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REGULAR ARTICLE

Stacking of triphenylene: characterization of the potential energy surface

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Abstract The interaction potential energy of triphenylene dimer has been calculated with Møller–Plesset second-order perturbation theory for various geometrical configurations. Different types of geometrical perturbations such as rotation, displacements and their combinations are studied in terms of their effects on the stability of the dimer. Minimum energy conformers for face to face, rotated, parallel displaced and T-shape structures are obtained. For the unsubstituted triphenylene, the 35° rotation of one of the monomers results in the global minimum. However, the dimer is still very flexible in terms of displacements. A helical structure seems to be the most stable form for the trimer. For large stacked clusters, the two body forces dominate the interactions while at small monomer–monomer separation, three body terms behave like z^{-9} where z is the vertical distance between two adjacent monomers.

1 Introduction

Recently the term "noncovalent interactions" has become one of the most coveted keywords in chemistry, biology and materials science [1]. Among the noncovalent interactions, the hydrogen bonding has been studied in detail from the early days of quantum chemistry mostly because of its importance in the stability of biological systems. They also play an important role in understanding the stability and mechanical properties of a large group of polymers. The mechanism of hydrogen bonding is relatively well understood. From the computational aspect, even simple calculations of ab initio or density functional theory (DFT) methodologies may provide reasonable geometries, energetics and mechanisms [2]. On the other hand, a newly emerging group of noncovalent interactions, namely the π–π stacking of organic polycyclic aromatic hydrocarbons (PAH) or their derivatives poses more complicated problems.

As the stacking interactions mostly consist of long range dispersion forces, they become one of the challenging computational problems of today. The proper description of the noncovalent interactions whether they are in forms of the stacking of base pairs in nucleic acids or graphenes in organic electronic devices is a complex task. A recent issue of *Phys. Chem. Chem. Phys.* [3] has been devoted to various methodologies used in computing and measuring the interactions between these units. In addition to the computational problems, the elucidation of the structures from experimental data is also a challenging task as most of the information on the structures is obtained indirectly and an accurate comparison of the computational and experimental results cannot be done properly.

The main difficulty of predicting the stacking interactions comes from the fact that the dominant contributions are long range London forces. It has been known for a long time that the standard DFT methods fail to express interactions in this range. There is a large number of studies to remedy this weakness by different exchange functionals [4, 5], or other methods such as the perturbation SAPT(DFT) [6] or dispersion corrected DFT (DC-DFT) [7].

Dedicated to the memory of Professor Jürgen Hinze and published as part of the Hinze Memorial Issue.

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For the ab initio methods, electron correlation must be included to get some meaningful answers. The most reliable results come from coupled cluster calculations involving single, double and triple (iteratively) excitations CCSD(T) and preferably at the complete basis set limit (CBS). However, in case of large extended systems such as PAHs which are the precursors of the graphenes, the complexity of these calculations allows such a search of the potential energy surfaces only for very small systems such as benzene [8] and in a more limited sense for naphthalene [9].

A computationally feasible method is the second-order Møller–Plesset perturbation (MP2) theory. However, large basis set calculations on benzene dimer have shown that MP2 overestimates the interaction energy. On the other hands, small basis sets underestimate the binding energy. A fortunate cancelation of these two errors results in a semi-accurate description of the general characteristics of the potential energy surfaces of stacked PAHs. This was first noted by Sherrill [10] and later by us in our studies of a large class of stacked PAHs [11].

In this work, we report on extensive studies of the interactions between vertically stacked triphenylene (Fig. 1) units.

This is the smallest PAH which has a disk-like shape and therefore a molecule likely to form columnar two-dimensional structures [12]. They could pack vertically and/or form helical structures as in hexabenzocoronenes [13] and they are thought to behave like one-dimensional conductors.

Triphenylene, upon substitutions by alkyl groups forms the so-called discotic liquid crystal species [14]. The structures are basically stacked triphenylene cores with alkyl groups orienting themselves in the molecular planes to form self-assemblies. These substituents will help to form the liquid crystalline phases while the PAH core should form the basis of the conductance mechanisms. Therefore, a characterization of the potential energy surface of triphenylene dimerization becomes an important question.

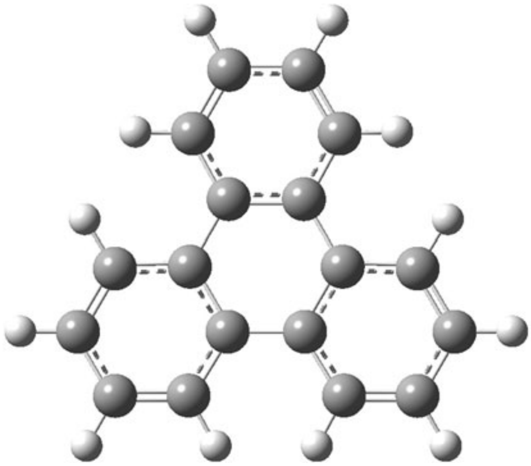


Fig. 1 Triphenylene

There is a recent report of triphenylene–triphenylene stacked dimer and the benzene–triphenylene system [15] with MP2 and using a modified 6-31G(d) basis set. They have calculated the potential energy curve of two face to face oriented triphenylenes as well as those for the cases where one of the monomers is rotated around the C_3 axis at 15° intervals. The results from these calculations are compared to OPLS [16] force field results. The optimized monomer–monomer distance was found to be 3.7 Å with the interaction energy of -12.8 kcal/mol.

In this work, we report a more extensive study of the potential energy surface including parallel-displaced dimers and T-shaped structures. The rotational potential energy curves are calculated at a large number of monomer–monomer distances, a rough PES is obtained for two triphenylene molecules on the same plane, and some characteristics of the trimer formation are studied. We will comment on several aspects of the parametrization of the potential energy surfaces. It is hoped that quantum mechanically generated force fields will help to understand at least the geometrical aspects of the disc-like and column-like structures formed by PAHs [17–19].

2 Calculations

After trying out various basis sets for the PES, we proceeded to employ two sets of MP2 calculations. The first set of results is by using the 6-31G(d) basis set and the Gaussian03 code [20]. The larger systems such as trimers and the PES over large grids are obtained with this methodology. The second set of calculations is obtained by employing the Molpro code [21] with a density-fitting MP2 [22] and a mixed correlation consistent basis set. In this basis set, carbon atoms are represented by an augmented basis of aug-cc-pVDZ while hydrogens have cc-pVDZ. When the augmented set is used also for hydrogens, the basis sets become linearly dependent especially at low monomer–monomer distances. Basis set superposition error is calculated by the standard counterpoise method. The second set of calculations is mostly used to check the small basis results.

Throughout the discussion, the z coordinate is along the C_3 axis and its value denotes the monomer–monomer distance. Molecules lie on the x–y plane where the y axis is the C_2 axis perpendicular to C_3. Therefore, x and y coordinates throughout the manuscript represent the shift from origin in x and y directions.

2.1 Parallel stacking

In order to establish the validity of the methods used, we plot in Fig. 2 the potential energy of the parallel stacked dimer as a function of z distance.

The minimum energy results are in Table 1. As in most of the unsubstituted PAHs [11], the potential energy curves are very flat around the minimum and both basis sets with and without BSSE corrections give the R_e as between 3.5 and 3.8 Å. The variation of the potential energy within this range is <1.0 kcal/mol. BSSE correction accounts about 50% of the calculated interaction. As in our former work, the results from method 6-31G(d) basis are very close to those obtained by Cinacchi and Prampolini [15] and not very far from a much improved calculation with aug-cc-pVDZ basis set with BSSE correction. Potential energy curves from these two methods differ by <1.0 kcal/mol after $z > 4.2$ Å. We proceed to use the BSSE-uncorrected 6-31G(d) for the remaining part of the calculations while checking the validity of calculations by employing the larger basis set in several cases.

Cinacchi et al. have reported that OPLS reproduces their MP2 potential energy fairly well. We observe that even a Morse or Lennard-Jones (LJ) potential function treating the complete molecule as a single particle can give a very reasonable description of the interaction. A Morse potential with $\alpha = 1.386$ Å^{-1} reproduces especially the left hand side of the potential well while LJ function with standard definition of parameters does a good job for distances larger than the equilibrium distance. A Buckingham potential describes the interactions much better than Morse and LJ functions. We obtain Buckingham parameters for the uncorrected 6-31G(d) curve as $A = 1{,}229{,}329$ kcal/mol, $B = 3.178$ Å^{-1} and $C = 56{,}832$ kcal/mol Å^6

$$V(z) = A\exp(-Bz) - C/z^6 \tag{1}$$

with these parameters, the average error in fitting is found to be 0.05 kcal/mol.

Table 1 Equilibrium bond length and the depth of the potential well for the stacked dimer

	Calculation	R_e (Å)	V (kcal/mol)
1	6-31G(d)	3.6	−13.06
2	6-31G(d) BSSE corrected	3.8	−6.04
3	Aug-cc-pVDZ	3.5	−16.31
4	Aug-cc-pVDZ BSSE corrected	3.7	−9.62

2.2 Rotation

The most stable forms of the stacked dimers of PAHs are obtained by the rotation of one of the monomers around the principal axis [23]. Especially in alkyl substituted cases, this rotation significantly reduces the steric hindrance of the substituents. In Fig. 3, the change in the potential energy by the rotational angle θ (around the C_3 axis) is plotted for $z = 3.6$ Å. The curves from both methods are superimposed by setting minimum V to zero. Both curves have almost the same characteristics. At this separation, the minimum energy conformation is at 35° and lowers the energy by 3.5 kcal/mol.

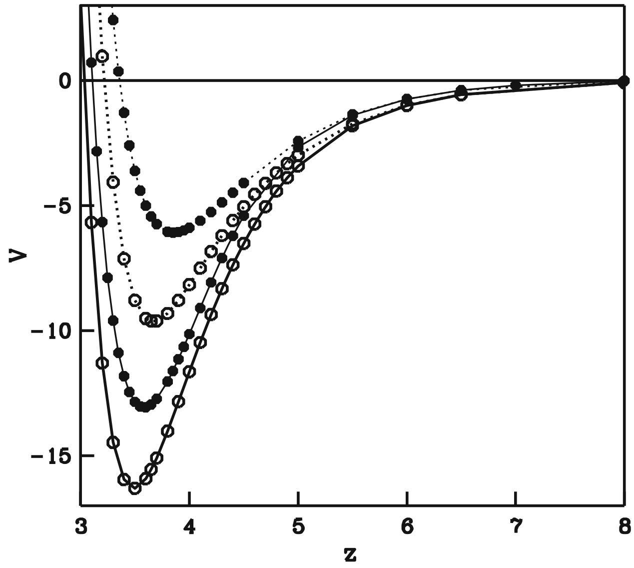


Fig. 2 $V(z)$ for stacked dimer of triphenylene. V is in kcal/mol and z is in Å. *Filled circles* are from 6-31G(d) and *empty circles* are from aug-cc-pVDZ basis sets. *Dotted lines* correspond to the BSSE corrected curves

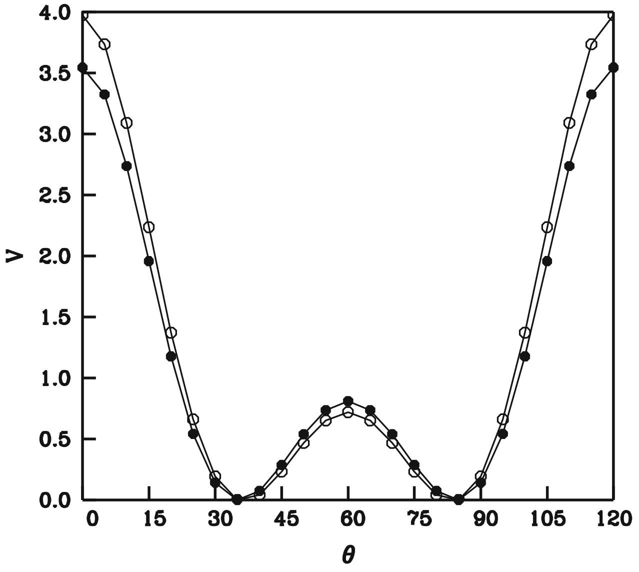


Fig. 3 Rotational potential energy function (in kcal/mol) at $z = 3.6$ Å. *Empty circles* are results from BSSE corrected aug-cc-pVDZ energies while *filled circles* are from uncorrected 6-31G(d)

The reduction of the steric hindrance by rotation should also reduce the monomer–monomer distance observed in face to face structures. We present the potential energy map as a function of the z and θ in Fig. 4. The lowest energy regime with -19 kcal/mol (compared to -13 kcal/mol at the parallel face to face position) is located at $3.2\ \text{Å} < z < 3.4\ \text{Å}$ and $30° < \theta < 40°$. This lowering of the energy is expected to be larger for alkyl substituted triphenylenes.

This contour plot also shows that the dimers are stable at very low separations provided that they are not fully face to face. The effect of the rotation becomes less prominent as z is increased. The long range behavior of the potential energy curves is such that V becomes around -1.0 kcal/mol only after $z > 5.5$ Å.

Unlike the case of the perfectly stacked structures, the interactions in the rotated dimers cannot be described by simple modifications of the Morse or LJ parameters. Even atom–atom potentials such as OPLS do not describe the variations of the potential energy by the rotational motion. So far, the best results from a classical approach for such systems have been obtained with a fluctuating charges model [19]. We are in progress of developing new functional forms for describing the rotational energy changes.

2.3 Parallel-displaced structures

Another possibility of reducing the steric repulsive forces is the shifting of one of the monomers from the center, the so-called “displaced dimers”. In Fig. 5, we present the changes in the potential with shifts in x and y direction, $V(x, 0)$ and $V(0, y)$, and their numerically obtained derivatives, $\partial V(x, 0)/\partial x$, $\partial V(0, y)/\partial y$, z is fixed at 3.6 Å. The minimum energy conformations are found when a monomer is displaced by 1.4 Å in either direction and this distance is approximately the width of a benzene ring. Similar to the rotational motion, one gains around 3.5–4.0 kcal/mol by forming such displacements. Studying the derivatives of the potential energy, which are more sensitive quantities than the actual energy, shows that there are several other key changes in the potential energy at 0.7, 2.0, 2.8 and 4.0 Å. They are all multiples of the width of a half benzenoid ring. This is significant in understanding the stacking interaction. First of all, it does not require much energy to shift one of the molecules though there are preferred sites. Then, the energy difference between a face to face dimer and a dimer with a shift of around 3 Å is zero. Therefore, the columnar structures should display a large degree of flexibility. The variations of the potential energy due to rotations as well as displacements imply that the

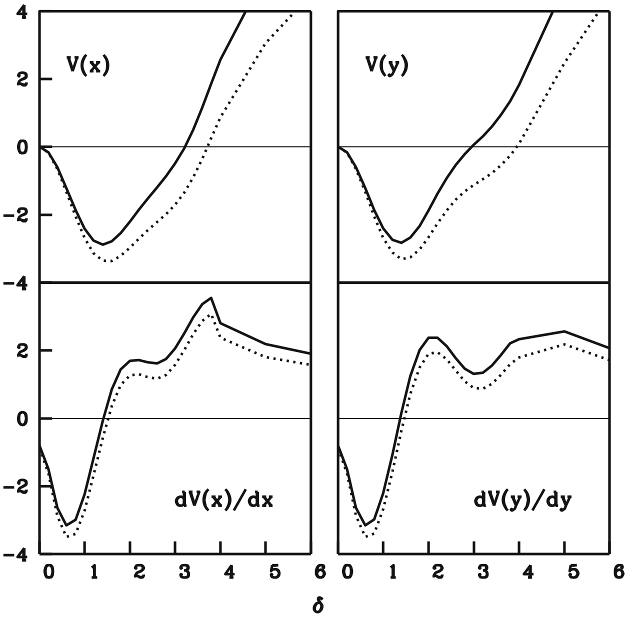
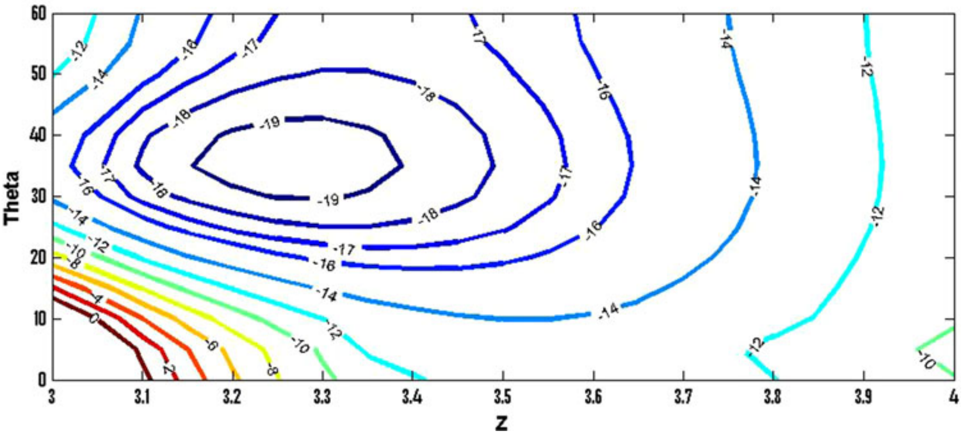


Fig. 5 Potential energy for $z = 3.6$ Å (in kcal/mol) and its derivatives as functions of the shift in x and y directions (in Å). *Solid lines* are results from BSSE corrected aug-cc-pVDZ energies while *dotted lines* are from uncorrected 6-31G(d)

Fig. 4 *Contour* diagram for the potential energy $V(z, \theta)$ in kcal/mol of the monomer–monomer distance z and the rotational angle θ



highly simplified bead models which use benzene rings as the building blocks of graphenes most probably are not suitable to describe such intricate interactions.

The complete PES of the displacement is seen in Fig. 6. The PES is reasonably isotropic with respect to displacements with a valley of minima which connects (0.0, 1.5) to (1.5, 0.0) points on the map. The potential energy becomes zero only after sliding one of the monomers around 3 Å in either direction.

As the displacement and the rotation help the stability of the dimer formation, one would think that a coupling of these two types of motion should even further stabilize the system. However, from the examples in Fig. 7, we see that the effect of the rotation is most prominent at the parallel position and as the displacement increases, the rotation is no longer a favorable motion.

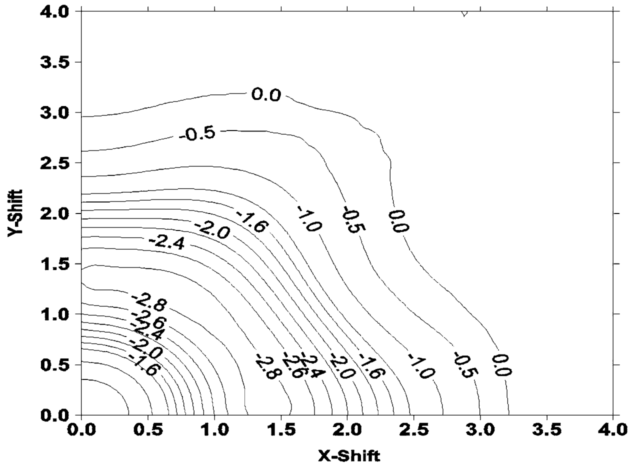


Fig. 6 PES at $z = 3.6$ Å. *Contours* are defined such that at the stacked conformation $V = 0$ kcal/mol

2.4 T-shaped conformer

For dimers of small systems like benzene, it is known that the T-shaped isomers are very stable. We would expect that this stability should decrease with the size of the PAH. For triphenylene, even though the T-shaped conformer is stable around 5 kcal/mol, it displays a much weaker well and at a larger separation of 7.1 Å (Fig. 8). The potential well around this structure is very floppy with a rotational barrier of <0.5 kcal/mol in the gas phase.

As a final note on dimers, we have searched the potential minima for the triphenylene dimer formation on a plane. The distance between the centers of mass should be around 10–11 Å for such structures to exist. In this range, the potential energy is only about 0.5 kcal/mol below zero for the lowest energy conformers. Considering the methods employed, these results are not very reliable. However, the columnar structures are thought to occur in bundles and we can conclude that the interactions between the triphenylene molecules and surfaces such as graphene should be the major contributor to the bundling.

2.5 Trimer

The characteristics of the dimer PES as given above can help to locate stable forms of the trimers. We have

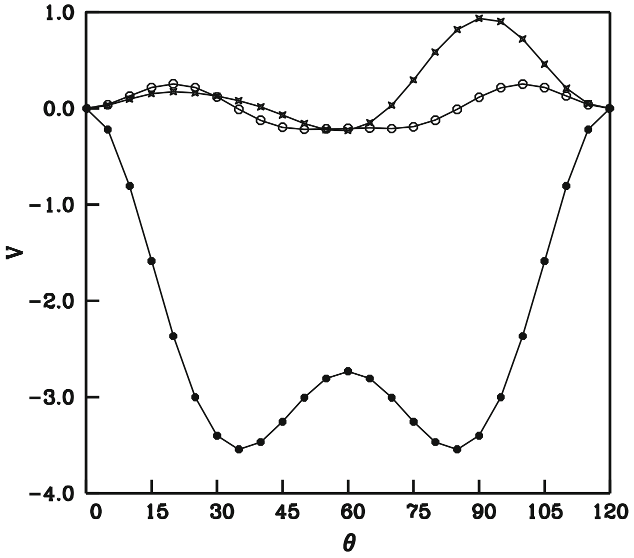


Fig. 7 Rotational potential energy functions (kcal/mol) for displaced dimers at $z = 3.6$ Å. *Filled circles* are for the stacked conformation for comparison. *Empty circles* are for $\delta x = 0.0$, $\delta y = 1.6$ and *stars* are for $\delta x = 1.4$, $\delta y = 0.0$ conformations

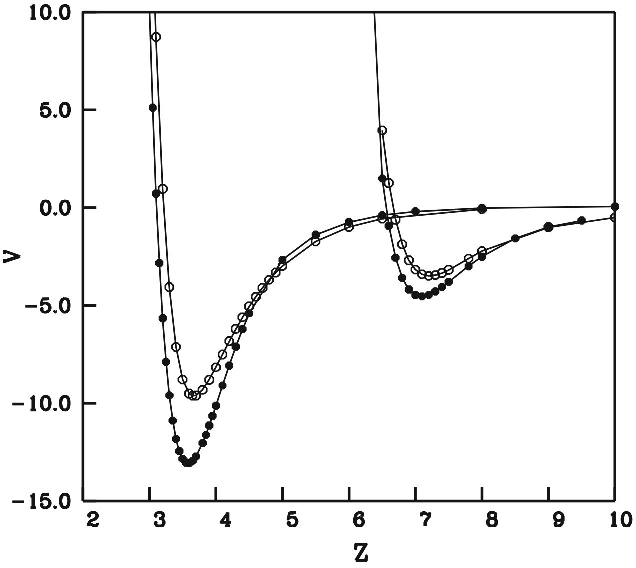


Fig. 8 Comparison of the interaction energies (kcal/mol) of stacked and T-shape structures. *Empty circles* are results from BSSE corrected aug-cc-pVDZ energies while *filled circles* are from uncorrected 6-31G(d)

calculated the interaction potentials of various types of trimers using the 6-31G(d) basis.

First of all, studying only trimers where $z_{12} = z_{23} = z$, the equilibrium distance in case of the perfect stacking in the dimer and the trimer is the same. We define the three body interactions as:

$$V_3(z) = (E_{\mathrm{trimer}}(z) - 3E_{\mathrm{monomer}}) \\ - 2(E_{\mathrm{dimer}}(z) - 2E_{\mathrm{monomer}}) \qquad (2)$$

At small separations, the three body forces contribute significantly. In Table 2, the results for Eq. 2 are given showing that the change in the three body terms with z is very monotonic. A least-square fitting shows that the magnitude of this term is proportional to z^{-9}.

We have studied two types of rotated structures: helical and zigzag conformations. These structures can be described by a single angle θ. Similar to the dimer case, the first molecule is placed in the $z = 0$ plane with the y axis coinciding with one of the C_2 axes. Then θ is the angle of rotation around the C_3 axis. The first molecule thus has coordinates as (0, 0) and the coordinate pairs (z, θ) and (2z, 2θ), respectively, are assigned to the other two molecules in the helical structure, whereas those in the zigzag structure are positioned in accord with the coordinate pairs (z, θ) and (2z, 0).

The energy differences between the helical and zigzag structures are found to be negligible. Even at a relatively dense structure for $z = 3.2$ Å, the differences are <0.5 kcal/mol.

In Fig. 9, we present the rotational potential energy of helical structures at two intermolecular separations. In both cases, $\theta = 30°$ shows minima. The effects of the rotation are more profound as the packing becomes denser. In fact, the lowest energy structure for $z = 3.2$ Å is more stable than any of the conformers of $z = 3.6$ Å.

Table 2 Three body interactions (kcal/mol) in terms of the intermolecular distance z (Å)

z	Three body interactions
3.2	−1.615
3.3	−1.270
3.4	−1.034
3.5	−0.924
3.5	−0.823
3.6	−0.728
3.6	−0.641
3.7	−0.562
3.7	−0.491
3.8	−0.371
4.0	−0.203

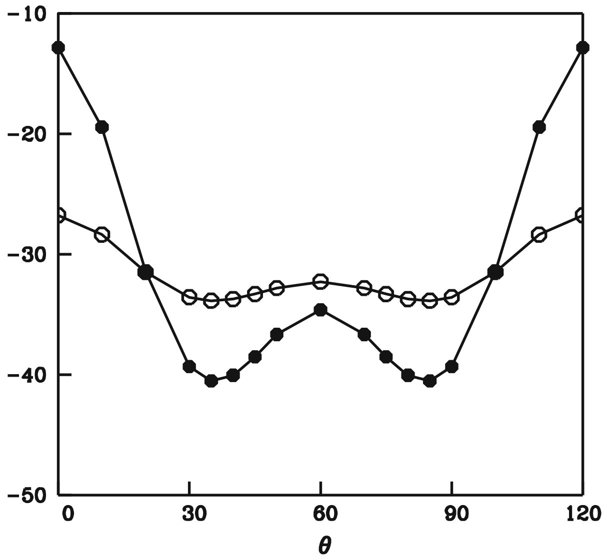


Fig. 9 Rotational potential energy of the trimer. *Filled circles* are at $z = 3.2$ Å and *empty circles* are at $z = 3.6$ Å

We have noted that the variation of the rotational potential energy of a helical trimer can be simple written as:

$$V_{\mathrm{trimer}}(\theta) - V_{\mathrm{trimer}}(0) = 2(V_{\mathrm{dimer}}(\theta) - V_{\mathrm{dimer}}(0)) \qquad (3)$$

We can safely conclude that at these separations the rotation is a simple two body interaction.

3 Conclusions

We presented various aspects of the potential energy surface of the dimer of triphenylene. A small basis set MP2 without BSSE correction seems to provide the correct characteristics of the PES. The minimum energy conformation of the stacked structure lies at $z = 3.6$ Å with a well depth of 13 kcal/mol. The potential energy function can be fitted to a Buckingham potential very accurately. The rotation of one of the monomers results in a more stable dimer conformation at $z = 3.3$ Å and $\theta = 30°$. The energy gained by this rotation is around 6 kcal/mol. The displacement of one of the monomers also finds another set of local minima which lowers the energy by another 3 kcal/mol. Both the displacement and the rotation do not have large barriers so gas phase structures of columnar triphenylene should display a rather large number of shapes. The global minimum of trimer has a helical conformation, though zigzag structures are energetically degenerate.

The majority of the experimental studies deal with alkyl substituted PAHs and applying highly accurate methods such as coupled-cluster theories with large basis sets to such systems is very prohibitive. This simplified approach could provide qualitative answers to the weakly bound PAHs.

Acknowledgments I have spent the years 1976–1980 working with Prof. Jürgen Hinze. I have learned a great deal from him and I am thankful for that. I also would like to thank the Turkish Academy of Sciences and Koç University for supporting this work.

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