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Twisted Nematics: Conformation of Chiral Dopants

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The conformational properties of binaphthol (BN) derivatives dissolved in a pentylcyanobiphenyl liquid crystalline (LC) matrix were determined by molecular dynamics (MD) simulation. Due to the influence of intermolecular interactions between the molecules of the LC matrix and the BN molecules, the conformations of the BN molecules in LC phase are found to change in the direction from transoid to cisoid on heating that results in decrease of observed helical twisting power (HTP). The changes of molecular conformation are mainly connected with orienting potential acting on solute molecule.

Keywords: Molecular dynamics; binaphthols; chirality; conformation

1. INTRODUCTION

The doped liquid crystalline systems attracted considerable attention during the last years. The experimental study of dopant orientation in different nematics with NMR or IR spectroscopy yields the information about intermolecular interactions if the appropriate model is chosen to analyse the results. The models are normally based on the mean field approximation. The more direct method of computer simulations of dopants in nematics using realistic atom-atom potentials is still very time consuming and,therefore, is applied rather rare. Just recently, new attempts were made to simulate the behaviour of dopants in nematic solutions [1–3]. In [1,2] the orientational order of benzene molecule was studied by molecular dynamics (MD) simulations with realistic atom-atom potentials. The behaviour of hexane molecule in a system of Gay-Berne molecules was studied in [3].

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The chiral dopants are of special interest in computer simulations because their conformation and ordering in nematics determine the pitch of observed helix and its temperature dependence. The pioneric work in this field was done by Allen [4]. The present work deals with recently synthesised class of chiral compounds [5,6]: open-chain binaphthyl-diethers (Fig1 a). In these compounds chirality originates from hindered rotation about single bonds (1,1′ -C-C) between the two naphthyl/naphthol moities that results in formation of conformationally stable optical antipodes: atropisomers. Binaphthyl derivatives (BN) have attracted attention in variety of applications because of their high twisting power, especially in biphenyl based LCs, and ability to undergo conformational changes [7,8].

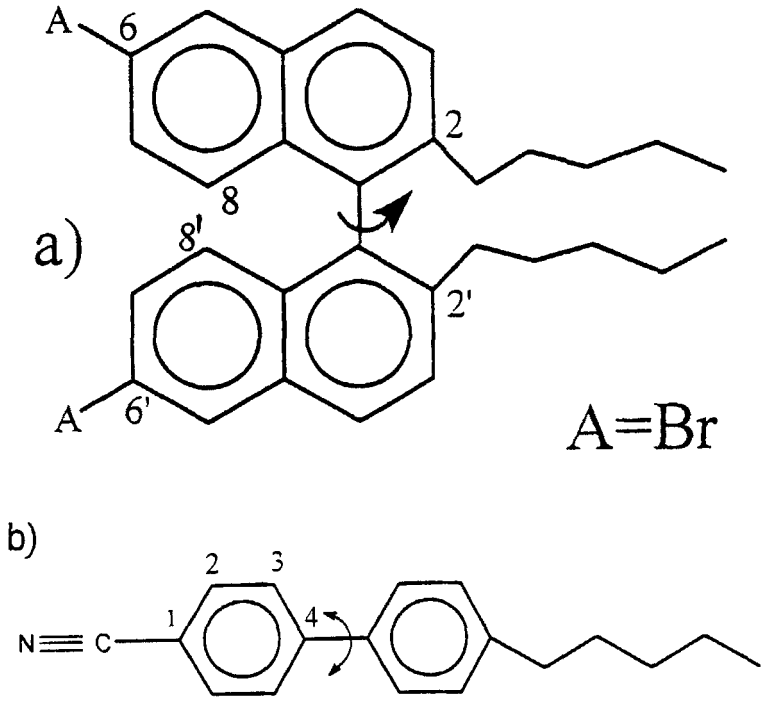

FIGURE 1 Structures of the open-chain binaphthol diethers and cyanobiphenyl (CB5) molecule

In [9,10] the high twisting power of the compounds was interpreted in terms of chirality transfer concept: correlations between solvent molecules and dopant lead to induction of the chirality with the same sign on the neighboring molecule.

This concept was firstly introduced by Gottarelli [10] for axially chiral biaryls dissolved in nematics of biphenyl type. It is well-known that pentylcyanobiphenyl molecules have the angle between benzene moities about $\theta = \pm 45°$. In fact, nematic based on cyanobiphenyl derivatives can become chiral if the population of two conformers with $\theta = -45°$, $\theta = +45°$ are not equal. It was assumed in [10] that presence of biaryls results in increasing concentration of molecules with certain sign of θ. The concept was never approved in direct experiments but got an indirect approvement in CD spectra measurements [11].

It was recently shown that the high HTP of BNs can be explained in the framework of shape model predicting crucial dependence of HTP on the angle between naphthalene moieties [12,13]. In accordance with [12,13], the maximum of HTP of unsubstituted BNs is theoretically predicted for a dihedral angle θ of 45° or 135°. The minimum of HTP is found for an angle θ of about 90°. It was proved in recent experiments [5,6] where bridged and open chain compounds were studied. The results revealed and described in [5] can be summarised as follows: bridged (type b) compounds have a high twisting power, whereas open-chain BN derivatives (type a) have smaller values of twisting power. HTP of BNs is increasing with increase of the length of the substituents in 6,6′- positions. The value of HTP seems to be dependent on the polarity and structure of the substituents but no evident correlation between polarity of the compound and HTP was found. The temperature dependencies of the HTP of the open (type a) and bridged (type b) BNs were found to be significantly different: The bridged compounds (type b) display slightly decreasing or constant HTP with increasing temperature, whereas the twisting power of unbridged compounds (type a) significantly decreases on heating [5].

Two different models are proposed to explain the temperature behaviour: The first one focuses on the influence of the shape of open-chain (type a) compounds. Since it is far from rod-like the expected HTP in a LC matrix is assumed to be very sensitive to temperature changes. Under increasing the temperature the order parameter of the dopant changes that leads to the change of HTP. As the molecule is assumed to be rigid, no internal degrees of freedom are considered. The second model which is confirmed by experimental results of optical rotation measurements takes conformational transformations of the molecule on heating into account [5] and relates conformation of BNs with changes of HTP.

The calculated internal potential of 1,1-binaphthyl given by MM2+ is very shallow in the region where the twist angle θ varies between 50° and 130°, showing that this molecule can twist very easily in this region by weak intramolecular interaction [14]. The calculated twist angle in the MM2+ approximation was found to be $\theta = 78°$, which is close to the angle in the racemic crystal taking into account that the conformation obtained from the solid state will be influenced by

packing effects [15]. Similar results were obtained by semiempirical methods and by tensor analysis of the first hyperpolarizability (for 6,6′-disubstituted BN derivatives) giving nearly perpendicular arrangements of the π -systems [16,17] for open-chain (type a) BNs.

Thus, the determination of the conformational properties of BN dopants in a LC matrix is an important step towards a better understanding of the nature of HTP behaviour of open-chain (type a) BNs and testing of the validity of existing theoretical models. The aim of this article is twofold: to study the preferable conformations of BNs by molecular dynamics (MD) simulations, both in vacuum and being dissolved in nematic LCs and to study intermolecular chirality transfer.

2. CONFORMATIONAL ANALYSIS IN VACUUM

As a BN derivatives we used Br-substituted compounds. The initial geometries were generated by building the fragments into a molecule using standard bond lengths and angles followed by minimizing the total energy of the molecule in vacuum. The molecular dynamic (MD) method applied has been revised recently [18]. In our calculations we used the BIOSYM package supplied with a Consistent Valence forcefield (CVFF). The parameters of this forcefield can be found in [19,20]. It is well-characterised and tested forcefield used to simulate organic molecules.

The following terms were considered in CVFF forcefield: (i) diagonal terms representing the energy of deformation of bond lengths, bond angles, torsion angles and out of plane interactions in a molecule, (ii) off- diagonal terms representing couplings between deformations of internal coordinates, (iii) non-bond terms describing interactions of chemically non-connected atoms.

The Discover-3 submodule of the BIOSYM package was used to perform the MD calculations.

In order to simplify the further analysis, we calculated the dependencies of the total energy of the open-chain (type a) BN molecule on the dihedral angle θ . There is one minimum for θ near 90° corresponding to almost perpendicular orientation of the two naphthyl moieties (Fig.2). The position of the minimum as well as the degree of assymetry of potential curve depend on the initial conformation of the molecule and the number of molecular fragments to be fixed. For example, if we constrain the conformation of alkyl chains the potential energy curve is almost symmetrical (Fig.2a). If we do not fix the geometry, then the potential energy curve becomes assymetrical (Fig.2b). Since the minimum is shallow it is difficult to determine if the molecule is in transoid or cisoid state. In

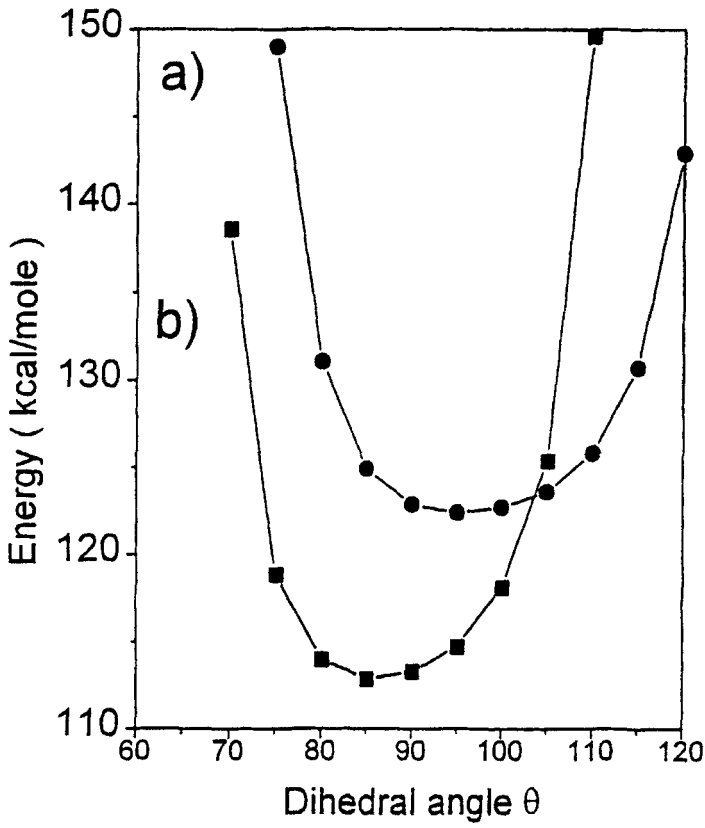

FIGURE 2 The energy of the molecule as a function of dihedral angle θ: a) fixed geometry of BN, b) non fixed geometry of BN

the interval of the dihedral angles θ=-60°...60° the potential is very flat that indicates it can be easily modified by external intermolecular interactions.

In order to span conformational space more efficient the MD runs of 10 initial conformers were performed. The total energy of the system was initially minimized as described above, then during first 300ps the system was equilibrated by running dynamics and kept at constant temperature for 1550ps. The calculated probability distribution function of finding molecule in certain conformation state is shown at Fig.3. It is easy to see that the maximum of probability distribution function shifts from lower angles ($\alpha < 90°$, cisoid conformation) to higher angles ($\alpha > 90°$, transoid conformation) with increasing the temperature.

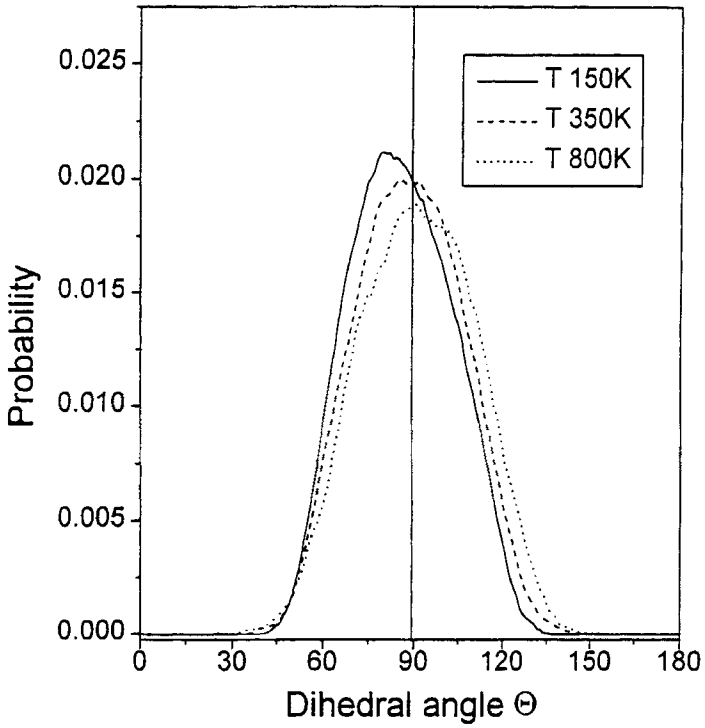

FIGURE 3 Distribution function of BN conformers (dihedral angle θ) calculated by MD in vacuum : a) at T=150K and b) T=350K c) T=800K

3. CONFORMATIONAL ANALYSIS IN LC STATE

A) Method of calculations

The MD simulations were performed for two types of system: LC cell containing only 113 4-cyano-4′-pentylbiphenyl molecules and LC cell containing 111 4-cyano-4′-pentylbiphenyl and two molecules of open-chain (type a) BNs. Periodic boundary conditions were applied, and NVT-ensemble was used. The atom-atom summation method of van-der-Waals interactions was used together with a cutoff distance of about 12Å. The choice of a cutoff distance of about 12 Å allows to calculate the molecular field acting on the solute molecule with reasonable accuracy (more than 85% of Van-der-Waals interactions). The 4-cyano-4′-pentylbiphenyl molecules were chosen to represent the nematic LCs which were used in our recent experiments [5] of HTP measurements. Both types

of LC cells were prepared for three different temperatures, T=280K, T=330K and T=360K (resembling the real temperature interval of the LC state of 4-cyano-4′-pentylbiphenyl). In order to simulate the change of the order parameter of the nematic phase for different temperatures, the longest axis of LC molecules was oriented along one of the axes of the cell and then while placing the molecules into the cell a special potential took care of the orientation of their axes in order to display a mesophase with a certain order parameter. The initial order parameters of the cell were established as 0.95 at 280K, 0.85 at 330K and 0 at 360K. The simulation box was choosen as rectangular parallelepiped with the longest axis about 1.5 longer than its width. The simulation box of practically the same size was recently used in [21] to study penthylcyanobiphenyl LC.

During computations the so-called SHAKE algorithm of constraining bond lengths. It was proven in a number of publications that this method permits at appropriate densities to use time step of about 1.8 fs. The equation of motion were integrated using the Verlet leapfrog algorithm. Basing on the data obtained in [22] the orientation of BN molecule was chosen in such a way that axis connecting two BN cores lies inside the cone angle forming by longest axis of cyanobiphenyl molecule and director. After molecules were put into the cell in accordance with initial order parameters the system was equilibrated during 400ps; the order parameters of the nematic and solute were rather stable during the following MD run. It is important to note here that it was not the aim of present study to investigate the behaviour of constituent LC molecules in details, but rather the behaviour of solute molecules. We believe that conformational changes of solute depends mainly on the orienting potential acting on it. It was stressed, for example in [3] where conformational properties of hexane molecule were studied in a liquid consisting of Gay-Berne particles and in [23] where the conformation of pentylcyanobiphenyl molecules itself has been studied by MC method. Nevertheless, in present study special care was taken to keep system in equilibrium conditions and to compare results obtained for equilibrated system with other available for penthylcyanobiphenyl [1,2,21,24].

In accordance with a number of studies [3,20] the conformation of solute molecule in LC matrix depends strongly on the orienting potential influenced by molecule. Such potentials depend mainly on the orientation of LC molecules. Obviously, the potential depending on the order parameter of the matrix is not the only one acting on the molecule in LC environment. The isotropic part of the potential acting on molecule in a matrix can also change dihedral angle distribution in comparison with that observed in vacuum. We checked this possibility by creating isotropic LC cell with BN molecules inside and study conformational changes under the heating in isotropic state..

B) System equilibration

The typical MD run was performed as follows: The total energy of the system was initially minimized as described above, then during first 400ps the system was equilibrated by running dynamics and kept at constant temperature and volume for 550ps. The total time used for MD was 950ps. It was shown in [21] that such a duration of MD run permits to reach equilibrium for a system of about 100 molecules.

The positional order in simulation box was also checked: in order to be sure that our system is nematic and not smectic state that may occur in MD simulations we have calculated the number density along the OZ direction of simulation box. The distribution was found to be very uniform for each particular configuration (Fig.4). The radial distribution function $g(r_{ij})$ also reflects positional order between sites *i* and*j* on different molecules. We have calculated this function for 4th carbon atom of aromatic ring in penthylcyanobiphenyl molecule. The distributions are similar and show a clear maximum at 5A (Fig.5). This is in agreement with the values derived from X-ray diffraction experiments giving 5A, but in disagreement with recent computations performed for penthylcyanobiphenyl [21]. To our opinion the source of disagreement is that united atom method employed in [21], in spite of its attraction from computational point of view, is not very accurate for distribution function calculations.

The nematic order parameter was calculated by using the formula

$$Q = \frac{1}{N}\sum_{j=1}(\frac{3}{2}n_j n_j - \frac{1}{2}) \qquad (1)$$

where n_j are the direction cosines between the longest molecular axes directed along the biphenyl core and OZ axes of the box. The time dependence of order parameter is shown at Fig.6. It is easy to see that after approximately 400ps the system reaches the state with practically constant order parameter. The same type of behaviour was revealed in [3]. Then MD runs and conformations of molecules are collected during 300ps. Each conformation is picked up after 90fs and averaged over four neighboring conformations. On the other hand, the limitation of computational time does not permit to explore the total phase space of the system. In order to take the effect of the centre of mass movement into account, we used 3 initial cells and then averaged the characteristics of them. In order to be sure that our system is not in a glassy state the diffusion coefficients were calculated for movements along D_{II} and across $D_{\perp}$ the director. The coefficients D_{II} and $D_{\perp}$ were found to be $3^{*}10^{-11}$ m^2/s and 10^{-11} m^2/s respectively. This result is in agreement with calculations performed in [21].

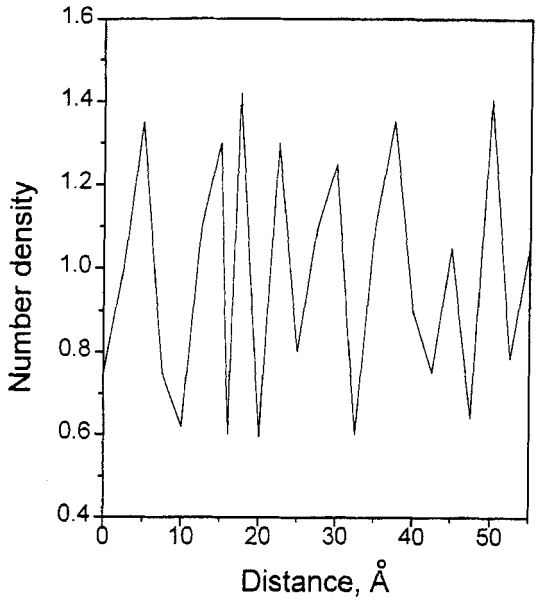

FIGURE 4 Snaphot of typical distribution density during MD run

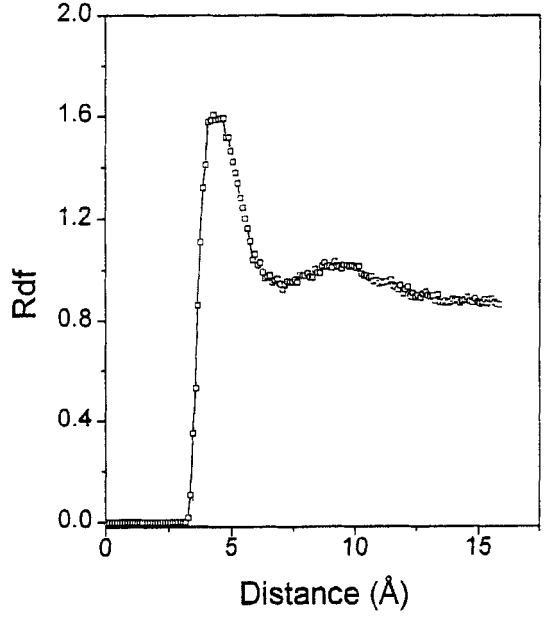

FIGURE 5 Radial distribution function

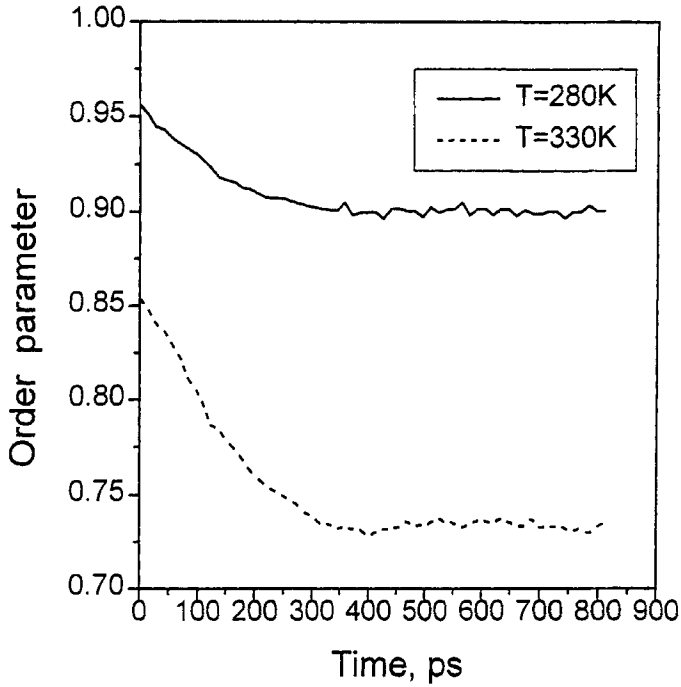

FIGURE 6 Time dependence of order parameter

C) Conformational analysis of BN molecule

In isotropic phase the conformation of BN molecule was found to be cisoid at T=360K.

In anisotropic LC state at lower temperature (T=280K) the preferable conformation of the open-chain BN molecule is transoid (Fig.7a). At higher temperature (T=330K) the preferable conformation of the molecule becomes cisoid (Fig.7b). This situation is quite different from the one observed in vacuum.This is the influence of intermolecular interactions which result in a preferable transoid state even at lower temperature. Thus, in the LC cell containing pentylcyanobiphenyl molecules there is a driving force towards the change of preferred conformation from transoid at lower temperature to cisoid at higher temperature. This driving force is obviously connected with degree of order in the system. The general trend in conformational changes in LC matrix is transformation from transoid to cisoid. These conformational changes are in accordance with our recent experimental findings [5]. In fact, the change of conformation from tran-

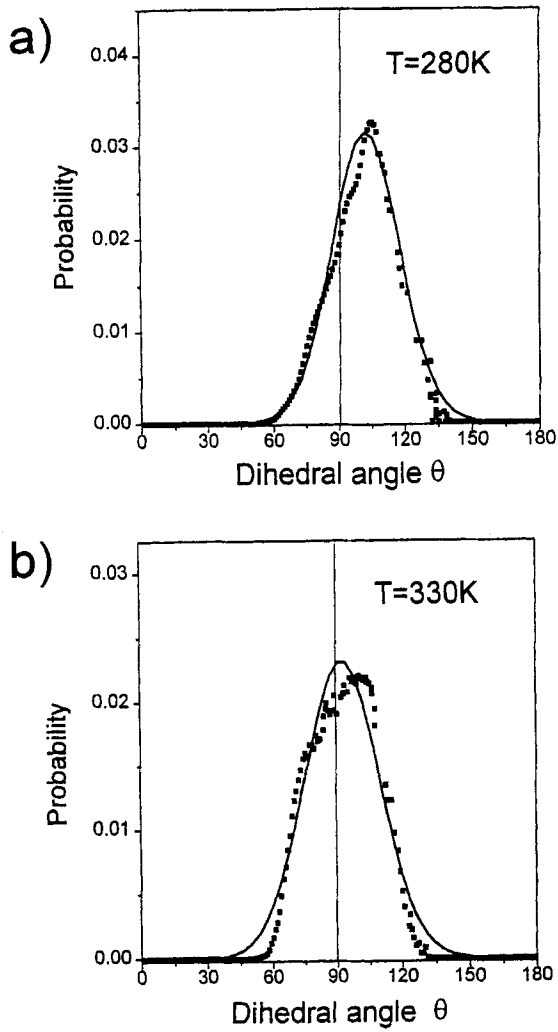

FIGURE 7 Distribution function of BN conformers (dihedral angle θ) calculated by MD in LC cell a) at T=280K and b) T=330K

soid to cisoid was supposed to be responsible for the decrease of HTP of open-chain (type a) BNs dissolved in the nematic LC host1277 (NIOPIK) consisting mainly of cyanobiphenyl derivatives [5]. The experimentally observed slope of HTP vs. temperature was determined to be $\frac{1}{\beta}\frac{d\beta}{dT} = 0.0125K^{-1}$.

The HTP of other binaphthol derivatives was shown to be dependent on temperature too. In case of assymetrically substituted binaphthols it may even change sign with increasing the temperature [25]. In [25] the temperature dependence and inversion of HTP were explained in terms of two-conformation model. No suggestions about the structure of conformers were made. In calculations performed by Ferrarini [12, 13, 26], the value of HTP was shown to be minimal at $\alpha = 90°$. If we assume that at $\alpha = 90°$ the HTP is equal to zero and, cisoid and transoid BN conformers produce helical twist of opposite sign and almost equal absolute value if the angle θ between naphthyl moieties is close to 90°, it becomes possible to estimate the changes of HTP basing on the MD calculations performed. Following the model developed by Ferrarini *et.al*in [12, 13, 22, 26], we can adopt the view here, that the total occupancy of transoid and cisoid states of BN approximately compensates each other in sense of the resulting HTP. If we assume that the HTP is proportional to the net difference in occupancy between cisoid and transoid conformers, it is possible to calculate the respective HTP by integrating the probability function for cisoid and transoid regions followed by subtraction. Assuming a linear dependence of HTP from the temperature, we get a slope of $\frac{1}{\beta}\frac{d\beta}{dT} = 0.0129K^{-1}$. Taking the approximate nature of interatomic potentials used as well as the error introduced by considering of only limited number of configurations in LC cell into account, this agreement between calculated and experimental observed slope is reasonable good.

Our calculations show that population of cisoid and transoid conformers may be responsible for observed changes of sign of HTP.

The effect of intermolecular transfer of chirality firstly introduced by Gottarelly, i.e. the transmission of chirality from the guest molecule to the LC host system was studied by picking up the penthylcyanobiphenyl molecules which are the nearest neighbours of BN molecule and calculating their conformation over the time when they are neighbours of BN molecule. The only nearest neighbours were picked up because it was expected that they are influenced by BN molecule more than all others. The conformation of LC molecules in a system with high concentration of dopants was compared with conformation of LC molecules in pure LC system. It was found that the distributions of dihedral angle round 35 degrees were almost identical. The results are presented at Fig.8. There is a slight excess of left handed conformers in comparison with right hand ones but this excess is lying within the estimated error interval.

Thus there is no evidence that chirality transfer mechanism play a significant role in cholesteric phase induction at least for the open-chain BN-penthylcyanobiphenyl. Of course, we should analyse results with certain care taking into acount small size of system and limited time of calculations. The BN molecule

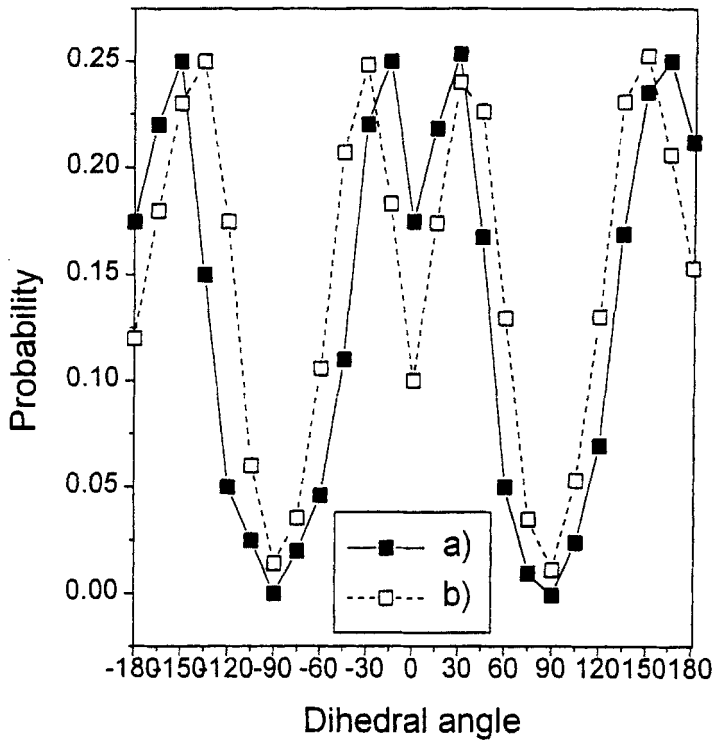

FIGURE 8 Distribution function for pentylcyanobiphenyl molecule in (a) a whole LC cell (b) near BN molecule

undergoes conformational changes around θ=90° where its degree of chirality is minimal and, therefore, surrounding BN molecules can effectively feel the only averaged chirality which is small. The chirality inducing in penthylcyanobiphenyls by open-chain BNs can be rather low and can not be detected with reasonable accuracy during MD run. The more precise technique is needed to feel such small changes or much longer computational times which could be achieved in simulation of model systems. The current studies are now in progress.

6. CONCLUSIONS

The MD simulations of BNs dissolved in penthylcyanobiphenyl LC was performed. For the best of our knowledge it is the longest simulation performed for

real system with full details of intermolecular interactions. The main results of simulation were compared with those of other simulations of real LC molecules. It was shown that full atomic description of molecules makes results closer to experiment in comparison with commonly used combined atom approach. The MD simulations performed show the changes of molecular conformation of BNs on heating.These changes were found to be responsible for the decrease of HTP observed experimentally.

The intermolecular chirality transfer to the host molecules was not identified for the system penthylcyanobiphenyl-BN. Such kind of chirality transfer was found in calculations of a system of chiral Gay-Berne particles with embedded nonchiral rotators [27]. It is clear that in that case the effect of chirality transfer was significantly enlarged. Moreover, it was pointed out in [27] that excess of rotamers has its maximum value at a dihedral angle close to the selected dihedral angle of the chiral dopant. It is not the case in a system BN-penthylcyanobiphenyl where dopant angle is close to θ=90° and the stable angle of stable conformer is close to θ=35°. Of course, all the restrictions caused by small system size and limited time of simulations should also be taken into account when analysing results.

Acknowledgements

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