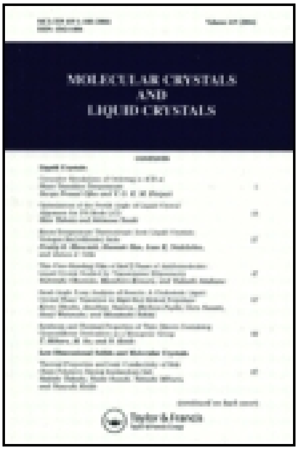

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Computer Simulation of P-Phenyls with Interaction Potentials from Ab-Initio Calculations

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COMPUTER SIMULATION OF p-PHENYLS WITH INTERACTION POTENTIALS FROM *ab-initio* CALCULATIONS

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The potential energy *surface (PES) of n-p-phenyls, with n from 2 to 5, has been obtained from ab initio calculations relevant to a few fragments into which the molecule can be decomposed. These PES have been fitted with a single Gay-Berne model that has been used in Monte Carlo NPT and Gibbs ensemble simulations.*

The results we obtain are in fairly good agreement with experiment in the case of biphenyl, while only a low density fluid phase (gas) is obtained for p-terphenyl and longer molecules.

Keywords: interaction potentials; computer simulations; n-p-phenyls

INTRODUCTION

The problem of building accurate potential functions for the simulation of molecular liquids becomes particularly severe in the case of liquid crystals. The complex nature of mesogenic molecules [1], combined with the wide range of length and time scales spanned by their dynamics, has been a powerful driving force for adopting simplified interaction models [2], in the attempt to capture the basic physics underlying their phenomenology. For the same reasons, first principles simulation techniques, as the Car-Parrinello approach [3], are still beyond current computational capabilities. Hence, it appears that also a straightforward application of *ab initio* calculations to sample the potential energy surface (PES) is out of question for a pair of mesogenic molecules.

In view of these considerations and of the growing interest for 'realistic' modelling of liquid crystals, we propose an approximate scheme to reconstruct the PES of mesogenic molecules from the *ab initio* interaction energies of the fragments into which they can be decomposed.

The basic idea behind this approach is that a very large number of potentially mesogenic molecules can be considered as composed of a very small number of moieties (phenyl rings and hydrocarbon chains are obvious examples). The size of the latter systems makes them amenable to *ab initio* calculations at a reasonable computational cost. From the PES of these 'building blocks' that of the whole molecules can be obtained with quite satisfactory accuracy.

In this paper we describe the application of this approach to the intermolecular potential of the series of p-phenyls, with a number of rings ranging from two to five. This series appears as an interesting test case as a variety of phases is observed in the higher members, (e.g. nematic for the p-quinquephenyl and smectic with six rings) even without flexible aliphatic chains. In addition, the computational cost is reduced as the only large building block is the phenyl ring. Of course, the use of the '*ab initio*' reconstructed PES in a simulation requires the choice of a model function that matches the PES as closely as possible.

From this point of view, we have adopted a multi-level strategy, starting from a rather simple and widely employed single site Gay-Berne (GB) model [4], whose results are discussed in the following. More complex and presumably realistic descriptions of the PES will be the object of future work.

Whatever model is chosen, however, the simulations are carried out under conditions of pressure relevant to the experimental and synthetic work, i.e. one atmosphere.

This constraint is of particular interest for the GB model, which has been almost always simulated at a *reduced* pressure close to one that means roughly three orders of magnitude larger than atmospheric pressure. Moreover, the parameters adopted in most simulations are not realistic, as first observed by Luckhurst and Simmonds [5]. They also used one of these systems (p-terphenyl modelled by a set of four Lennard-Jones sites) to parameterize the GB potential, and obtained values significantly different from that of Gay and Berne. The advantage of using a PES from *ab initio* calculations is that the latter can be improved in a totally controlled way, if the comparison of simulation results with experimental data is not satisfactory, even with a more flexible and 'realistic' description of the interactions, such as an atomic-detail model.

This paper contains an overview of the approach to decompose the molecule and reconstruct its PES, which is then modelled by the GB function. The second part reports the results obtained via computer simulation, and discusses possible improvements over this first, simple level of description provided by the GB potential.

INTERMOLECULAR POTENTIALS

The molecule is considered composed of a number of fragments which are the building blocks to be used to reconstruct the PES of the whole molecule. We want to develop a theoretical method which allows expressing the intermolecular interaction energy of the dimer as a sum of energy contributions from pairs of such fragments [6].

Decomposition Scheme

The choice of the molecular decomposition is led by the requirement that the ground state electronic density around the atoms of each fragment be as close as possible to that observed around the same group of atoms in the full molecule. This criterion may be verified by comparing the ground state equilibrium geometry of the isolated fragments with that observed in the molecule under study.

When applied to biphenyl, e.g., the above idea means that we can formally write the molecule as composed of two (equal) fragments A and B, as follows

$$A - B = AH_a + H_bB - H_a - H_b$$

where $A = B = C_6H_5$ and where the symbolic operators $+/-$ put in evidence the H atoms which disappear passing from the fragment sequence to the real whole molecule. Then H_a and H_b are the hydrogen atoms present in the two benzene molecules and absent in the biphenyl molecule, they will be called “intruder atoms”.

In both members of the above equation, the geometry of A and B coincides with the ground state equilibrium geometry of the biphenyl molecule, and the position of the “intruder atoms” is dictated by the spatial distribution of the atoms in the pertinent fragment. For instance the distance between the H_a and the nearest carbon atom of the benzene fragment is about 1.1 Å, as in the benzene ring.

According to Claverie [7], the interaction energy of a pair of molecules can be written, to a good approximation, as a sum of atom-atom interactions.

Therefore, the interaction energy between the AB molecule and a generic molecule X, is

$$E(AB \cdots X) = \left(\sum_{i}^{A} + \sum_{i}^{B} \right) \sum_{j}^{X} U(R_{ij}, Z_i, Z_j)$$

where the $U(R_{ij}, Z_i, Z_j)$ expresses the dependence of the atom-atom energy terms on both the internuclear distance R_{ij} and the atomic numbers Z_i and Z_j.

By the present approximation, the interaction energy of a biphenyl molecule, decomposed as described above, with a generic molecule X, may be written as

$$\begin{aligned}
&E([AH_a + H_bB - H_a - H_b]\cdots X)\\
&\quad = \left(\sum_i^{AH_a} + \sum_i^{H_bB}\right)\sum_j^{X} U(R_{ij}, Z_i, Z_j) - \sum_j^{X} U(R_{H_aj}, 1, Z_j) - \sum_j^{X} U(R_{H_bj}, 1, Z_j)\\
&\quad = E(AH_a\cdots X) + E(H_bB\cdots X) - E(H_a\cdots X) - E(H_b\cdots X)
\end{aligned}$$

This way, the full intermolecular potential is decomposed into a sum of interaction energies between the hydrogenated fragments (closed shell molecules) and the X molecule. To obtain the proper $AB\cdots X$ energy, the contribution of the intruder hydrogen atoms has to be removed. This formal decomposition of the interaction energy as suggested by Claverie [7], leads to obvious computational advantages. In fact this approximation requires the calculation of interaction energies of systems much smaller than the whole $AB\cdots X$ system.

The main conceptual problems in the present approach come from the contribution of the atoms involved in the linkage between the fragments in the full molecule and, in general, from the effects due to the linkage itself. From a physical viewpoint, if the A and B fragments are linked by a single σ bond, the effects of the *A-B* bond on X is considered equivalent to that of an *A-H* bond plus a *B-H* bond minus the contribution of two intruder hydrogen atoms. Moreover the spatial distribution of the group wavefunction of A is considered unaffected by the substitution of the H_a atom with the B fragment. Obviously the same has to be supposed for B.

In the case of biphenyl, as the two rings are far from being coplanar, this is expected to be verified also for the π cloud which accounts for a large part of the dispersion energy.

Using this approximation, we can write for the AB dimer

$$\begin{aligned}
E(AB\cdots A'B') &= E([AH_a + H_bB - H_a - H_b]\\
&\qquad \cdots [A'H'_a + H'_bB' - H'_a - H'_b])\\
&= E(AH_a\cdots A'H'_a) + E(AH_a\cdots H'_bB')\\
&\quad + E(H_bB\cdots A'H'_a) + E(H_bB\cdots H'_bB')\\
&\quad - E(AH_a\cdots H'_a) - E(AH_a\cdots H'_b)\\
&\quad - E(H_bB\cdots H'_a) - E(H_bB\cdots H'_b)\\
&\quad - E(H_a\cdots A'H'_a) - E(H_a\cdots H'_bB')\\
&\quad - E(H_b\cdots A'H'_a) - E(H_b\cdots H'_bB')\\
&\quad + E(H_a\cdots H'_a) + E(H_a\cdots H'_b)\\
&\quad + E(H_b\cdots H'_a) + E(H_b\cdots H'_b)
\end{aligned}$$

where the primes indicate the second *AB* molecule. In this case the interaction between all couples of intruder hydrogen atoms has to be added. It can be easily verified that, if N is the number of electrons of *AB*, the above expression for the interaction energy correctly includes N^2 interactions.

The above equation can be easily extended to three or more fragments without increasing the dimension of all the possible dimers whose contribution to the interaction energy has to be computed from quantum mechanical calculations.

In the case of p-phenyls, the above expression requires the *ab initio* calculations only for three pairs, i.e. benzene-benzene, benzene-H and H-H.

We notice that this is not just a reduction of computational effort, as it means that one can obtain an *ab initio* potential for molecules as large as p-quinquephenyl that cannot be tackled with a straightforward application of quantum mechanical methods.

Over 130 configurations have been selected to sample the benzene-benzene PES and the corresponding interaction energies evaluated within a second order perturbation theory in the supermolecular approach (see Ref [6] for details). The results obtained for the three pairs benzene-benzene, benzene-H and H-H, have been fitted with a combination of atom-atom functions $U(R_{ij}, Z_i, Z_j)$ including Coulombic, dispersion, Yukawa and Buckingham potentials cantered on the carbon nuclei as well as on extra sites to improve the overall agreement with the *ab-initio* data.

It is worth stressing that, at this stage, one can disregard any problem of computational convenience, as the resulting analytic potential is to be used once and for all to reconstruct the PES of the whole molecule, according to the procedure outlined above.

The accuracy of the reconstructed PES has been tested by comparison with two truly *ab-initio* interaction energies, calculated for the biphenyl dimer in its face-to-face configuration, with exactly the same quantum chemical machinery. As can be seen in Figure 1 there is a satisfactory agreement between the results.

Modelling the p-phenyls Potential

The availability of an analytical expression for the *ab-initio* PES reconstructed through the atom-atom functions has allowed us to generate a large data base of interaction energies ($>10^4$ values). These data can be used to parameterize the model that will be employed in the simulation. As stated in the Introduction, we chose a uniaxial single site Gay-Berne potential as the simplest description of the interaction of the p-phenyls.

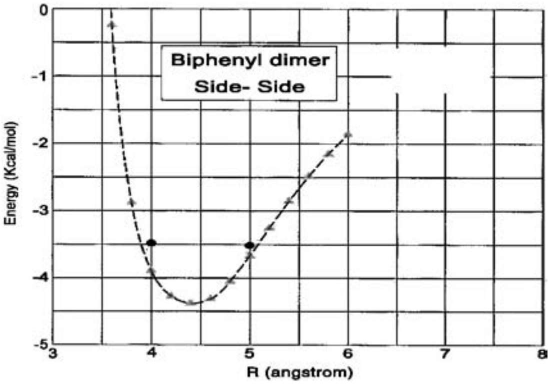

FIGURE 1 *Ab-initio* (dots) and reconstructed (curve with triangles) interaction energies of a biphenyl dimer in the side-by-side configuration.

This model can be considered as an extension of the Lennard-Jones potential to anisotropic interactions and its form is

$$U(\hat{u}_i,\hat{u}_j,\vec{r}) = 4\varepsilon(\hat{u}_i,\hat{u}_j,\hat{r})\left[\left(\frac{\xi\sigma_0}{r-\sigma(\hat{u}_i,\hat{u}_j,\hat{r})+\xi\sigma_0}\right)^{12} - \left(\frac{\xi\sigma_0}{r-\sigma(\hat{u}_i,\hat{u}_j,\hat{r})+\xi\sigma_0}\right)^{6}\right]$$

where the unit vectors $\hat{u}_i, \hat{u}_j$ define the orientation of particle i and j and the strength function is defined as follows

$$\varepsilon(\hat{u}_i,\hat{u}_j,\hat{r}) = \varepsilon_0\varepsilon^{\nu}\left(\hat{u}_i,\hat{u}_j\right)\cdot\varepsilon'^{\mu}(\hat{u}_i,\hat{u}_j,\hat{r})$$

with

$$\varepsilon(\hat{u}_i,\hat{u}_j) = \left[1-\chi^2\left(\hat{u}_i\cdot\hat{u}_j\right)\right]^{-1/2}$$

$$\chi = \frac{k^2-1}{k^2+1} \qquad k = \frac{\sigma_{ee}}{\sigma_{ss}}$$

$$\varepsilon'(\hat{u}_i,\hat{u}_j,\hat{r}) = 1 - \frac{\chi'}{2}\left(\frac{(\hat{u}_i\cdot\hat{r}+\hat{u}_j\cdot\hat{r})^2}{1+\chi'(\hat{u}_i\cdot\hat{u}_j)} + \frac{(\hat{u}_i\cdot\hat{r}-\hat{u}_j\cdot\hat{r})^2}{1+\chi'(\hat{u}_i\cdot\hat{u}_j)}\right)$$

$$\chi' = \frac{1-k'^{1/\mu}}{1+k'^{1/\mu}} \qquad k' = \frac{\varepsilon_{ee}}{\varepsilon_{ss}}$$

while the shape function is

$$\sigma(\hat{u}_i, \hat{u}_j, \hat{r}) = \sigma_0 \left[1 - \frac{\chi}{2} \left(\frac{(\hat{u}_i \cdot \hat{r} + \hat{u}_j \cdot \hat{r})^2}{1 + \chi(\hat{u}_i \cdot \hat{u}_j)} + \frac{(\hat{u}_i \cdot \hat{r} - \hat{u}_j \cdot \hat{r})^2}{1 + \chi(\hat{u}_i \cdot \hat{u}_j)} \right) \right]$$

while the parameter ξ has been introduced by Kabadi [8] to vary the width of the potential well.

As in the work by Luckhurst and Simmonds [5], we have to eliminate the biaxial nature of the PES of biphenyl. Rather than attempting a rotational average with Boltzmann weights, we carried out a sort of geometrical average as outlined below. Looking at a biphenyl molecule along its long (C_2) molecular axis, one can notice that the molecular section has an ellipsoidal envelope, because of the angle (~40°) between the ring planes. We modelled this shape as a circle with a diameter given by the geometrical average of the long and short axes of the ellipse. The latter are taken as the contact distance for molecules approaching each other in the face-to-face (3.48 Å) or side-by-side (6.13 Å) configuration. This diameter (4.62 Å) defines the σ_0 of the corresponding GB and is used to pick the curve that crosses the distance axis at σ_0, among that obtained at various angles of rotation around the C_2 (long) axis of one biphenyl, in the cross or side-by-side configuration. This way, also ε_0 and ε_{SS} are fixed as the well depth of this curve.

The same procedure readily yields σ and ε for the end-to-end configuration, while the corresponding parameters for the other basic configurations (T-shaped and cross) are obtained exploiting the relations provided by the analytic expression of the GB potential.

Repeating the whole process for the other p-phenyls we obtained the final set of optimized parameters collected in Table I.

As can be seen from this Table, along with the obvious increase of anisotropy along the series, measured by *k* and *k*', there is also a deeper well depth that moves to larger distances going from biphenyl to p-quinquephenyl. The value of the parameter ξ does not deviate much from one, especially for the longest molecule.

TABLE I Value of the Parameters of the GB Potential of Biphenyl (First Row) to p-quinquephenyl (Last Row), Obtained by a Fitting of the Reconstructed PES

k	k′	μ	ν	ξ
2.448	0.096	11.31	6.00	1.29
3.022	0.087	−12.0	0.87	1.10
3.736	0.062	−1.64	1.27	0.93
4.538	0.052	−2.94	1.02	0.99

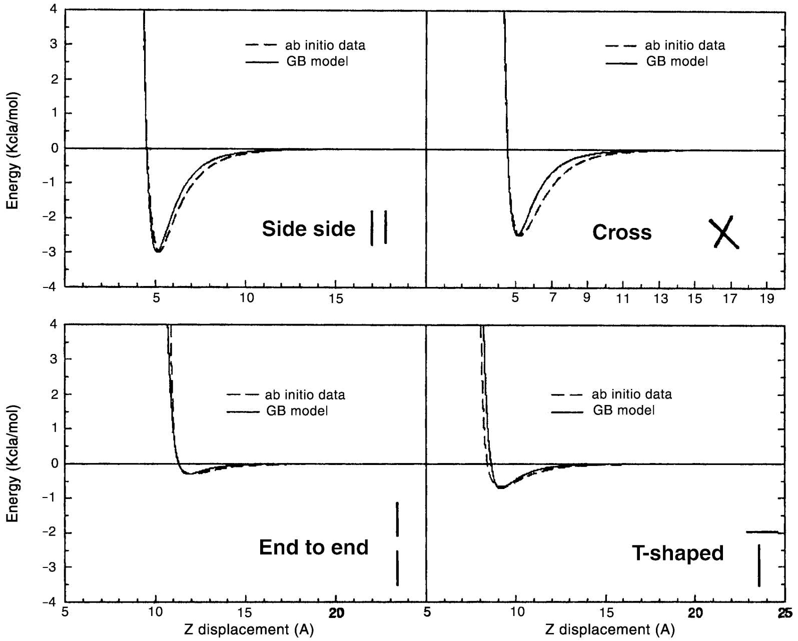

FIGURE 2 *Ab-initio* (dashed) and optimized Gay-Berne (full curve) interaction energy for four configurations of biphenyl.

A comparison of the *ab-initio* and GB results for the usual four 'basic' configurations of biphenyl is shown in Figure 2.

Essentially the same accuracy is achieved for the same geometrical arrangements of the longer p-phenyls.

RESULTS

Monte Carlo Simulations

A series of Monte Carlo simulations has been carried out in the isothermal-isobaric ensemble on a system composed of $N = 600$ GB particles. The temperature has been varied between 100 and 600 K in steps of 25 K, while the pressure has always been kept fixed at 1 atm as we wanted to test the possibility of the simple GB model under conditions close to the usual experimental ones.

At all temperatures, an ordered initial configuration has first been equilibrated for a number of cycles (i.e. N attempted particle moves plus an attempted volume move) large enough to guarantee elimination of any slow drift of the monitored properties. Then, the results have been averaged over an additional 10^5 cycles.

The final configuration at T = 500, 525, 550, 575 and 600 K has been used as a starting configuration for another series of MC simulations in the Gibbs ensemble [9] at the same temperature, aimed at calculating the critical temperature and density of this model.

In these runs, 25000 MC cycles (including particle swaps) have been carried out after equilibrating for 5000 cycles.

The results for density, enthalpy and second rank orientational order parameter (P_2) are shown in Figure 3 as a function of temperature. These functions have also been fitted with polynomials to obtain an estimate of the constant pressure heat capacity, C_P, and thermal expansivity, α.

Two transition temperatures can be identified in these plots, the first (360 K) marks the melting of the ordered solid phase to a dense disordered fluid, and the second (560 K) is the vaporization temperature of this GB model of biphenyl.

There is a fair agreement between MC and experimental values of transition temperatures, as can be seen in Table II, so that the range of stability of the liquid phase (200 K) is only slightly larger than that of the real biphenyl (184 K).

As for the enthalpy change at the transitions, the ΔH of melting is still acceptable while that of vaporization is largely underestimated. The same can be observed for the C_P values, where the error is larger in the liquid phase.

Density, as well as its temperature dependence, is close to the experimental data. This is reflected by the fairly good agreement of our results of expansivity with the measured data, again better for the solid than the liquid phase.

Finally, we obtain a critical temperature well below the experimental one, which suggests that the quantitative reproduction of the measured critical density is likely accidental.

From the set of results collected in Table II and plotted in Figure 3 we can conclude that the GB model of biphenyl, parameterized on the *ab-initio* PES, is able to describe the solid phase with a fair amount of realism. The quality of the GB description, however, significantly worsens for the liquid phase and for the transition to the gas phase.

This behaviour seems to indicate that our procedure to eliminate the biaxial nature of the PES of the n-phenyls is physically sound, but that the role of some important configurations for the liquid phase is somewhat underestimated by the GB model.

Among the latter, certainly the parallel-displaced is poorly described, as can be seen from the comparison shown in Figure 4. Presumably, their importance in stabilizing the liquid phase increases along the series of the

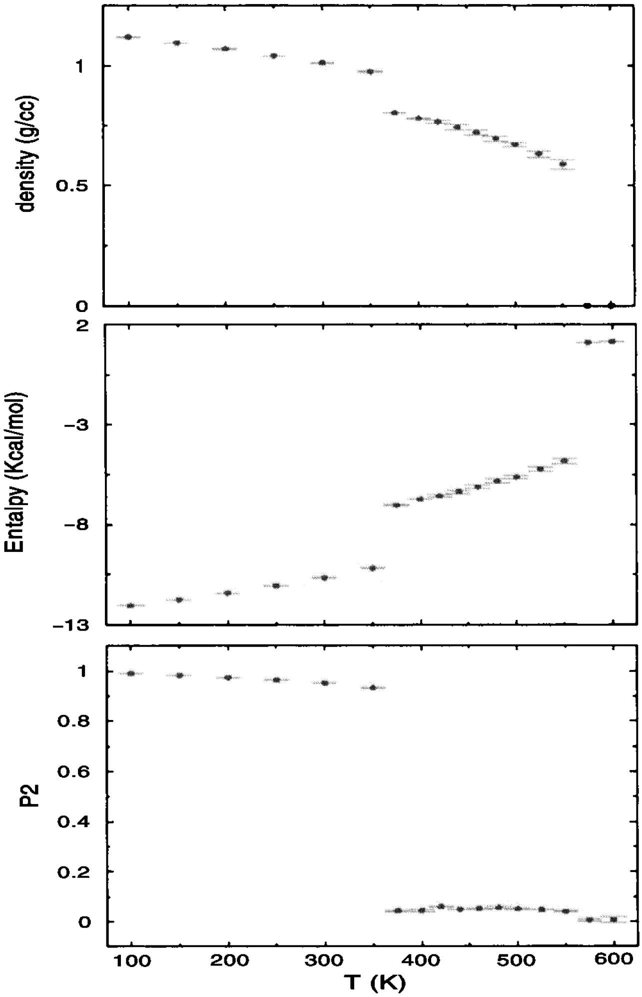

FIGURE 3 MC NPT results of density, enthalpy and orientational order parameter of biphenyl as a function of T.

n-phenyls. This interpretation is also supported by the failure of the GB model, with the parameters of Table I, to give a stable liquid phase for all n-phenyls longer than biphenyl.

In this case we have carried a less extensive series of NPT MC simulations than for biphenyl. The practical details are the same described above, except that a larger system (N = 2160) has also been employed in the

TABLE II Experimental and Calculated (GB model) Values of Some Thermodynamic Properties of Biphenyl

		MC NPT	EXP
T (K)	melt	360	343[a]
	vap	560	527[b]
$\Delta\mathrm{H}(\frac{Kcal}{mal})$	*melt*	2.9	4.4[c]
	vap	3.7	11.5[d]
$C_P(\frac{cal}{mol \cdot K})$	*sol*	7.4	47.4[c]
	liq	12.5	68.2[e]
$\alpha \times 10^3$ (K^{-1})	*sol*	0.53	0.77[a]
	liq	0.98[f]	1.08[f]
$\mathrm{T_c}$ (K)		601	773[b]
$\rho_c\left(\frac{g}{cm^3}\right)$		0.307	0.310[b]

[a] Ref. [10].

[b] Ref. [11].

[c] Ref. [12].

[d] Ref. [13].

[e] Ref. [14].

[f] T = 378 K, from experimental data of density *vs.* Temperature.

simulation of p-quinquephenyl, to test for possible size effects. However, a stable liquid phase was never obtained.

We can conclude that the simplest level of description of the *ab-initio* PES of the n-phenyls, namely the single site GB potential, does perform an

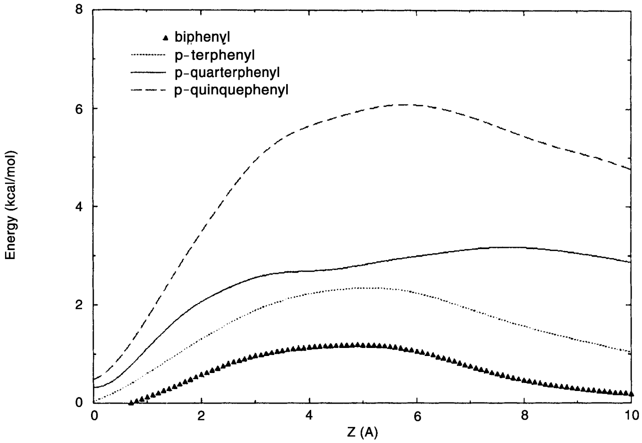

FIGURE 4 Difference between GB and *ab-initio* interaction energy for a pair of n-phenyls in the parallel-displaced configuration as a function of z. The two molecules are parallel to the y axis and 5.7 Å apart.

overall good job in the simulation of equilibrium properties of biphenyl under conditions relevant to the experimental work. There are however several drawbacks, more noticeably so in the representation of the liquid phase of biphenyl and especially of the longer n-phenyls, where this phase is missing.

We are currently pursuing some improvements of the GB model in the direction suggested by the results collected so far. In particular, we aim at a better description of the *ab-initio* PES using, e.g., GB sites for each phenyl ring of the molecule plus electric multipoles. This way, both the biaxial nature of the molecules and their torsional degrees of freedom could be taken into account leading, hopefully, to a closer agreement with the experimental data and to the observation of the nematic phase for the p-quinquephenyl.

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