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How the Odd-Even Effects on the Inter-Molecular Potentials Propagate to the Order Parameter in the 4-Cyano-4′n-Alkylbiphenyl Series

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How the Odd-Even Effects on the Inter-Molecular Potentials Propagate to the Order Parameter in the 4-Cyano-4′*n*-Alkylbiphenyl Series

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We present a study on the dimers of the 4-cyano, 4′n-alkyl biphenyl (nCB) aimed at capturing information connected to the measured odd-even effects on the meso-phase properties.

The interaction energy of dimers of the 4-cyano, 4′n-alkyl biphenyl (nCB) is computed by a model atomistic potential. The latter has been derived for the 5CB molecule by ab initio *calculations that include correlation energy, with an approach that has already provided accurate results. The analyzed inter-molecular energy profiles for selected parallel and antiparallel conformations along the nCB series (n = 5,6,7,8), present some features that might be at the root of the odd-even effect of this class of compounds. Preliminary molecular dynamics results yield a stable nematic phase for each homologue, whose computed order parameter show an evident odd even alternation, in good agreement with the experimental findings.*

Keywords: ab initio force-fields; condensed matter; liquid crystals; simulation methods

INTRODUCTION

The potential energy is the key quantity which embodies the chemical specificity of the single molecule and provides a link between the microscopic properties and macroscopic phase behaviour and stability,

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as obtained through bulk simulation methods like Molecular Dynamics (MD) and Monte Carlo (MC). The molecular potential is usually given by a simple sum of analytical atom-atom functions (the force field) whose derivatives are easily computed and implemented in the simulation program codes. For molecules without "soft" internal degrees of freedom, the standard intra-molecular part [1–4] is accurate enough in order to account for the phase stability, whereas the inter-molecular part is generally more sensible to the molecular details. In other words, the concept of transferability, which assumes that each atomic species in similar molecular environments takes identical terms in the force field, is generally more suited for the intra-molecular energy. Nevertheless, there are many cases in which transferability can be extended to the inter-molecular part of the force field with sufficient precision.

For molecules showing mesophases, the quality of the inter-molecular force field is very important, since the thermodynamic stability of the nematic or smectic phases often results from a delicate interplay between energetic and entropic contributions to the free energy. Moreover, the presence of aliphatic chains bonded to aromatic moieties in the monomer, can originate torsional potentials which require an accurate description of the energy profile [5,6]. For instance, it is well know, that in the 4-cyano, 4′*n*-pentylbiphenyl series the conformation of the aliphatic tails is different in going from crystalline to isotropic liquid phases [7–10].

In summary, whereas the rigid internal degrees of freedom can be confidently transferred from molecule to molecule, the transferability of both flexible internal and inter-molecular energy terms has to be used with caution in order to obtain accurate force fields.

In a previous article [11] we set up an atomistic inter-molecular force field for 5CB (4-cyano,4′*n*-pentyl biphenyl) derived by a comparison with Quantum Mechanical calculations performed through the Fragmentation Reconstruction Method (FRM) [12]. This method was devised in our group with the aim of computing intermolecular energies for large molecules and in particular was specifically designed for mesogenic molecules. In the present article we want to transfer that force field to the higher homologues of the nCB series with n = 6,7,8 and to study the intermolecular energy of some relevant dimer arrangements, in order to put in evidence some peculiarities that can be traced back to the odd-even effect.

The validation of this extension involves the study of the condensed phase properties of these systems through by very long MD simulations [13] that are currently under way.

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METHOD AND COMPUTATIONAL DETAILS

The FRM approach to the calculation of the inter-molecular energy of a dimer, is based on the assumption that each molecule can be fragmented in a number of moieties through a cut along some single bonds. The valence of the resulting fragments is then saturated by suitable "intruder" hydrogen atoms. The resulting formal molecule contains a number of closed shell overlapping molecules which are considered the basis entities of the inter-molecular energy, which can be expressed as a sum of contributions of all the resulting pairs of fragments. Obviously, the intruder atoms have to be subsequently cancelled from the molecule and their energy contribution properly subtracted in order to recover the correct interaction energy. For example, the A–B molecule may be split into $A–H_a + H_b–B$ fragments through a cut along the single A–B bond and then saturated with hydrogen atoms. Thus, the whole molecule can be formally written as

$$A–B = (A–H_a) + (H_b–B) – (H_a–H_b)$$

and the interaction energy between the dimer AB...AB is (the pedicels are omitted for brevity)

$$\begin{aligned} E(AB-AB) = {} & E(AH–AH) + E(HB–HB) \\ & + E(AH–HB) + E(HB–AH) \\ & - E(AH–H_2) - E(HB–H_2) \\ & - E(H_2–AH) - E(H_2–H_2) + E(H_2–H_2) \end{aligned}$$

For the nCB series (n = 5,6,7,8) the fragmentation scheme involves a cut along the inter-ring single bond and along the C(aromatic)-C (aliphatic) bond

$$\begin{aligned} nCB = {} & (NC - C_6H_5 - H_a) + (H_b - C_6H_4 - H_c) \\ & + (H_d - C_nH_{2n+1}) - (H_a - H_b) - (H_c - H_d) \end{aligned}$$

and the dimer interaction energy is reconstructed accordingly.

To account for the dispersion energy, which plays a crucial role in the description of van der Waals complexes, the correlation energy has to be included. FRM calculations are carried out at MP2 level of theory using a 6-31G* basis set in which polarization functions are more diffuse than the standard ones. The counterpoise correction scheme [14] was applied to all the computed energies in order to reduce the basis set superposition energy error.

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Calculations were carried out for the 5CB dimer for a large number of geometries and the resulting energy vs. geometry database was fitted with an atomistic force field of Amber type [1] with some modification of the Lennard-Jones functions [11]. The united atom (UA) approach, which allows us to save computational time, was restricted to the alkyl chain, whose methyl and methylene groups have been considered as single interaction sites. On the contrary, all aromatic hydrogens were taken into account for a total number of 27 interaction sites for 5CB. In order to facilitate transferability to longer nCB homologues, the three internal methylene groups of the chain were treated as equivalent UA's with no net charge. In this way the extension of the inter-molecular FF from 5CB to n-CB (n = 6, 7, 8) is straightforward, since the methylene group to be inserted take the same FF parameters as in the 5CB. Notice that this can be done with no additional MP2 calculation.

The intra-molecular FF is the same as Amber [1] with two relevant *ad hoc* differences concerning internal coordinates, whose value may be phase dependent, i.e., the value they assume does not necessarily match that found in the isolated molecule at the energy minimum energy. The inter-ring dihedral degree of freedom was parameterized on the basis of DFT calculations on the single 5CB molecule [15]. The rotation around the aliphatic C−C bond closest to the aromatic ring shows peculiar features that are hardly reproduced by the Amber FF. Indeed, due to the effects of the steric repulsion between the chain and the aromatic hydrogen atoms, a very high rotational barrier is obtained by DFT calculations [15], very different from the standard rotational curves in the aliphatic chains. The extension of this intra-molecular FF from 5CB to 6–8CB is even more straightforward, since the newly methylene groups can be equipped with the Amber force field with no further QM calculation.

The mechanical phase stability was checked by MD simulations carried out at constant pressure and several temperatures on systems of 192 nCB molecules. A positionally and orientationally ordered starting configuration was created for each homologue by replicating an antiparallel dimer arrangement 3, 4 and 4 times along the X, Y and Z directions, respectively. Long runs, ranging from 30 to 60 ns, have been performed to ensure reliable results, as the dynamics of these systems, monitored e.g., by the diffusion coefficients, is significantly slower than that of most molecular liquids under ordinary conditions.

All MD simulations were carried out with a parallel version of the suitably modified Moscito 3.9 package [11,16]. Temperature and pressure were kept constant using the weak coupling scheme of Berendsen *et al.* [17]. The short range intermolecular interactions have been truncated at $R_c = 10\,\text{Å}$, employing standard corrections for energy and virial [18]. Charge-charge long range interactions were treated

with the particle mesh Ewald (PME) method [19,20]. Since a timestep of 1 fs was used, bond lengths were fixed at their equilibrium value using the SHAKE algorithm [21].

The main order parameter P_2 was obtained by diagonalizing the Saupe ordering matrix $\mathbf{Q}$ defined [22] as

$$Q_{ij} = 1/2\langle(3u_i u_j - \delta_{ij})\rangle$$

where the mean value $\langle \ldots \rangle$ is obtained averaging on all molecules composing the system, and u (i, j = x, y, z) is the eigenvector corresponding to the minimum eigenvalue of the molecular inertia tensor, i.e., the principal axis. The maximum eigenvalue of $\mathbf{Q}$ is then taken to be the principal order parameter P_2, with the corresponding eigenvector representing the phase director $\mathbf{n}$. Another choice might have been to compute P_2 with respect of the more rigid part of the molecule, i.e., the cyanobiphenyl core. However, since no significant differences were found, all the reported P_2 refer to the former procedure.

RESULTS AND DISCUSSION

In a previous article [11], the absolute energy minimum of the 5CB dimer was found for a nearly slipped antiparallel conformation with the cyano group close to the internal ring (that bonded to the chain) and amounts to about -40 kJ/mol. Owing to the complexity and flexibility of the nCB molecules, many other relative energy minima were found for the 5CB dimer. In all the corresponding geometrical arrangements the aromatic core-core interactions play the main role, due to high polarizability of their π molecular orbitals. The aliphatic chain generally contributes less, although not negligibly, in the total binding energy. However, its flexibility is very important for the stability of the nematic phases, since the chain may be driven towards different favourable inter-molecular arrangements at a very low expense of internal conformational energy. Also, it was verified [15,23] that the all-trans conformation of the chain is the most populated in the nematic phase, and for this reason we will consider nCB dimers made by monomers in their elongated conformation.

In this article we are not interested in a general study of the relative energy minima of the nCB dimers. Rather, we will consider some of their conformations with the aim of analyzing the effects of adding methylene groups to the aliphatic chain, and in particular to discriminate between the member of the nCB series having an even or an odd number of aliphatic Carbon atoms.

The energy curves of the four nCB dimers (n = 5,6,7,8) for three significant parallel arrangements are displayed in Figures 1 and 2. In all

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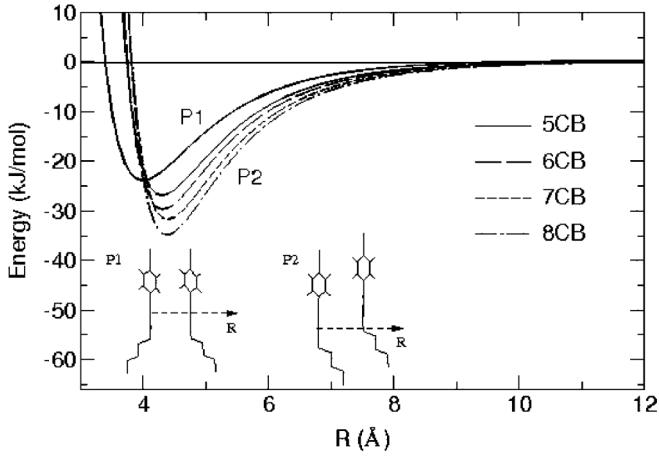

FIGURE 1 Energy curves for the P1 and P2 parallel conformations of nCB dimers. The dimer arrangements are displayed in the figure, together with the inter-molecular coordinate corresponding to the abscissa. In the P2 conformations the right molecule is shifted of 2 Å along the C_2 rotation axis of the cyano-biphenyl moiety. The chain sketched is that of 5CB.

figures the relative position of the two molecules is sketched and the inter-molecular coordinate corresponding to the abscissa axis is indicated in the molecular plots. In both Figures 1 and 2 the abscissa corresponds to the distance between the planes of the rings bonded to

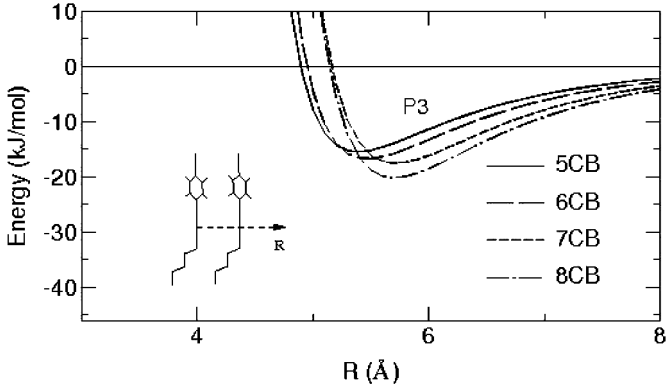

FIGURE 2 Energy curves for the P3 parallel conformations of nCB (n = 5, 6, 7, 8) dimers. The dimer arrangement is displayed in the figure for 5CB, together with the intermolecular coordinate corresponding to the abscissa.

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the aliphatic chain; which are parallel for all the P1, P2 and P3 arrangements.

The P1 curves refers to an arrangement where the chains play a negligible role and, as expected, do not indicate any relevant difference in the series, giving superimposed energy profiles. Nevertheless, the P1 curves allow us to evaluate the packing energy between the cores for parallel displacements also to be used for a comparison for the energy of the next geometrical arrangements.

In the arrangements that correspond to the P2 curves, the second molecule is shifted by 2 Å along the C_2 rotation axis of the cianobiphenyl moiety, and a translation along the C_6 rotation axis of the ring bonded to the chain defines the abscissa of Figure 1. The four P2 curves clearly show the differences in the attraction energy due to the different length of the chain. The interaction between the aliphatic moieties is emphasized by the "parallel" arrangement of the carbon chain, in which many methyl(ene)-methyl(ene) pairs contribute when the two molecules approach to each other. It is apparent that there is a monotonic increase of the binding energy between contiguous homologues, with smaller differences in the repulsive region. The net increase of the well depth in going from nCB to (n + 1) CB ($\sim$4 kJ/mol) can be mainly ascribed to the chain-chain interaction and could be roughly expected from simple considerations on the previously computed intermolecular energy of the pentane dimer. The energy minimum of the pentane dimer for the parallel conformation is about 6 kJ/mol, with both molecules in the elongated form. The number of methylene (methyl) pairs is 25 and a rough estimate of the energy contribution of each pair is $6/25 = 0.24$ kJ/mol. Since the number of new methylene-methylene interactions in going from nCB to (n + 1) CB is about 2n, the expected increase of attraction energy in the minimum is (0.24 kJ/mol)*2n which is close to the observed increase along the series (about 3 kJ/mol).

The P3 curves of Figure 2 correspond to a parallel translation along the C_6 rotation axis of the ring bonded to the chain with, unlike from the P2 arrangements, no other spatial operations. It is apparent that the difference between the 5CB and 6CB curves is similar to that between the 7CB and 8CB curves: an increase of the minimum energy of about 3 kJ/mol is observed with no relevant change in the position of the minimum. On the contrary, on going from 6CB to 7CB the minimum energy does not change appreciably but the minimum position is shifted of about 0.3 Å. The reason is related to the orientation of the terminal methyl group which is different for the odd and even members of the series. For 5CB and 7CB the threefold rotation axis of CH_3 is almost parallel to the long axis of the core, whereas for 6CB

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and 8CB it forms an angle of 120°. This feature, which is invoked in the rationalization of the odd-even effect for the clearing temperature in the nCB series, affects the binding energy of the P3 arrangements at small intermolecular distances and the differences between the curves of nCB and (n + 1)CB are different for n even or odd. The ultimate reason is found in the interaction between the last Carbon atom of the right molecule (Fig. 2) and the second last one of the left molecule. For even homologues, the (n + 1)CB atoms collide at a shorter distance and this leads to the shift of the whole curve to larger separations.

The energy curves of the four nCB dimers for three significant antiparallel arrangements (A1–A3) are displayed in Figures 3 and 4. For all the considered geometries, the abscissa corresponds to the distance between the planes of the parallel rings bonded to the aliphatic chain, followed by a rotation of one molecule of 180° around the C_6 axis of the ring bonded to the chain.

In the A1 geometries, as the aliphatic chains are well separated, no major differences appear between different homologues, being all curves almost superimposed, similarly to the P1 arrangements. From a comparison with the latter, the small shift (∼7 kJ/mol) of the well depth to more negative values can be ascribed to the antiparallel arrangement of the aromatic cyanobiphenyl cores.

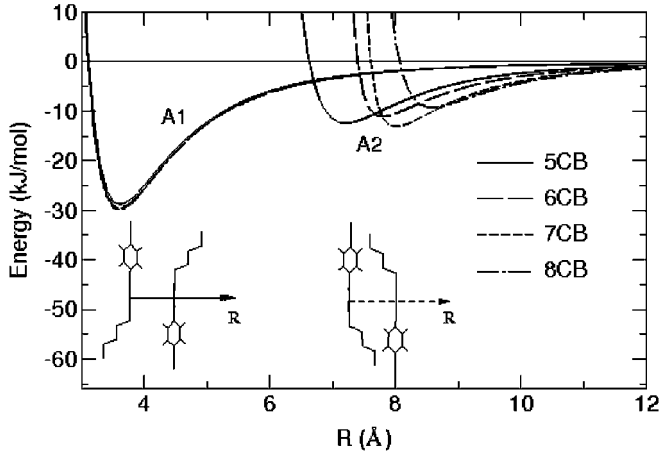

FIGURE 3 Energy curves for the A1 and A2 antiparallel conformations of nCB (n = 5, 6, 7, 8) dimers. The dimer arrangement is displayed in the figure, together with the intermolecular coordinate corresponding to the abscissa.

On the contrary, the A2 arrangements are obtained by rotating the second molecule around the centre of the internal ring in such a way that the two rings are again in a face-to-face relative position, but both aliphatic chains point toward each other, as shown in the Figure 3. The effect of the chain increase along the series, shown by the four A2 curves, may be related to the well known odd-even effect [10] on the clearing temperatures of the nCB. Indeed, whereas the energy minima are similar for all homologues, their position does not increase regularly and a smaller difference is apparent on going from 6CB to 7CB with respect to 5CB-6CB and 7CB-8CB.

Therefore, the increase of the colliding distance is evident for an addition of an odd methylene group, which makes the terminal methyl group to form a angle of 120° with the C_2 axis of the cyanobiphenyl moiety. In other words the addition of an odd methylene group increases the molecular length to breadth ratio more than the addition of an even one.

In the A3 arrangements of Figure 4, the rings bonded to the chain are parallel to each other and the terminal methyl group of one molecule is constrained to be on the C_6 axis of the corresponding ring of the other molecule. Therefore the shifting of the second molecule,

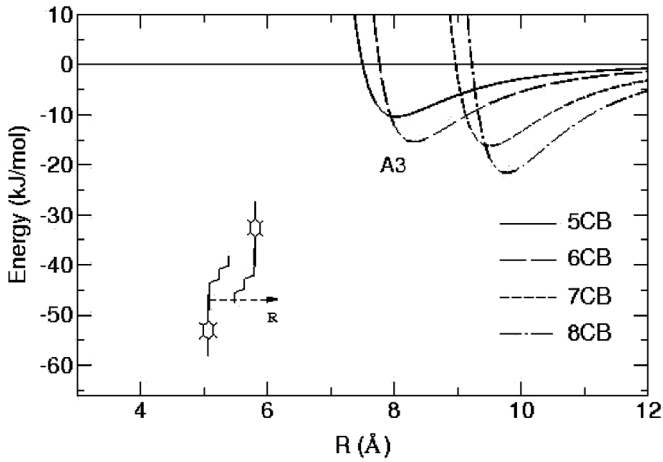

FIGURE 4 Energy curves for the A3 antiparallel arrangements of nCB (n = 5, 6, 7, 8) dimers. The dimer arrangement is displayed in the figure, together with the intermolecular coordinate corresponding to the abscissa. The rings bonded to the chain are parallel to each other and the terminal methyl group of one molecule points towards the barycentre of the ring of the other molecule for all members of the series.

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along the C_2 rotation axis of the cyanobiphenyl moiety, increases with n in the nCB series. In particular, according to the orientation of the methyl group for odd or even nCB, the increase corresponds to the length of an aliphatic C−C bond ($\sim$1.5 Å) for odd nCB's, and the half of this for even nCB's. This causes the colliding distance between the chains to vary in a different way depending on whether n is odd or even. For instance on going from 5CB to 6CB the colliding R value increases of about 0.3 Å whereas from 6CB to 7CB the increase is greater than 1 Å.

The lowering of the binding energy along the series arises from a combined effect of the chain-chain and of the methyl-ring interaction, and is the result of the different number of interacting atoms involved as well as of the shift of the energy minimum to larger distances. Therefore these combined effects lead to regular changes of the energy profile along the series on going from nCB to (n + 2) CB but not from nCB to (n + 1) CB. All in all, the A3 potential energy curves show a remarkable odd-even effect which, due to the large depth of the wells,

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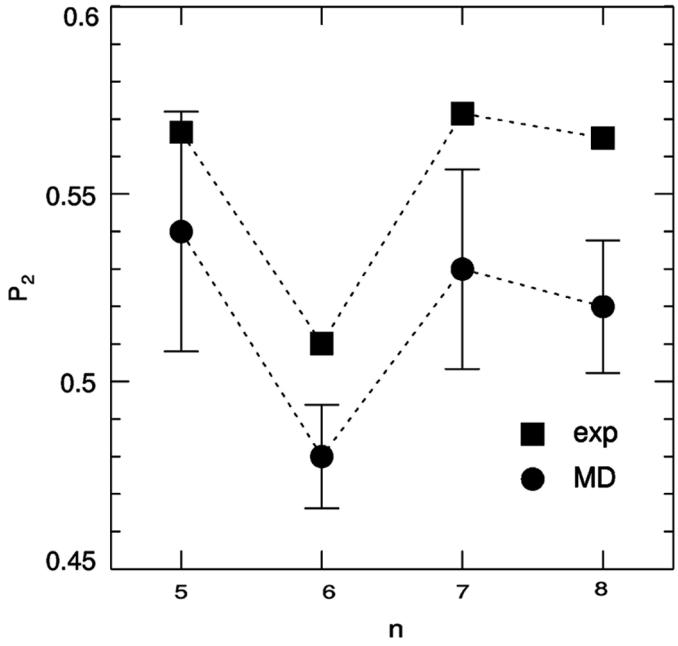

FIGURE 5 Comparison between experimental [23] and computed order parameter P_2 for the nCB series at atmospheric pressure and $T = 0.99T_{NI}$, where T_{NI} is the experimental clearing temperature [10].

is expected to affect to some extent the behaviour and the stability of the mesophase.

All the above considerations should be kept in mind when the results obtained by MD simulations on the condensed phases are examined. A property of particular interest for mesogens is obviously the orientational order parameter P_2, whose value is compared to the experimental data [23] for the nCB series in Figure 5. The MD data is obtained from NPT simulations at atmospheric pressure and at equal reduced temperature for the series. It is apparent that the odd-even effect is correctly accounted for by the model, although the single values appear slightly underestimated. It should also be noted that the simulation data are affected by an uncertainty of about 10%, despite runs which covered tens of nanoseconds in all cases. This error is however less than the difference between the P_2 values calculated along the series, so that the zig-zag trend can be considered a reliable result. This is particularly rewarding as the odd-even effect in the nCB series entails fairly small differences of clearing temperature, much smaller than in other systems, e.g., the aminocynamates [24].

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CONCLUSIONS

In this article we have showed and analyzed several dimer conformations of the nCB series. Even considering many other dimer arrangements, the effects of the differences in the attraction energy are hard to be translated into the difference of stability. However, we were able to put in evidence that the odd-even effects, found for the clearing temperatures of the nCB series, has a correspondence in some features of the energy curves. In particular, the addition of one methylene group has a different effect if it leads to an even or odd number of Carbon atoms in the aliphatic chain. Although no quantitative relation with the odd-even effect can be obtained by simple considerations on the energy curves, we feel that the observed microscopic features are connected with the macroscopic measurements of the thermodynamic parameters of the involved mesophases. It is clear that MD simulation, which probes the full accessible intermolecular potential energy of the dimers, is the appropriate way to find more significant links between microscopic and macroscopic properties of the systems of interest. Such a study is currently in progress in our laboratory [13].

REFERENCES

[1] Cornell, W. D., Cieplak, P., Bayly, C. I., Gould, I. R., Merz, K. M., Ferguson, D. M., Spellmeyer, D. C., Fox, T., Caldwell, J. W., & Kollmann, P. A. (1995). *J. Am. Chem. Soc.*, *117*, 5179.

[2] Jorgensen, W. L. & Tirado-Rives, J. (1988). *J. Phys. Chem. B*, *110*, 1657.
[3] Brooks, B. R., Bruccoeri, R. E., Olafson, B. D., States, D. J., Swaminanthan, S., & Karplus, M. (1983). *J. Comp. Chem.*, *4*, 187.
[4] Hermans, J., Berendsen, H. J. C., van Gusteren, W. F., & Postma, J. P. M. (1984). *Biopolymers*, *23*, 1.
[5] Adam, C. J., Clark, S. J., Wilson, M. R., Ackland, G. J., & Crain, J. (1998). *Mol. Phys.*, *93*, 947.
[6] Cheung, D. L., Clark, S. J., & Wilson, M. R. (2002). *Phys. Rev. E*, *65*, 051709.
[7] Hanemann, T., Haase, W., Svodoba, I., & Fuess, H. (1995). *Liq. Cryst.*, *19*, 699.
[8] Adam, C. J., Ferrarini, A., Wilson, M. R., Ackland, G. J., & Crain, J. (1999). *Mol. Phys.*, *97*, 541.
[9] Emsley, J. W., Luckhurst, G. R., & Stockley, C. P. (1982). *Proc. R. Soc. Lond. A*, *381*, 117.
[10] Gray, G. W. & Mosley, A. (1976). *J. Chem. Soc., Perkin Trans.*, *21*, 97.
[11] Bizzarri, M., Cacelli, I., Prampolini, G., & Tani, A. (2004). *J. Phys. Chem. A*, *108*, 10336.
[12] Amovilli, C., Cacelli, I., Campanile, S., & Prampolini, G. (2002). *J. Chem. Phys.*, *117*, 3003.
[13] Cacelli, I., De Gaetani, L., Prampolini, G., & Tani, A. (2007). in press.
[14] Boys, S. F. & Bernardi, F. (1970). *Mol. Phys.*, *19*, 553.
[15] Cacelli, I., Prampolini, G., & Tani, A. (2005). *J. Phys. Chem. B*, *109*, 3531.
[16] Paschen, D. & Geiger, A. (2000). *MOSCITO 3.9*, Department of Physical Chemistry: University of Dortmund.
[17] Berendsen, H. J. C., Postma, J. P. M., van Gusteren, W. F., Di Nola, A., & Haak, J. R. (1984). *J. Chem. Phys.*, *81*, 3684.
[18] Allen, M. P. & Tildesley, D. J. (1987). *Computer Simulation of Liquids*, Clarendon: Oxford.
[19] Darden, T. A., York, D., & Pedersen, L. (1993). *J. Chem. Phys.*, *98*, 10089.
[20] Essmann, U., Perera, L., Berkowitz, M. L., Darden, A., Lee, H., & Pedersen, L. (1995). *J. Chem. Phys.*, *103*, 8577.
[21] Ryckaert, J. P., Ciccotti, G., & Berendsen, H. J. C. (1977). *J. Comput. Phys.*, *55*, 3336.
[22] Luckhurst, G. R. & Veracini, C. A. (1994). *The Molecular Dynamics of Liquid Crystals*, NATO ASI series, Kluwer: Dordrecht.
[23] Kobinata, S., Kobayashi, T., Yoshida, H., Chandani, A. D. L., & Maeda, S. (1986). *J. Mol. Struct.*, *146*, 373.
[24] Berardi, R., Muccioli, L., & Zannoni, C. (2004). *Chem. Phys. Chem.*, *5*, 104.

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