**Structures, stability, and growth sequence patterns of small homoclusters of naphthalene, anthracene, phenanthrene, phenalene, naphthacene, and pyrene**

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**ABSTRACT:** Growth sequence patterns of molecular clusters have not been well elucidated. To examine structures of planar-molecule clusters, naphthalene, anthracene, phenanthrene, phenalene, naphthacene, and pyrene clusters with up to 10 molecules were theoretically investigated with the all-atom OPLS potential. The global-minimum geometries of the naphthalene dimer, trimer, and tetramer are consistent with the experimental data, suggesting that the model potential is useful for predicting the cluster geometries. The growth sequence patterns of the naphthalene, anthracene, phenanthrene, and naphthacene clusters are based on herringbone structures whereas the structures of the phenalene and pyrene clusters are amorphous. The magic numbers of the clusters are 7 or 8 except for the phenalene clusters. These numbers are used to discuss structural motifs of the clusters.

Keywords: polycyclic aromatic hydrocarbon; all-atom OPLS potential; herringbone structure; amorphous structure

**1. Introduction**

Recently the present author has investigated global-minimum structures of molecular clusters to clarify structural features of the clusters. In the latest study of the author [1], structures of planar-molecule clusters, benzene clusters (C6H6)*n* (*n* ≤ 30), were optimized with the all-atom OPLS (optimized parameters for liquid simulation) potential [2]. Magic numbers of the clusters were calculated to be 13, 19, 23, 26, and 29, in excellent agreement with the results of the Lennard-Jones atomic clusters. This is explained by regarding icosahedral structures constructed by 13 nearest-neighboring molecules as building units of the benzene clusters. The growth sequence of the benzene clusters with *n* ≥ 14 was continuous with a few exceptions. The stepwise construction of the icosahedron leads to the continuity found for the growth sequence. However, clusters of different kinds of planer molecules, ethylene clusters, display amorphous structures not icosahedral ones [3]. To understand structural features of homoclusters of planar molecules, clusters of polycyclic aromatic hydrocarbon (PAH) molecules, naphthalene, anthracene, phenanthrene, phenalene, naphthacene, and pyrene, are investigated in the present study.

Many investigations deal with homoclusters of the PAH molecules [4 – 34]. The multiphoton ionization spectra observed for (naphthalene)2 [4, 6, 8] show that the transitions of the dimer are broad. Hence no geometrical information on the dimer is obtained. On the other hand, in the spectra of the naphthalene dimer-Ar*n* (*n* = 1 – 3) [4], some sharp peaks are observed as the evidence that two inequivalent molecules are present in the clusters. The structure of (naphthalene)3 was determined from the rotational constants [5]; the naphthalene trimer has *C*3h symmetry with the intermolecular distance (the distance between the centers of mass of molecules) of 4.93 ± 0.02 Å. According to the experimental studies of Fujiwara and Lim [6] and Saigusa and Lim [7], the naphthalene trimer has *C*3h symmetry and the tetramer has a core structure similar to the trimer structure. From the *S*1 – *S*0 transitions of the naphthalene trimer and tetramer, Syage and Wessel [8] suggested that one configuration predominantly exists for each cluster. The trimer and the tetramer may take a triangular shape and a herringbone structure, respectively [8, 9]. Mass-selective, ionization-loss simulated Raman spectra of the trimer and tetramer [10] show that the trimer has three equivalent sites whereas the tetramer has four inequivalent sites.

The anthracene clusters are experimentally investigated in Refs [11 – 13]. Two configurations were detected for the jet-cooled dimer [11, 12]. Piuzzi et al. [13] revised the erroneous assignment of a band in the studies [11, 12] and reported the conclusion that the dimer exists in only one configuration. For the trimer [13], they detected two configurations. Other experimental information has never been available for the PAH clusters with a few molecules.

Theoretical investigations on the PAH clusters are limited for naphthalene, anthracene, pyrene, and naphthacene [13 – 34]. Most of the investigations are related to the naphthalene dimer and the anthracene dimer. Ab initio calculations of the structures of small clusters (four or less molecules) are reported. Geometries of larger clusters are obtained with model potentials; the maximum cluster size in the literature is six for naphthalene and anthracene clusters [13, 27]. Since the data reported previously were insufficient to discuss structural features of the PAH clusters, the present author optimized the geometries of the PAH clusters with the all-atom OPLS (OPLS-AA) potential [2]. The present study is aimed at examining structure growth sequences of the PAH clusters with up to 10 molecules.

**2. Calculation**

*2.1 Intermolecular potential*

The OPLS-AA potential [2] was used in the present study after the study on the benzene clusters [1]. The potential energy of the *n*-molecule cluster takes the pairwise-additive form:

 (1)

Here *V*(*i*, *j*) denotes the potential energy between molecules *i* and *j*. In the OPLS-AA model, intermolecular potential consists of Coulomb and Lennard-Jones terms:

 (2)

In Eq. (2), *k* and *l* represent atoms in the two molecules *i* and *j*, respectively, and *rkl* means a distance between the atoms. The following assumptions are made: (1) the structures of PAHs are rigid and planar; (2) C-H and C-C bond lengths are 1.08 and 1.40 Å, respectively; (3) all CCC and CCH bond angles are 120°. The coefficients in the equation [2] are: *B*CC = 4.69343 × 106 kJ mol-1 Å12; *C*CC = 2.34488 × 103 kJ mol-1 Å6; *B*CH= 3.08336 × 105 kJ mol-1 Å12; *C*CH = 4.86287 × 102 kJ mol-1 Å6; *B*HH = 2.02562 × 104 kJ mol-1 Å12; *C*HH = 1.00847 × 102 kJ mol-1 Å6; *Q*CC = −*Q*CH *= Q*HH =18.37422 kJ mol-1 Å. Since fusion carbons have no charge, no Coulomb term is needed for them. The intermolecular potential curves for a few clusters are shown later to explain structure growth sequences of the PAH clusters.

*2.2 Geometry optimization*

The global optimization of atomic/molecular clusters is one of the most difficult problems. Recently the present author developed the heuristic method combined with geometrical perturbations (HMGP) for geometry optimization of molecular clusters and applied it to benzene clusters to examine its efficiency [35]. In the study, the potential function of Williams and Starr [36] was employed since the benzene clusters (C6H6)*n* (*n* ≤ 15) expressed by the potential have been regarded as benchmark problems for optimization methods. The global minima for *n* ≤ 30 proposed in [35] were recently confirmed by Llanio-Trujillo et al. [37] with an evolutionary algorithm.

In HMGP, starting geometries were generated by randomly placing molecules in a sphere with a volume of *nr*e3 (*r*e denotes the equilibrium distance of the dimer). These geometries were locally optimized with a quasi-Newton method (the L-BFGS method [38]). The number of starting geometries of each cluster is listed in Table 1.

For each of the clusters with *n* = 2 – 5, the global minimum was easily located after local optimizations of starting geometries since several optimizations yielded the same lowest energy. However, it was difficult to obtain the same lowest energy for each of larger clusters after local optimizations of starting geometries. Hence three geometrical-perturbation operators [35] with subsequent local optimizations were used for searching for lower-energy configurations.

The geometry is modified with interior, surface, and orientation operators [35]. The interior operator perturbs a cluster configuration by moving some molecules to the neighborhood of the center of mass of a cluster. The surface operator partially modifies a cluster configuration by moving them to the most stable positions on the surface of a cluster. The orientation operator randomizes orientations of all molecules in a cluster. The modified geometry is always optimized with the L-BFGS method.

The number of molecules moved by the interior operator is randomly selected from 1 to 5. As a molecule or molecules moved by the operator, the highest-energy molecule or the highest-energy group of molecules is selected. The numbering of the selected molecules is represented by *s*1, *s*2, …, *sm*. The selected group has the highest energy for the expression [ 35]:

 (3)

The number of molecules surrounding a moved molecule generally increases after the operator moves it. Hence its potential energy obtained after local optimization is expected to be lower than that at the original position. This leads to a probability that the potential energy of the cluster is improved with the operator.

The surface operator also moves the highest-energy molecule or group. The most stable set of positions on the surface is selected as positions of the moved molecules. The number of moved molecules *m* is initially set at 1. It increases to 4 at an interval of 1 when the energy of the cluster is not lowered with this operator. In the operator with *m* = 1, the second highest-energy molecule and the third highest-energy molecule are also selected as a moved molecule. This enhances the optimization efficiency because the operator often lowers the energy of the cluster.

The global minimum of each of the clusters with *n* ≥ 6 was found at least twice by means of HMGP as shown in Table 1. For the naphthalene cluster with *n* = 10, the phenanthrene clusters with *n* = 4, 5, 8 – 10, the phenalene clusters with *n* = 7 – 10, and the pyrene clusters with *n* = 4 – 6, 8 – 10, it is difficult to search for their global minima (successful rates of *N*s/ *N*i are below 0.05, see Table 1). The difficulty is related to the complexity of the potential energy surface of these clusters as described later.

Calculation was executed with dual core 3 GHz Intel Xeon 5160 processors. The geometry optimization of each cluster was carried out on a single core. The Cartesian coordinates of the global-minimum geometries are available from Supplementary Material. The lowest-energy configurations of (naphthalene)2,3,4, and (anthracene)2,3 are shown in Figs. 1 and 2, respectively. The global-minimum geometries of the PAH clusters with *n* ≤ 10 are shown in Fig. 3.

*2.3 Determination of saddle points*

It was necessary to calculate saddle points on the potential energy surface of the naphthalene dimer for discussing the configurations. The saddle point connected to two minima was calculated from the geometries of the minima (endpoints) using the nudged elastic band (NEB) method [39]. In the calculations, the linear interpolation was used to generate the initial value of the geometrical parameter *i* of *n*th intermediate configuration

 (4)

Here *m* is a predefined value (20) and *n* represents integers between 1 and *m* – 1. The geometrical parameters *i* of the two endpoints (Cartesian coordinates of centers of mass of molecules and Euler angles of molecules) are denoted by *g*end1,*i* and *g*end2,*i*, respectively.

**3. Discussion**

*3.1. Structures of small naphthalene clusters*

To examine the efficiency of the OPLS-AA potential, the calculated results of the naphthalene dimer, trimer, and tetramer were compared with the experimental ones. The global-minimum configuration of the dimer takes the T-shaped form with *C*s symmetry as shown in Fig. 1. If the saddle point connected to the configuration and its mirror image corresponds to a parallel or parallel-displaced form with two equivalent monomers and its energy is close to that of the global minimum, the geometry averaged over the large-amplitude motion including the saddle point and global minimum may take a parallel configuration. To clarify the configurational behavior of the dimer, the saddle points around the minimum were searched with the NEB method [39]. The saddle point with the lowest energy took the T-shaped form where the short axis of one molecule was perpendicular to the plane of the other molecule. Its energy was 1.2 kJ mol-1 higher than that of the global minimum. The parallel-displaced configuration was also found as the saddle point but was less stable than the T-shaped saddle-point configuration by 0.9 kJ mol-1 in energy. Consequently the structure of the dimer is considered to have inequivalent monomers. The calculated geometry is consistent with the experimental result that two monomers are inequivalent in the dimer [4]. It should be noted that the T-shaped configuration shown in Fig. 1 has never been taken into account in the ab initio calculations and density functional theory calculations [13 – 21, 24 – 26, 29 – 34].

The OPLS-AA geometry of the naphthalene trimer takes the triangular shape with *C*3h symmetry and the intermolecular distance is calculated to be 4.97 Å, a value slightly larger than the experimental value (4.93 Å). The calculated values (167 and 139 MHz) of the rotational constants of *B* and *C* are equal to the experimental ones (167 ± 1 and 141 ± 1 MHz [5]) within 2 MHz. Hence the OPLS-AA geometry is in good agreement with the experimental one. The MM3 [23], MP2/6-31+G//MP2/6-31G [23], and model potential [27] calculations also show that the lowest-energy structure of the naphthalene trimer is the cyclic form with *C*3h symmetry.

The global-minimum geometry of the tetramer takes *C*1 symmetry whereas the second lowest-energy configuration takes a herringbone structure with *C*2h symmetry (see Fig. 1). According to the experimental results [6, 7, 10], the tetramer is composed of four symmetrically inequivalent molecules and its core takes a structure similar to the trimer. Hence the global-minimum geometry calculated with the OPLS-AA potential is consistent with the experimental results. The above agreement between the calculated geometries and experimental data on the dimer, trimer, and tetramer suggests that the OPLS-AA model is useful for predicting global-minimum configurations of the PAH clusters.

Fujiwara and Lim [6] determined the binding energies of the dimer, trimer, and tetramer to be 12.1, 36.2 and 50.7 kJ mol-1, respectively. These values are calculated to be 19.6, 57.1, and 91.0 kJ mol-1 (see Table 1), respectively. The binding energies of the OPLS-AA clusters are considerably overestimated.

*3.2. Anthracene dimer and trimer*

The experimental study [13] shows that the anthracene dimer and trimer take one and two configurations in the supersonic expansion, respectively. The present study proposes the candidates of these configurations. The OPLS-AA model predicts that the crossed form is the most stable for the dimer. In the ab initio studies on the anthracene dimer [14, 24, 29, 30], the crossed configuration is the most stable, in good agreement with the results of the exp-6-1 [27] and OPLS-AA potentials. Accordingly it is considered that the crossed configuration corresponds to the global minimum of the dimer. It is interesting to notice that the anthracene clusters with *n* ≥ 3 include no crossed dimer fragment as shown in Fig. 3. The dimer structure is not a building unit of the larger clusters.

The global-minimum configuration of the trimer takes the cyclic structure with *C*3h symmetry as found for the naphthalene trimer. The results obtained with the potential in Ref [13] show that the most stable and second most stable configurations are similar to those in Fig. 2. In the study based on the Hartree-Fock dispersion model [22], the *C*3h cyclic and stacked geometries were taken into account and the former was more stable than the latter (the third most stable configuration in Fig. 2). This is reasonable because the cyclic configuration has three pairs with close contact whereas the stacked configuration has two pairs. According to the number of the pairs, the minima 1 and 2 are candidates of the trimer configurations.

*3.3 Relative stability and structures of the PAH clusters*

In the global-minimum structures of the phenanthrene, phenalene, naphthacene, and pyrene dimers, two molecular planes in each cluster are parallel or nearly parallel. The T-shaped configuration is observed for the dimers of small aromatic hydrocarbon molecules, the naphthalene and benzene dimers [1].

To calculate the relative stability of the PAH clusters, the potential energies of the clusters (Table 1) were substituted into the equation

*S*(*n*) = *V*(*n* – 1) + *V*(*n* + 1) − 2*V*(*n*) (5)

A positive value of *S*(*n*) indicates that the *n*-molecule cluster is more stable than the clusters with the sizes of *n* ± 1. Fig. 4 shows that the anthracene, phenanthrene, and naphthacene clusters have the magic number of 7. Usually clusters are stabilized when construction of a building unit is just completed. Fig. 3 shows that the herringbone structure formed by 7 molecules is a building unit. The stability of the herringbone structure is confirmed by the result that the anthracene, phenanthrene, and naphthacene clusters with *n* = 10 take double herringbone structures (two 7-molecule herringbone structures are overlapped).

The structure of a building unit can be analyzed with the maximum number of molecules surrounding a molecule. In the analysis, the number of the intermolecular distances shorter than a cutoff distance (6.5 Å) is counted for each molecule. From the numbers for all molecules in the cluster, the maximum number *N*max is determined. The results are plotted in Fig. 5. For the anthracene, phenanthrene, and naphthacene clusters, the *N*max value increases up to 6. This indicates the existence of the building unit consisting of 7 molecules.

The naphthalene and phenalene clusters are considered to have no building unit since no striking stability is observed for these clusters (Fig. 4). On the other hand, the pyrene cluster with *n* = 8 is relatively stable. At the cluster size, the value of *N*max is 2 and thereby a building unit is formed by three nearest-neighboring molecules. The number of the building units in (pyrene)8 was found to be 8 whereas that in (pyrene)7, 9 was 5. Hence the pyrene clusters have the magic number of 8.

Fig. 3 shows that structural growth sequence of the anthracene clusters is similar to that of the naphthacene clusters except for the 4-molecule clusters. The herringbone structures found for the clusters with *n* ≥ 7 are similar to those in the crystal as described in Refs [13, 28]. This indicates that the growth sequence patterns of the anthracene and naphthacene clusters are based on the structures in the crystal.

The geometries of the naphthalene clusters with *n* = 3 – 7 are similar to the corresponding ones of the anthracene clusters. For the naphthalene clusters with *n* ≥ 8, one or two molecules are on the two-dimensional herringbone structures. The typical dimer geometries found in (naphthalene)8 are shown in Fig. 6. The configurations 1 and 2 are similar to the parallel-displaced and T-shaped ones of the naphthalene dimer. The configuration 3 does not correspond to the local minimum of the dimer. Only the parallel-displaced and T-shaped configurations are found in the anthracene and naphthacene clusters with *n* ≥ 3. To examine the relative stability of the configuration 3, the intermolecular potentials were calculated for the configurations 1 – 3 of the naphthalene, anthracene, and naphthacene dimer. In the calculations, the molecular orientations in these geometries were fixed and the intermolecular distance was varied. The obtained intermolecular potentials are shown in Fig. 7. The equilibrium distances of the configurations 1 and 2 are approximately independent of the clusters whereas the corresponding distance of the configuration 3 considerably varies from 8.47 Å (naphthacene) to 6.07 Å (naphthalene) because of the lengths of the long axes of the molecules. The lowest energy of the configuration 3 is lower than that of the configuration 1 for the naphthalene dimer and this is not the case for the other two dimers. Consequently the configuration 3 is not observed for the anthracene and naphthacene clusters.

The geometrical parameters (Fig. 8) of the configurations 1 and 2 in (anthracene)7 and (naphthacene)7 are listed in Table 2. The parameter values for anthracene are close to the corresponding ones for naphthacene. The comparison of these values with the data taken from the crystal structures of anthracene and naphthacene [40, 41] shows that significant differences between the clusters and the crystals are found for *θ*1 and *θ*2 of the configuration 2 of anthracene and the configuration 1 and one of the configurations 2 of naphthacene. This indicates that some molecules in the clusters are more perpendicular to the intermolecular axes than those in the crystals.

The longest C…C distance in the phenanthrene molecule, 7.0 Å, is longer than that in the naphthalene molecule, 5.0 Å and shorter than that of the anthracene molecules, 7.4 Å. This suggests that the phenanthrene clusters have features between the naphthalene and anthracene clusters. This is confirmed in Fig. 3, that is, the structure growth sequence of the phenanthrene clusters with *n* = 5 – 9 is similar to that of the naphthalene clusters and the geometry of the 10-molecule phenanthrene cluster is similar to that of the corresponding anthracene cluster.

Contrary to the above clusters, the phenalene and pyrene clusters take amorphous structures. This must be related to the fact that the shapes of these molecules are more oblate than those of the other molecules.

The global-minimum configurations of the benzene clusters [1] have the icosahedral building unit. The phenalene molecule is oblate as well as the benzene molecule but the phenalene clusters take the amorphous structures in contrast with the benzene clusters. Hence the structures of the clusters of the oblate planar molecules depend on the sizes of the molecules. For small planar molecules, anisotropy of molecular interactions would be small. Consequently the benzene clusters are considered to prefer icosahedral structures.

As described before, it is not easy to search for the global minima of (naphthalene)10, (phenanthrene)4, 5, 8 – 10, (phenalene)7 – 10, and (pyrene)4 – 6, 8 – 10. Most of these geometries take amorphous structures or three-dimensional structures based on herringbone geometries. Hence several stable configurations are possible compared with two-dimensional herringbone structures. The complexity of the potential energy surfaces of these clusters would be enhanced by the number of possible configurations.

**4. Conclusions**

Geometry optimization of the PAH clusters with up to 10 molecules was performed with the OPLS-AA potential. The structural growth sequence of the PAH clusters is different from the icosahedron-based growth sequence of the benzene clusters. The PAH clusters are classified into two categories: (1) the naphthalene, anthracene, phenanthrene, and naphthacene clusters taking herringbone structures; (2) the phenalene and pyrene clusters with no regularity (amorphous structures). The oblate planar molecules (benzene and phenalene) exhibit icosahedral or amorphous cluster structures. On the other hand, the prolate planar molecules (ethylene, naphthalene, anthracene, phenanthrene, and naphthacene) display amorphous or herringbone cluster structures not icosahedral ones.

**Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at doi:xxxxxxxx/j.computc.xxxxxxx.

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**Table 1**

The number of the initial geometries used in the geometry optimization (*N*i), the number of the initial geometries from which the global minima are found (*N*s), and the lowest energy of the cluster with *n* molecules, *V*(*n*) (in kJ mol-1)

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| size | naphthalene | | | anthracene | | | phenanthrene | | |
| *n* | *N*i | *N*s | *V*(*n*) | *N*i | *N*s | *V*(*n*) | *N*i | *N*s | *V*(*n*) |
| 2 | 100 | 86 | -19.6 | 100 | 31 | -33.2 | 100 | 92 | -33.4 |
| 3 | 100 | 56 | -57.1 | 100 | 47 | -87.9 | 100 | 9 | -82.8 |
| 4 | 100 | 39 | -91.0 | 100 | 15 | -140.5 | 100 | 3 | -133.2 |
| 5 | 500 | 47 | -127.8 | 500 | 50 | -198.1 | 1000 | 3 | -185.0 |
| 6 | 100 | 75 | -164.7 | 100 | 92 | -255.7 | 100 | 23 | -238.7 |
| 7 | 100 | 55 | -210.4 | 100 | 94 | -328.1 | 100 | 21 | -307.8 |
| 8 | 100 | 15 | -254.4 | 100 | 90 | -390.0 | 800 | 16 | -364.2 |
| 9 | 200 | 30 | -294.9 | 200 | 151 | -451.5 | 600 | 7 | -425.6 |
| 10 | 200 | 5 | -338.5 | 200 | 132 | -526.1 | 1000 | 3 | -486.2 |
|  | phenalene | | | naphthacene | | | pyrene | | |
| *n* | *N*i | *N*s | *V*(*n*) | *N*i | *N*s | *V*(*n*) | *N*i | *N*s | *V*(*n*) |
| 2 | 100 | 74 | -27.7 | 100 | 76 | -43.9 | 100 | 67 | -38.0 |
| 3 | 500 | 22 | -63.6 | 100 | 11 | -119.0 | 100 | 11 | -77.1 |
| 4 | 500 | 39 | -104.5 | 100 | 9 | -191.2 | 100 | 3 | -128.1 |
| 5 | 500 | 6 | -144.3 | 100 | 13 | -269.4 | 1000 | 3 | -178.8 |
| 6 | 100 | 6 | -191.9 | 100 | 85 | -348.1 | 1000 | 10 | -238.8 |
| 7 | 100 | 5 | -241.5 | 100 | 96 | -447.8 | 1000 | 65 | -302.8 |
| 8 | 2500 | 16 | -293.1 | 100 | 86 | -532.3 | 1000 | 7 | -373.4 |
| 9 | 2500 | 4 | -348.4 | 200 | 175 | -616.4 | 1000 | 3 | -431.5 |
| 10 | 7000 | 5 | -402.4 | 200 | 159 | -718.6 | 11000 | 2 | -493.8 |

**Table 2**

Geometrical parameters of the dimers in (anthracene)7 and (naphthacene)7 and in the crystals of anthracene and naphthacene

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| parametera | 7-molecule clusterb | | |  | crystal | | |
|  | conf. 1c | conf. 2c | |  | conf. 1c | conf. 2c | |
| anthracened |  |  |  |  |  |  |  |
| *r* | 5.94 | 4.67 | 4.76 |  | 6.02 | 5.23 | |
| *θ*1 | 82.7 | 84.1 | 82.3 |  | 82.8 | 61.5 | |
| *θ*2 | 97.0 | 95.6 | 96.4 |  | 97.2 | 109.4 | |
| *φ*1 | -0.7 | -1.1 | -0.8 |  | 0.0 | 12.3 | |
| *φ*2 | 25.1 | 29.5 | 29.9 |  | 26.2 | 27.6 | |
| *φ*3 | 22.9 | 74.8 | 79.5 |  | 26.2 | 74.9 | |
| naphthacenee |  |  |  |  |  |  |  |
| *r* | 5.94 | 4.67 | 4.76 |  | 6.14 | 4.93 | 5.14 |
| *θ*1 | 82.5 | 83.8 | 82.5 |  | 73.3 | 86.2 | 66.8 |
| *θ*2 | 97.4 | 96.0 | 96.8 |  | 106.7 | 93.0 | 111.6 |
| *φ*1 | -0.4 | -0.7 | -0.4 |  | 0.0 | 1.8 | 1.4 |
| *φ*2 | 24.8 | 29.8 | 29.7 |  | 26.6 | 28.8 | 27.4 |
| *φ*3 | 23.1 | 75.0 | 79.6 |  | 26.6 | 77.5 | 75.7 |

a Structural parameters *r*(Å), *θ*(°), and *φ*(°) are defined in Fig. 8.

b The values are taken from the dimer geometry including the central molecule in the cluster.

c The configurations 1 and 2 are shown in Fig. 6. Two distinct geometries are obtained for the configuration 2 except for the crystal structure of anthracene.

d The crystal data at 295 K taken from [40].

e The crystal data taken from [41].

Figure Captions

Fig. 1. Top and side views of the lowest-energy configurations of the naphthalene dimer and trimer, and the two lowest-energy configurations of the tetramer. The relative energies Δ*V* are given for the tetramer in units of kJ mol-1.

Fig. 2. Top and side views of the lowest-energy configuration of the anthracene dimer and the three lowest-energy configurations of the trimer. The relative energies Δ*V* are given for the trimer in units of kJ mol-1.

Fig. 3. The global-minimum geometries of the polycyclic aromatic hydrocarbon clusters with *n* ≤ 10.

Fig. 4. The relative stability *S*(*n*) of the global-minimum configurations of the polycyclic aromatic hydrocarbon clusters.

Fig. 5. The maximum number of molecules surrounding a molecule in each of the polycyclic aromatic hydrocarbon clusters.

Fig. 6. Top and side views of three types of molecular pairs in the naphthalene cluster with *n* = 8.

Fig. 7. Intermolecular potentials of the naphthalene, anthracene, and naphthacene dimers. The solid, dashed, and dotted curves represent the potential curves of the configurations 1, 2, and 3 shown in Fig. 6, respectively. The relative orientations of the molecules are fixed as shown in Fig. 6 and the distance between the centers of mass of molecules *r* is varied.

Fig. 8. Geometrical parameters of the anthracene dimer. Five straight lines are drawn: (1) one line connecting the centers of mass of molecules; (2) two lines coinciding with the long axes of the molecules; and (3) two lines along the C-C bonds. The intermolecular distance *r* is the length of the line (1), the angles*θ* are formed by the two lines (1) and (2), and the dihedral angles *φ* are defined by the three connected lines.

Fig1.tiff

Fig. 1

Fig2.tif

Fig. 2

Fig3.tif

Fig. 3

Fig4.tif

Fig. 4

Fig5.tif

Fig. 5

Fig6.tif

Fig. 6

Fig7.tif

Fig. 7

Fig8.tiff

Fig. 8