.66	15	6,2,3
		20.50	17	6,2,4
		20.86	16	6,2,9
	C_{2h}	20.86	15	6,2,11
		20.76	17	6,2,2
		21.20	12	6,2,7
$C_{26}H_{16}$	D_{2h}	22.60	7	6,0,36
		21.74	11	6,0,35
	C_{2h}	21.16	16	6,0,29
	C_{2v}	21.30	17	6,0,32
		21.54	14	6,0,31
		21.42	13	6,0,30
		21.82	14	6,0,33
	C_{2v}	21.16	16	6,0,34
		20.84	19	6,0,14
		21.54	20	6,0,18
		21.47	18	6,0,17
	C_{2h}	21.46	15	6,0,16
		20.94	18	6,0,15
		21.66	19	6,0,22
		21.17	19	6,0,26
		20.83	17	6,0,28
	C_{2v}	21.19	19	6,0,19
		21.18	17	6,0,27
		21.41	19	6,0,12
		21.59	20	6,0,20
		21.51	18	6,0,21
	C_{2v}	21.83	15	6,0,24
		21.60	19	6,0,25
		20.79	22	6,0,13
		21.34	21	6,0,9
	C_{2v}	21.37	21	6,0,8
		21.06	23	6,0,7
		21.80	22	6,0,3
	C_{2h}	21.58	21	6,0,2
	C_{2h}	20.83	21	6,0,11
	C_{2v}	21.74	22	6,0,10
	D_{2h}	21.44	24	6,0,1

[a] The fourth column has the Kekule numbers while the fifth is the Zagreb notation for the isomer.

TABLE 3: Average Potential (kcal/mol) in Terms of the Number of Rings

h	$\langle V \rangle$	h	$\langle V \rangle$
3	9.17	5	17.01
4	13.05	6	21.15

the eigenvalues of the vertex adjacency matrix. This matrix defines the connectivity of C atoms; that is, each element is 1 if two atoms are connected and 0 otherwise. The sum of the positive eigenvalues (S) could be used as a topological measure.

$$S = 1/N \sum_{k}^{N/2} \alpha_k \tag{1}$$

where α_k denotes the kth eigenvalue with N being the number of carbon atoms. Similarly. the product of these eigenvalues could also be used; however, this product is shown to be equal to the Kekule number.[27] To isolate the effects of the number of rings, we plot only the results of $C_{26}H_{16}$ in Figure 5.

There are two points which are noteworthy. First of all, the energies vary very slightly from isomer to isomer, the maximum difference being 2.2 kcal/mol. The second point is that even though this measure is in fact a distinguishing factor for all isomers,[1] it does not really correlate with the interaction potentials.

The other measure (A) is the ratio of two axes of the moment of inertia which describes the elongation of the molecule.

$$A = \sigma_1/\sigma_2 \tag{2}$$

σ_1 and σ_2 are the smaller and larger axes of the two-dimensional moment of inertia tensor. For totally symmetric cases, this ratio is 1.0 and drops as the molecule is stretched. Because V depends linearly on the number of carbons (or h), we present the scaled quantity V/N as a function of the aspect ratio of all dimers studied in Figure 6. Similar to the adjacency matrix based measure, the aspect ratio does not distinguish the stacking energies, at least for small PAHs up to $h = 6$.

We have mentioned the Kekule number which signals the extent of the conjugation and has strong connections to the aromatic stability of PAHs. For example $K = 0$ cases should be unstable biradicals. In Figure 7, we plotted the V with respect

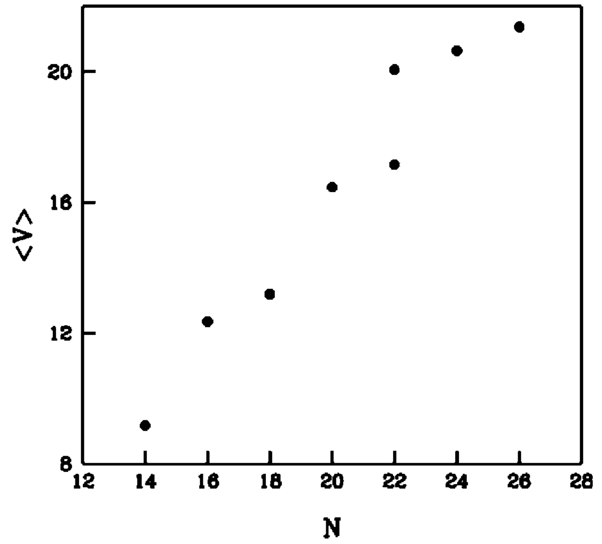


Figure 4. Average interaction potential as a function of the number of carbon atoms.

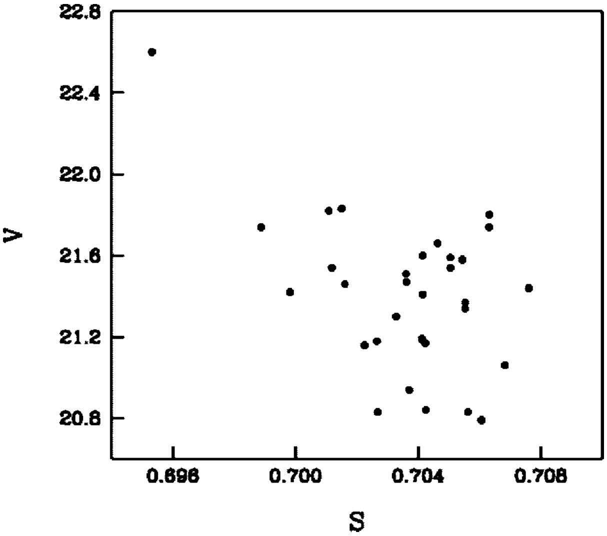


Figure 5. *V* vs for *S* for $C_{26}H_{16}$..

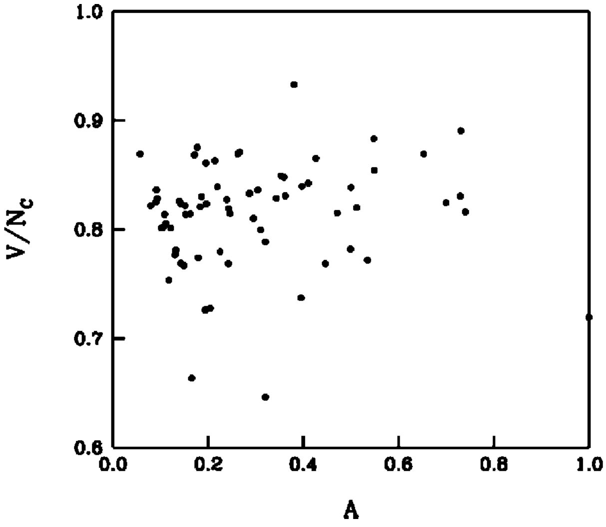


Figure 6. *V*/*N* in terms of the aspect ratio.

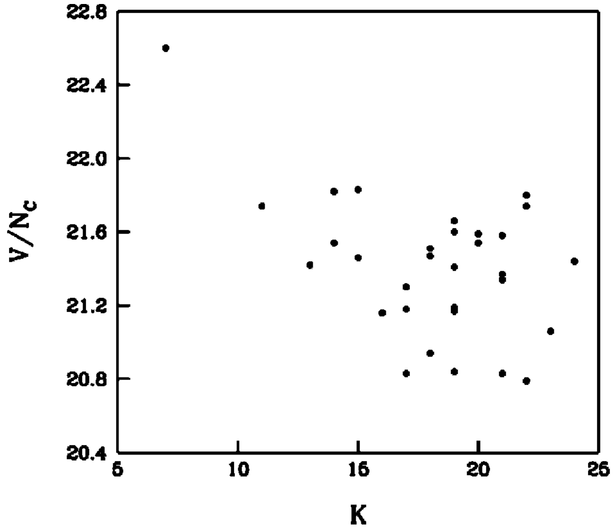


Figure 7. *K*-number dependence of the stacking energy.

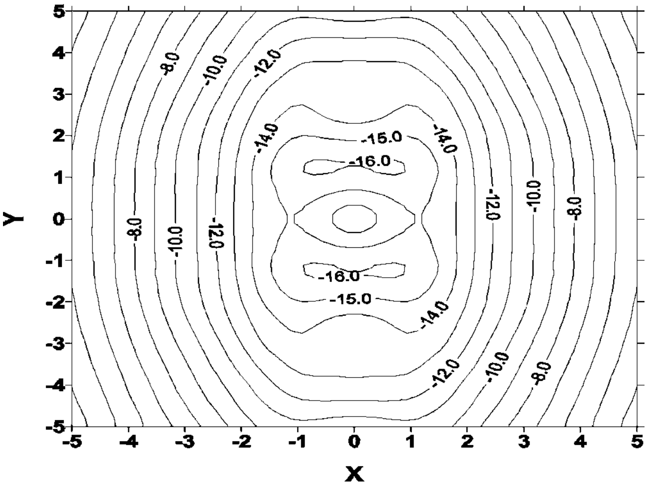


Figure 8. PES for the slipping motion of tetracene. *Y* is the long axis along the molecule. Distances are in angstroms, and the potential energy is in kilocalories per mole.

to the *K*-number for the same set of molecules. Surprisingly, the *K*-number is not a determining factor for the strength of the stacking. In fact if there is a trend, then it is the opposite of what we expect. That is the more stable PAHs have smaller *K*-numbers. Our calculations for two $K = 0$ molecules from Figure 3 give dimerization energies of 70 and 90 kcal/mol though one should not pay much attention to these figures as they are closed-shell calculations.

Shifting and Rotation. It is clear that packings of these small systems are not necessarily composed of simple vertical displacements. This was demonstrated in very small systems as well as in N-containing PAHs.[28] To study the energy variations between parallel stacked dimers and their off-centered conformations, we have selected a small set of molecules which possess D_{2h} symmetry and one additional molecule with D_{3h} symmetry. In Table 4, we present these molecules and the energy differences. ΔV(shift) is the energy difference between the aligned and offf-center minima. In all cases, the off-center conformation is lower in energy. The shifts in the molecular planes vary from 1.4 to 1.6 Å. The linear molecules have global minima if one of the monomers is shifted about 1 Å in molecular axis and 1 Å in perpendicular direction. It is not possible to describe the global minima in such simple terms for the other cases.

A sample potential energy surface for the slipping motion is given for tetracene obtained again with 6-31g(d) basis in Figure 8.

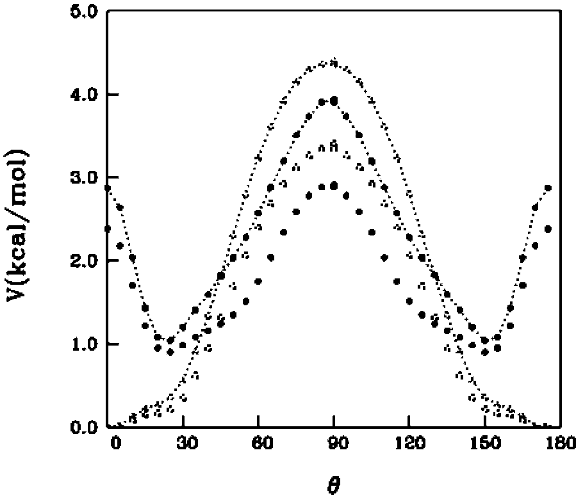
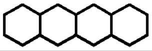
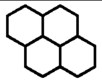
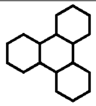
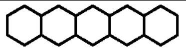
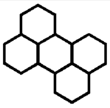
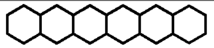
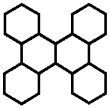
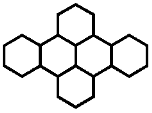


Figure 9. Rotational energy barriers for tetracene. Filled markers are from the sandwiched structure and empty ones are for the shifted conformation. Results from BSSE corrected aug-cc-PVDZ basis are connected with dotted lines whereas uncennected plots are for 6-31g(d) (uncorrected).

TABLE 4: Energy Differences (kcal/mol) for Shifting and Rotating One of the Monomers from BSSE Uncorrected MP2/6-31g(d) Calculations

Closed Formula	Structure	ΔV(Shift) /kcal/mol)	ΔV(Rotation) /kcal/mol)
$C_{18}H_{12}$		2.4	3.4
$C_{16}H_{10}$		2.8	2.8
$C_{18}H_{12}$		2.3	3.0
$C_{22}H_{14}$		3.5	6.8
$C_{20}H_{12}$		3.2	4.4
$C_{26}H_{16}$		4.1	11.1
$C_{26}H_{16}$		4.5	5.4
$C_{24}H_{14}$		3.3	4.3

The minimum energy conformation is found by shifting one of the tetracenes by 1.0 Å along the molecular axis and 0.7 Å perpendicularly. The important observation is that the noncovalent interaction changes very slowly even when one of the molecules is shifted perpendicularly to the molecular axis. In fact, the potential energy reaches 1.0 kcal/mol only when a molecule is shifted about 7 Å. This observation is valid for other PESs studied. The use of the aug-cc-PVDZ basis does not change the characteristics of the PES. In fact we have computed the same PES over a rather sparse grid, and the correlation coefficient for these two basis sets comparison is found to be 0.997.

The rotational motion of one of the monomers can be described by three angular degrees of freedom. We have studied only the rotational motion around the z-axis which keeps the molecules on two parallel planes at a fixed distance. Two similar rotational potential functions are calculated both with 6-31g(d) and BSSE-corrected aug-cc-PVDZ basis sets starting from the vertically stacked dimers and their off-center conformations. In Figure 9. the example for tetracene rotational functions is given. In tetracene, the ratio of the lengths of molecular axes is much smaller than 1; still the rotations in both cases require around 4 kcal/mol. The rotational barriers are calculated as the differences between the minimum energy (off-center) conformations and the conformation with the maximum energy.

General characteristics of both basis sets are very similar. They both find the sandwich structure to be around 2.5−3.0 kcal/mol less stable and locate the minimum of the sandwiched structure at θ as 25°, and the rotational barrier around 4.0 kcal/mol.

Conclusion

We have presented extensive calculations of the noncovalent interactions in the π-stack dimers of small PAHs. The benzoids studied here have four to six hexagons and are all planar structures. We have shown that MP2/6-31g(d) produces reliable results for the variations of the potential energy.

Interaction potential energy values show a strong correlation with the size of the PAH and seem to be unaffected by the shape of the molecule. We do not claim to study the correlations between the potential energy and a large number of graph theoretical measures proposed for these systems; however, two measures of the elongation of the molecule and the eigenvalue spectrum of the adjacency matrix do not show any important relation to the dimerization strength. Much more significanly, we did not observe correlations to the Kekule-numbers which signify the aromaticity of benzeoids.

The variations from the aligned conformations require small energies. The disturbances of the exact alignment (as in the slipping motion) work in favor of the dimer. Rotation around the perpendicular axis also is possible even to the extent of 90° rotations. These observations point out that the stacking of small PAHs is (theoretically) feasible. There may be a large variance in the structures obtained by parallel stacking of PAHs due to the relatively small amount of energy required for the rotational motion.

Finally, by also using our preliminary results on larger oligomers, we predict that simple force fields can be generated for the noncovalent interactions of PAHs in terms of vertical potentials, 2-D potential energy functions describing the slipping in the molecular planes, and rotational functions. These terms are reasonably additive: hence, it is possible to write empirical functions for each type of motion, and together one can simulate the formation of columnar structures of PAHs and graphenes.

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