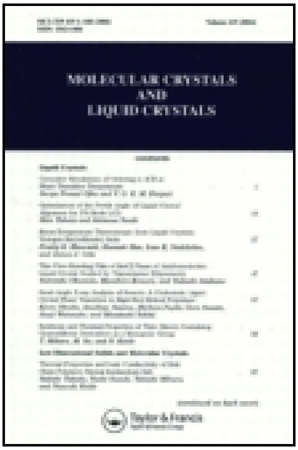

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Ordering in Homologous Series of 4-Cyano-4′-Alkylbiphenyls(*n*CB)—A Statistical Study

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A comparative study of molecular ordering in three homologous series of 4-cyano-4′-alkylbiphenyls **(*n*CB)** with alkyl groups pentyl **(5CB)**, hexyl **(6CB)**, and heptyl **(7CB)** have been carried out with respect to translatory and orientational motions. The **CNDO/2** method has been employed to evaluate the net atomic charge and atomic dipole components at each atomic center of the molecule. Modified Rayleigh-Schrodinger perturbation theory along with multicentered-multipole expansion method has been employed to evaluate the long-range intermolecular interactions, while a *6-exp* potential function has been assumed for short-range interactions. The total interaction energy values obtained through these computations were used to calculate the probability of each configuration at room temperature using Maxwell-Boltzmann formula. On the basis of stacking, in-plane, and terminal interaction energy calculations, all possible geometrical arrangements of molecular pair have been considered, and the most favorable configuration of pairing has been obtained among the compounds. An attempt has been made to develop a molecular model for liquid crystalline molecules.

Keywords: *n*CB, liquid crystal, quantum chemistry, computer simulation

INTRODUCTION

Liquid crystal phases are characterized by their long-range orientational order. There have been many attempts to measure this property and to explain it in terms of the behavior and structure of the molecules [1,2]. In recent years there has been increasing interest in stable phases mediating the transition between different liquid crystalline phases [3–7]. Further,

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computer speed has led to the use of computer simulation as a tool for understanding liquid crystal phases [8–13]. However, it is essential to study simple models in some depth in order to understand the forces responsible for mesophase formation. The possibility also exists of extending these simple models by building in realistic features such as molecular flexibility, complicated structural anisotropy, and electrostatic forces.

The characteristics of mesomorphic behavior, which occur at phase transitions, are primarily governed by the intermolecular interactions acting between sides, planes, and ends of a pair of molecules [14–17]. The melting point, the temperature at which an ordered geometrical arrangement collapses and gives rise to the disordered isotropic melt, depends to very large extent on the nature of intermolecular interaction existing within the system. Since mesogenic properties are related to molecular aggregation in a specific manner, probability calculations based on interaction energy results will provide information regarding the most probable molecular aggregation. It therefore seems important to investigate the relative freedom of the molecules to depart from the minimum energy configuration in terms of (1) variation in orientation and (2) translation along the long molecular axis. Through these computations one is able to obtain information of dimer complex, the relative freedom of a molecule in terms of variations in inclination, separation, or sliding of one molecule over the other, etc.

In the present paper, an attempt has been made to identify the characteristic features of nematogens in terms of configurational probabilities based on intermolecular interaction energy calculation of three homologous series of 4-cyano-4′-alkylbiphenyls **(*n*CB)** with alkyl group: pentyl **(5CB)**, hexyl **(6CB)**, and heptyl **(7CB)** molecules at an intermediate distance for stacking, in-plane, and terminal interactions. The choice of the distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the short and medium range interactions.

COMPUTATIONAL DETAILS

The molecular geometry of ***n*CB** ($n = 5$, 6, and 7) has been constructed on the basis of the published crystallographic data with standard values of bond lengths and bond angles [18].

The computations have been carried out in two parts.

1. The **CNDO/2** method [19] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule. According to the second order pertubation theory as modified for

intermediate-range interactions [20], the total interaction energy (E_{total}) between a pair molecule is given by

$$E_{total} = E_{el} + E_{pol} + E_{disp} + E_{rep},$$

where E_{el}, E_{pol}, E_{disp}, and E_{rep} respectively, represent the electrostatic, polarization, dispersion, and repulsion components.

Again, electrostatic term is expressed as

$$E_{el} = E_{QQ} + E_{QMI} + E_{MIMI} + \cdots,$$

where E_{QQ}, E_{QMI}, and E_{MIMI}, etc. are monopole-monopole, monopole-dipole, and dipole-dipole, etc. terms, respectively. In fact, the inclusion of higher order multipoles does not affect significantly the electrostatic interaction energy and the calculation gives satisfactory result only up to dipole-dipole term [21]. The computation of electrostatic term has, therefore, been restricted only up to dipole-dipole energy term. The necessary formulae may be found elsewhere [22].

In this case, the origin on an atom has been chosen close to the center of mass of the molecule. The X-axis has been chosen along the long molecular axis, while the Y-axis lies in the plane of the molecule and Z-axis perpendicular to the molecular plane.

2. The total interaction energy values obtained by these computations were used as input to calculate the intrinsic probability of each configuration with the help of the Maxwell-Boltzmann formula [22]:

$$P_i = \exp(-\beta\varepsilon_i) / \sum_{i} \exp(-\beta\varepsilon_i); \quad \beta = 1/kT,$$

where P_i is the probability of a particular configuration and ε_i the energy of configuration i relative to the minimum energy configuration.

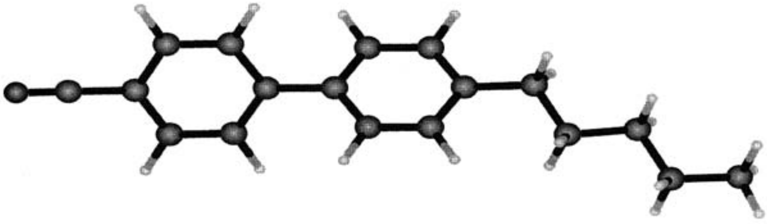
RESULTS AND DISCUSSION

The molecular geometry of *n***CB** is shown in Figure 1. Table 1 presents a comparative picture of the total energy, binding energy, and the total dipole moments of **5CB**, **6CB**, and **7CB**. As is evident from Table 1, the total energy and binding energy of these nematogens magnitude-wise exhibit the following order:

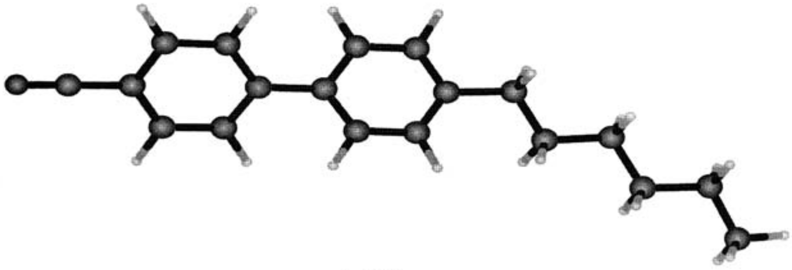
$$\mathbf{7CB} > \mathbf{6CB} > \mathbf{5CB},$$

while the dipole moments are

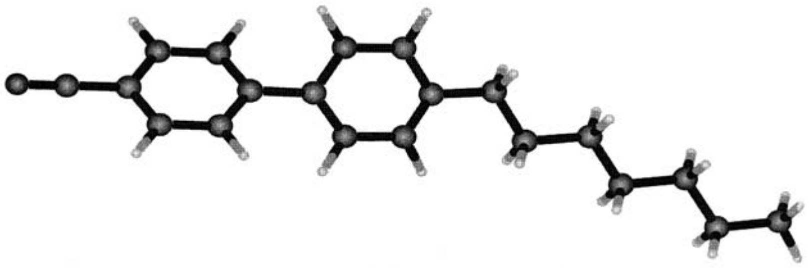
$$\mathbf{6CB} > \mathbf{7CB} > \mathbf{5CB}.$$



a. 5CB



b. 6CB



c. 7CB

FIGURE 1 Molecular geometry of ***n*CB** molecules.

The results of probability distribution corresponding to different modes of interactions are discussed below.

Figure 2 shows the variation of probability with respect to rotation about X-axis during stacking interactions. A maximum in the probability is observed near the equilibrium position. Further, it may be observed that the rotational rigidity about the long molecular axis indicates a strong binding at low temperature. With the increase of temperature the molecules obtain sufficient freedom to rotate about the long molecular axis. Having refined

TABLE 1 Total energy, binding energy, and total dipole moment of the homologues of ***n*CB** molecule

Molecule	*Total energy** *(a.m.u.)*	*Binding energy*** *(a.m.u.)*	*Total dipole moment* *(Debyes)*
4-cyano-4′-pentylbiphenyl **(5CB)**	−154.03	−19.85	2.58
4-cyano-4′-hexylbiphenyl **(6CB)**	−162.72	−21.09	2.65
4-cyano-4′-heptylbiphenyl **(7CB)**	−171.42	−22.35	2.64

*Total energy corresponds to the sum of atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

**Binding energy of a molecule is the difference between the total energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms.

the interacting configuration with respect to translation along Z-axis and rotation about Z-axis at the equilibrium position, the energy is brought down and the probability is further investigated with respect to translation along the X-axis (Figure 3). Sharp maxima corresponding to the minimum energy point with more than 20% probability occurs for **5CB** at room temperature (300 K). The variation of probability is almost constant for region −1.4 Å ± 0.4 Å, which shows that a sliding of one molecule over the other is energetically allowed for a small range. It may be correlated with the fluidity of compound maintains its alignment in the mesophase.

Again, similar calculations have been performed for in-plane interactions at an intermediate separation. Figure 4 shows the results corresponding to

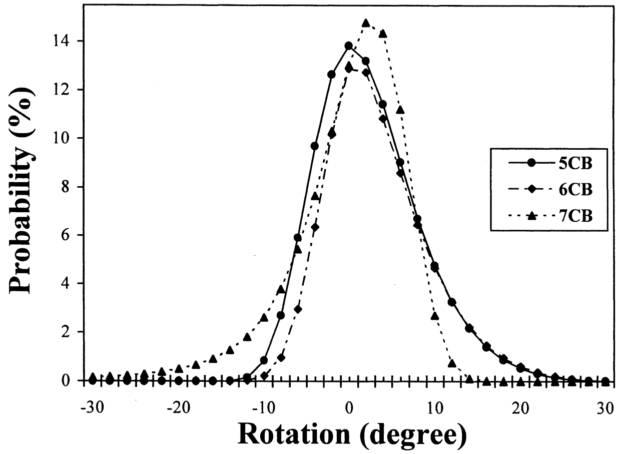


FIGURE 2 Variation of probability with respect to rotation about X-axis during stacking interactions at room temperature (300 K).

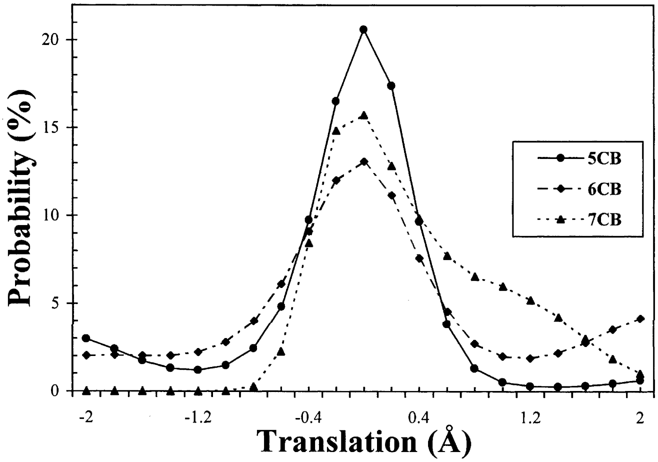


FIGURE 3 Variation of probability with respect to translation along X-axis during stacking interactions at room temperature (300 K).

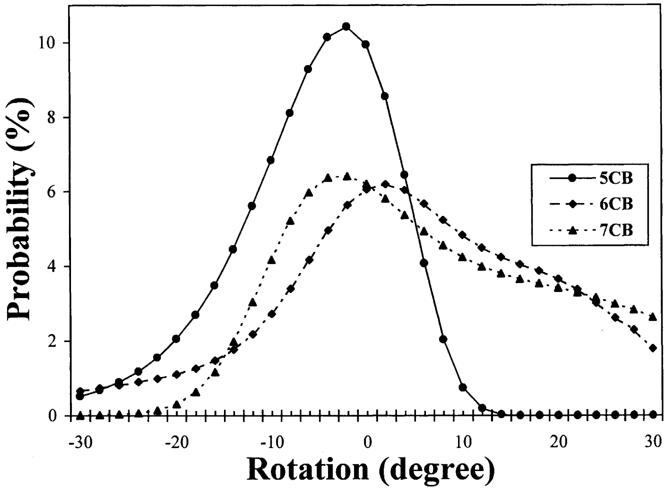


FIGURE 4 Variation of probability with respect to rotation about X-axis during in-plane interactions at room temperature (300 K).

the rotation about X-axis during in-plane interactions. It is clear that there is no drastic preference for the aligned structure; the smooth rise near the equilibrium position indicates the existence of an aligned structure at low temperature when the thermal agitation does not drastically disturb the molecular alignment. Figure 5 shows the results with respect to translation along the long molecular axis. It may be observed that the translational freedom is much more pronounced than the stacking interactions.

Terminal interactions are much weaker as compared to stacking or in-plane interactions. Figure 6 shows the results of rotations about X-axis. In this case molecules are completely free to rotate about their long molecular axis. A further maximum of probability is observed to various inclinations for **5CB**, **6CB**, and **7CB**. It is also clear that the lowering of terminal interaction energy (maximum of probability) for **7CB** is partially due to dimer energy and also due to the increased interactions between alkyl chains.

The most prominent energy minimum of the above-mentioned interactions are further refined with an accuracy of 0.1 Å in translation and 1° in rotation. It has been observed that the refined corresponding to stacking energy is maximum, and the ultimate magnitude of the stacking energy is larger than the in-plane and terminal interaction energy. Further, all possible geometrical arrangements between a molecular pair of **5CB**, **6CB**, and **7CB** molecules have been considered during stacking, in-plane, and terminal interactions and provide an insight of molecular arrangements inside bulk materials. The most favorable stacked configuration of pairing has been obtained among the compounds (**5CB**, **6CB**, and **7CB**) for **6CB** at an interplanar separation of 3.79 Å with energy −12.64 kcal/mole (Figure 7).

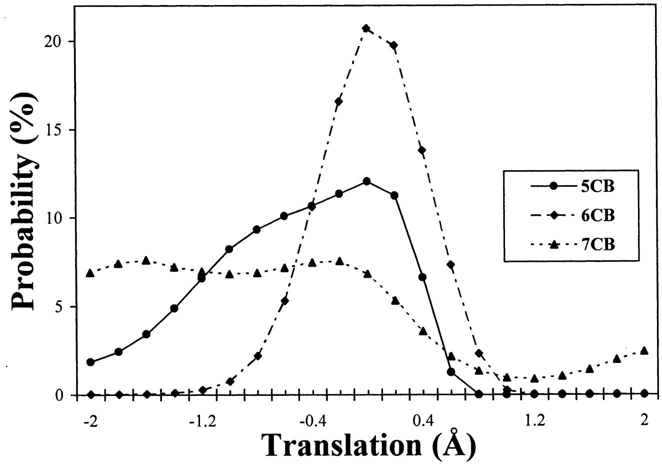


FIGURE 5 Variation of probability with respect to translation along X-axis during in-plane interactions at room temperature (300 K).

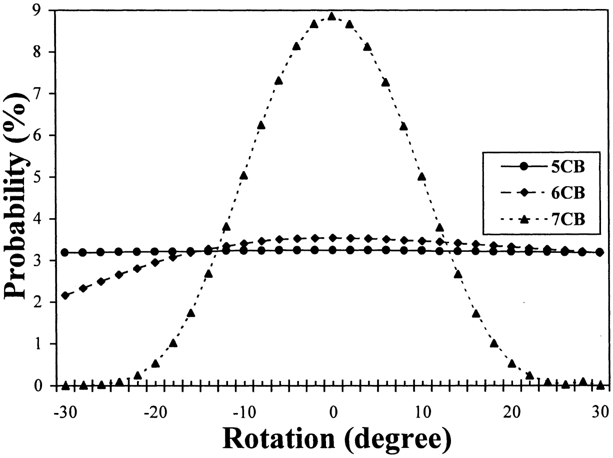


FIGURE 6 Variation of probability with respect to rotation about X-axis during terminal interactions at room temperature (300 K).

Thus in a molecular assembly a number of local minimum energy configuration exists; all of them have their own importance. As in the case of close molecular packing, any molecule, depending on its own spatial position may be forced to assume a local minimum energy configuration. The global minimum is, however, of paramount importance because while coming down from a very high temperature when the molecules have a complete disorder distribution, the global minimum has the maximum probability of occupancy and the other minima have sequential preference depending on their individual relative probability.

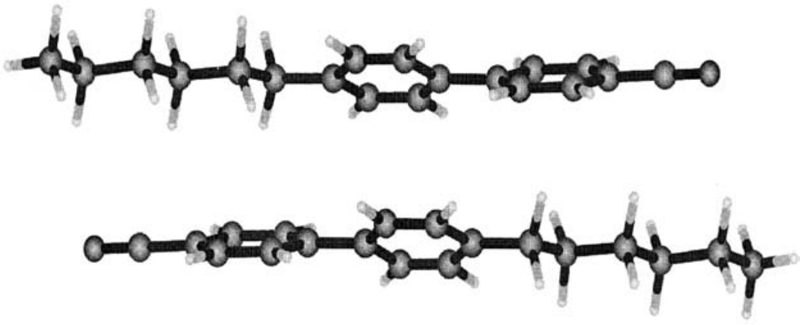


FIGURE 7 The most favorable stacked configuration among the compounds obtained for 6CB at an interplanar separation of 3.79 Å with energy −12.64 kcal/mole.

EFFECT OF TRANSLATION

The nematic character of liquid crystals is generally manifested by its translational freedom along the long molecular axis. Therefore, for stacked and in-plane interactions, the changes in probabilities for translations at interval of 0.2 Å are reported.

Figure 3 shows the results obtained for stacking interactions. It may be observed that stacking interactions have lesser translational freedom. The ratio of probability being at the maximum probable point to having ±0.2 Å displacement along the long molecular axis is 0.52 at room temperature (300 K), but with the increase of temperature the molecules obtain sufficient freedom to slide along the long molecular axis. Such translational freedom is much more pronounced in planar interactions. It may be noted that (see Figure 5) although the freedom is considerable for smaller translation, longer translations are not in general permitted. Thus, small movements of the molecules are only possible in the mesomorphic range. However, the comparable values in both cases (i.e., stacking and in-plane interactions) show that the molecules do not show extraordinary preference in forming stacked layers, hence justifying the nematic character.

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