Ab initio-based intermolecular carbon–carbon pair potentials for polycyclic aromatic hydrocarbon clusters
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Citation: The Journal of Chemical Physics 122, 031102 (2005); doi: 10.1063/1.1845432
View online: http://dx.doi.org/10.1063/1.1845432
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/122/3?ver=pdfcov
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Ab initio studies on the van der Waals complexes of polycyclic aromatic hydrocarbons. II. Naphthalene dimer and naphthalene–anthracene complex

Ab initio studies on the van der Waals complexes of polycyclic aromatic hydrocarbons. I. Benzene–naphthalene complex
Ab initio-based intermolecular carbon–carbon pair potentials for polycyclic aromatic hydrocarbon clusters

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(Received 4 November 2004; accepted 16 November 2004; published online 30 December 2004)

We derived the carbon–carbon pair potentials for polycyclic aromatic hydrocarbon (PAH) clusters, which exhibited a strikingly similar geometry to that of the two-layer graphite. The binding energy of PAH clusters ranging in size from the benzene dimer to the pyrene dimer obtained by ab initio calculations at the MP2 level was used to extract the pair potentials in the form of the Lennard-Jones and Exponential-6 functions. Identical binding energy and equilibrium interlayer distance were reproduced by these functions to those calculated by the ab initio method. The pair potentials for PAHs yield the same equilibrium C–C distance as the known pair potentials for graphite and fullerenes, but nearly twice the well depth because of the polarization of the C–H bond.

The lattice sum method using atomic pair potentials has been widely used to estimate the binding energy and other physical properties of conjugated carbon materials such as graphite, fullerenes, and nanotubes. In the case of graphite, its interlayer binding energy and compressibility have been calculated from the Lennard-Jones (LJ) and exponential-6 (Exp-6) type potentials. Likewise, for conjugated hydrocarbon systems such as polycyclic aromatic hydrocarbons (PAHs), the pair potentials of Exp-6-1 type have been derived for benzene (Bz), naphthalene (Np) and anthracene (At) from the crystal structure and partial atomic charges. In the rapidly growing area of materials and supramolecular chemistry, a pair potential for larger PAH systems is in great demand. Calculation of the partial atomic charges for a large PAH is a daunting task, however, and thus there is no universal pair potential available for PAHs to date.

In this paper, we report the intermolecular carbon–carbon (C–C) pair potentials for the PAH clusters based on their binding energy obtained by MP2 level ab initio calculations. The resulting pair potentials turn out to describe the interactions of PAH clusters very well and are even closely related with the C–C interactions of graphite in a scalable way. All PAH clusters examined in our study, up to the pyrene (Py) dimer, were found to have a common geometry of parallel-displaced type as if they were embedded in a two-layer graphitic structure.

We have shown in our recent theoretical study of the PAH clusters ranging in size from (Bz)2 to Np–At that their stable geometry is remarkably identical to that of the two-layer graphite and that their binding energy is proportional to the number of overlapping hexagons between the pair of PAHs ("the integer rule"). The optimized interplanar distance of these clusters decreases as the size of the PAH molecule increases, reaching the graphitic value of 3.35 Å at (Np)2 with no further change. For the smallest cluster of (Bz)2, it is well-known that there exist two local minima of nearly equal energy between the T-shaped and parallel-displaced structures. As the size of the PAH molecule increases, the parallel-displaced form that resembles the two-layer graphite becomes more stable than the T-shaped one. The dominant force in the former is the π–π stacking interaction, which increases with the size of the PAH system, in contrast to the more localized π-hydrogen bond that governs the latter. The graphitic structural motif becomes predominant as early in the PAH series as Bz–Np. The result of our newly refined calculation for clusters up to (Py)2 at a higher scanning resolution of 0.05 Å in interplanar distance is summarized in Table I and Fig. 1. In PAH clusters, the dispersion force that governs the attractive interaction favors the geometry with the largest π–π overlap, while the electrostatic interaction tends to avoid a direct (face-to-face) overlap of carbon atoms between the two layers in order to minimize the π electron repulsion and the quadrupole-quadrupole moment interaction. The parallel-displaced graphitic geometry of the PAH clusters appears to be the result of a compromise between these two opposing factors.

In an attempt to take advantage of the striking geometrical resemblance between the PAH clusters and graphite, we tried to derive the LJ and Exp-6 type potential functions for the interlayer C–C pair from our ab initio binding energies for the PAH clusters fixed at the geometry of graphite (Table II). In the lattice sum, we assumed that the self-consistent-field energy, ΔE_{SCF}, from the ab initio result corresponds to the repulsive term of the pair potential, while the electron correlation energy, ΔE_{COR}, accounts for the attractive term, in view of the fact that ΔE_{COR} of the PAH clusters is well represented by a function that varies as r^{−6}. We obtained three simple equations, two for the repulsive interaction and one for the attractive one:

\[ \Delta E_{SCF} = A \sum_{ij} 1/r_{ij}^{12} + B/n_{ij}, \]  

(repulsive term for LJ)
TABLE I. The geometrical coordinates and the binding energy of polycyclic aromatic hydrocarbon clusters shown in the top panel of Fig. 1 calculated at the MP2/6-31G* (0.25) level.2

<table>
<thead>
<tr>
<th>Clusters</th>
<th>$\Delta x^b$</th>
<th>$\Delta y^b$</th>
<th>$\Delta z^b$</th>
<th>$\Delta E^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) benzene dimer</td>
<td>0.2</td>
<td>0.1</td>
<td>3.50</td>
<td>-0.112</td>
</tr>
<tr>
<td>(b) benzene–naphthalene</td>
<td>0.0</td>
<td>-0.1</td>
<td>3.45</td>
<td>-0.214</td>
</tr>
<tr>
<td>(c) naphthalene dimer</td>
<td>0.0</td>
<td>0.3</td>
<td>3.35</td>
<td>-0.333</td>
</tr>
<tr>
<td>(d) naphthalene–anthracene</td>
<td>0.0</td>
<td>0.2</td>
<td>3.35</td>
<td>-0.456</td>
</tr>
<tr>
<td>(e) pyrene dimer</td>
<td>0.1</td>
<td>0.0</td>
<td>3.35</td>
<td>-0.772</td>
</tr>
</tbody>
</table>

The same computational method as in Refs. 8 and 9 was employed for all calculations, except for a higher scanning resolution of 0.05 Å in interplanar distance. The geometry of the pyrene monomer was newly calculated at the MP2/6-31G* level with geometry optimization and used in the calculation for the dimer.

The binding energy, $\Delta E$ (in eV), is evaluated from $\Delta E = E(AB) - E(A) - E(B)$, where $E(AB)$, $E(A)$, and $E(B)$ are the molecular energies of the A–B complex, monomer A, and monomer B, respectively.

\[
\Delta E^{SCF} = A^{ij} \sum \exp(-\alpha r_{ij}) + B^{ij}/n_{ij}, \quad \text{(repulsive term for Exp-6)} \tag{2}
\]

\[
\Delta E^{COR} = C \sum \frac{1}{r_{ij}^6} + D/n_{ij}, \quad \text{(attractive term for LJ)} \tag{3}
\]

where $i$ and $j$ are the indices for the carbon atoms of the two different constituent planes, $r_{ij}$ is the inter-carbon distance, and $n_{ij}$ is the total number of counted pairs in the cluster. The additional terms $B/n_{ij}$, $B^{ij}/n_{ij}$, and $D/n_{ij}$ to the original potential functions are introduced in order to ensure convergence to zero energy in the graphitic limit (the infinite PAH).17

Equations (1)–(3) are plotted in Figs. 2(a)–2(c), which demonstrate that the binding energy of the PAH clusters is remarkably well-described by these interlayer C–C pair potential functions. The binding energy $\Delta E$ is obtained from $\Delta E = \Delta E^{SCF} + \Delta E^{COR}$ for both the LJ and Exp-6 pair potentials, whose working formulas are given by Eqs. (4) and (5), respectively:

\[
\Delta E^{LJ} = 36.04 \times \sum_{ij} (1380.34/r_{ij}^{12} - 1/r_{ij}^6) + 3.56/n_{ij} \tag{4}
\]

\[
\Delta E^{Exp-6} = \sum_{ij} \exp(-\alpha r_{ij}) + \sum_{ij} \exp(-\beta r_{ij}) \tag{5}
\]

### Table II. The binding energy (in eV) of polycyclic aromatic hydrocarbon clusters of graphitic geometry shown in the bottom panel of Fig. 1 calculated at the MP2/6-31G* (0.25) level.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>$\Delta E^{SCF}$</th>
<th>$\Delta E^{COR}$</th>
<th>$\Delta E$</th>
<th>$\Delta E$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f) benzene dimer</td>
<td>0.317</td>
<td>-0.415</td>
<td>-0.098</td>
<td>-0.316</td>
<td>-0.065</td>
</tr>
<tr>
<td>(g) benzene–naphthalene</td>
<td>0.403</td>
<td>-0.611</td>
<td>-0.208</td>
<td>-0.510</td>
<td>-0.204</td>
</tr>
<tr>
<td>(h) naphthalene dimer</td>
<td>0.491</td>
<td>-0.818</td>
<td>-0.327</td>
<td>-0.718</td>
<td>-0.339</td>
</tr>
<tr>
<td>(i) naphthalene–anthracene</td>
<td>0.584</td>
<td>-1.034</td>
<td>-0.450</td>
<td>-0.932</td>
<td>-0.460</td>
</tr>
<tr>
<td>(j) benzene–pyrene</td>
<td>0.407</td>
<td>-0.759</td>
<td>-0.352</td>
<td>-0.709</td>
<td>-0.335</td>
</tr>
<tr>
<td>(k) naphthalene–pyrene</td>
<td>0.621</td>
<td>-1.143</td>
<td>-0.522</td>
<td>-1.043</td>
<td>-0.538</td>
</tr>
<tr>
<td>(l) anthracene–pyrene</td>
<td>0.725</td>
<td>-1.396</td>
<td>-0.671</td>
<td>-1.299</td>
<td>-0.682</td>
</tr>
<tr>
<td>(m) pyrene dimer</td>
<td>0.752</td>
<td>-1.517</td>
<td>-0.765</td>
<td>-1.438</td>
<td>-0.759</td>
</tr>
</tbody>
</table>

The same computational method was employed as in Refs. 8 and 9, except that the interlayer distance of all clusters is now fixed at 3.35 Å with their lateral geometry fixed to the graphitic geometry with the direct overlap of the reference carbon atoms of both moieties. This approach yields an error of less than 0.1 Å in geometry (Ref. 13). Because the binding energy difference due to the displacement of 0.1 Å at the graphitic geometry is very small (0.007 eV) even for the largest system treated here, the error in binding energy arising from our graphitic geometry is negligible. $\Delta E^{SCF}$ is the self-consistent-field energy and $\Delta E^{COR}$ is the electron correlation energy: $\Delta E = \Delta E^{SCF} + \Delta E^{COR}$.

The binding energy calculated by the Lennard-Jones pair potential of Eq. (4).

The binding energy calculated by the Exponential-6 pair potential of Eq. (5).

The SCF uncorrected values.
the minimum, but in the repulsive region the Exp-6 potential gives a better result than the LJ potential. In order to see the basis set dependency, another basis set (6-31+G*) was employed in the same manner, which again yielded the linearity [see Figs. 2(a)–(c)], with a slight change in the slope and intercept [Eqs. (6) and (7)]:

\[
\Delta E_{\text{LJ}} = 34.00 \times \sum_{ij} (1455.53/r_{ij}^{12} - 1/r_{ij}^6) + 4.07/n_{ij},
\]

and

\[
\Delta E_{\text{Exp-6}} = 34.00 \times \sum_{ij} (45.80 \times \exp(-3.3/r_{ij}) - 1/r_{ij}^6)
+ 3.98/n_{ij}.
\]

The recalculated binding energy of each cluster by these potentials also agreed well with the ab initio results (Table III). In all the cases, the deviation in binding energy was largest for clusters containing benzene, as expected from its highest hydrogen/carbon ratio. It is significant that these pair potentials seem to yield the interlayer binding energy and interplanar distance remarkably well for a generic system of PAH clusters, regardless of their sizes all the way up to (Py)₂.

Since a single graphite layer amounts to an infinite-size PAH without peripheral hydrogens, it is interesting and worthwhile to examine the differences in the interlayer C–C interaction between PAH systems and other all-carbon materials such as graphite, fullerenes, and nanotubes. It is also of immense interest to check whether the PAH clusters can be used, within a scale factor, as a mimic system for “nanographite” that is within the reach of a high level ab initio calculation unlike graphite itself. The potential functions for PAH clusters derived by our method yield nearly the same equilibrium C–C distance (\(x_0\)) as for all-carbon materials, while its potential well depth (\(e\)) is nearly twice larger (Fig. 3). The latter is a direct result of the fact that both the repulsive and attractive constants [\(A\) and \(C\) in Eqs. (1) and (3)] for PAHs are about twice those for graphite. In comparison with graphite, the polarization of the C–H covalent bond in PAH leads to an increase in not only the repulsive

**TABLE III.** The binding energy (in eV) of polycyclic aromatic hydrocarbon clusters of graphitic geometry shown in the bottom panel of Fig. 1 calculated at the MP2/6-31+G* level.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>(\Delta E_{\text{SCF}})</th>
<th>(\Delta E_{\text{COR}})</th>
<th>(\Delta E)</th>
<th>(\Delta E_{\text{LJ}})</th>
<th>(\Delta E_{\text{Exp-6}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f) benzene dimer</td>
<td>0.294</td>
<td>-0.350</td>
<td>-0.055 (= -0.244)</td>
<td>-0.031</td>
<td>-0.032</td>
</tr>
<tr>
<td>(g) benzene–naphthalene dimer</td>
<td>0.372</td>
<td>-0.526</td>
<td>-0.154 (= -0.443)</td>
<td>-0.164</td>
<td>-0.160</td>
</tr>
<tr>
<td>(h) naphthalene dimer</td>
<td>0.459</td>
<td>-0.715</td>
<td>-0.256 (= -0.652)</td>
<td>-0.291</td>
<td>-0.291</td>
</tr>
<tr>
<td>(i) naphthalene–anthracene</td>
<td>0.542</td>
<td>-0.911</td>
<td>-0.369 (= -0.885)</td>
<td>-0.402</td>
<td>-0.402</td>
</tr>
<tr>
<td>(j) benzene–pyrène</td>
<td>0.370</td>
<td>-0.700</td>
<td>-0.330 (= -0.823)</td>
<td>-0.290</td>
<td>-0.290</td>
</tr>
<tr>
<td>(k) naphthalene–pyrène</td>
<td>0.574</td>
<td>-1.067</td>
<td>-0.493 (= -1.181)</td>
<td>-0.474</td>
<td>-0.474</td>
</tr>
</tbody>
</table>

*aThe same computational method was employed at the MP2/6-31+G* level as in Table II. The geometry of the pyrène monomer was newly calculated at the MP2/6-31G* level with geometry optimization and used for the calculation of the clusters. Due to the large size of these clusters, the calculation was performed only up to naphthalene-pyrène. \(\Delta E_{\text{SCF}}\) is the self-consistent-field energy and \(\Delta E_{\text{COR}}\) is the electron correlation energy. \(\Delta E = \Delta E_{\text{SCF}} + \Delta E_{\text{COR}}\).

*bThe binding energy calculated by the Lennard-Jones pair potential of Eq. (6).

*The binding energy calculated by the Exponential-6 pair potential of Eq. (7).

**BSSE uncorrected values.
electrostatic and exchange-repulsion interactions between a pair of PAHs but also the attractive dispersion force by enhancing the electron densities on carbon atoms. The relatively large H/C ratios for the PAHs of our study enhancing the electron densities on carbon atoms. The relative importance of these interactions decreases as the size of the PAH increases, becoming totally negligible in the limit of graphite.

We thank Professor H. Park of Harvard University for helpful discussions. This work was supported by the National R & D Project for Nanoscience and Technology of MOST and CRM-KOSEF. Computational resources were provided by the Grand Challenge Project of KISTI.

12See Refs. 8 and 9 for a detailed account of computational method.
13Because the carbon–carbon covalent bond lengths of polyacrylamidic aromatic hydrocarbons are not identical, varying from 1.39 to 1.45 Å, we measured the deviation from the directly overlapping positions of the carbon atoms of the two planes. The reference carbon atom was selected as the one located at the center of the cluster, but the error due to the bond length difference was always smaller than 0.1 Å, which was our scanning resolution in lateral directions.
15With respect to the accuracy of the binding energy, the MP2/6-31G* (0.25) level calculation is known to be efficient for aromatic stacking interactions, yielding 75%–90% of the intermolecular correlation stabilization. The PAH clusters considered in this work are too large for a more sophisticated ab initio method, such as CCSD(T), with current computational resources. See P. Hobza and J. Šponer, J. Am. Chem. Soc. 124, 11802 (2002).
16The SCF energy for the electrostatic interactions such as the π electron repulsion and quadrupole–quadrupole moment interaction of PAH clusters is known to be repulsive at the stacking geometry (Refs. 8 and 14). On the contrary, the electron correlation energy that represents the dispersion force governs the attractive interaction of PAH clusters (Refs. 8 and 14) and is well described by the r−6-type function. See, for example, R. L. Jaffe and G. D. Smith, J. Chem. Phys. 105, 2780 (1996).
17There are interactions that are present in the PAH clusters but absent in graphite, including the van der Waals interaction between interlayer carbon and hydrogen atoms and the quadrupole–quadrupole moment interaction due to the polarization of carbon–hydrogen covalent bond. The relative importance of these interactions decreases as the size of the PAH increases, becoming totally negligible in the limit of graphite.
20Equilibrium distance $x_0 = (2A/C)^{1/6}$ and potential well depth $\varepsilon = C^2/4A$. 

FIG. 3. The Lennard-Jones C–C pair potentials for graphene–graphene (Ref. 2), graphene–C₆₀ (Ref. 5), C₆₀–C₆₀ (Ref. 2), and PAH–PAH of this work [Eq. (4)].