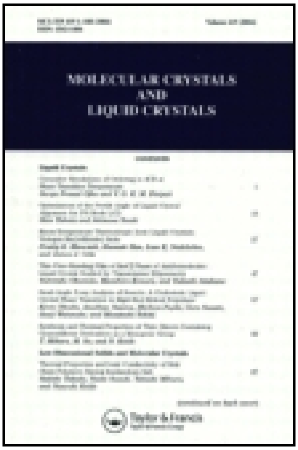

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COMPUTER SIMULATIONS OF MOLECULAR ORDERING IN DISUBSTITUTED BIPHENYLCYCLOHEXANES (BCHs) AT PHASE TRANSITION TEMPERATURE

Durga Prasad Ojha [a] , N. Ajeetha [a] & V. G. K. M. Pisipati [a]

[a] Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar-522 510, A.P., India

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COMPUTER SIMULATIONS OF MOLECULAR ORDERING IN DISUBSTITUTED BIPHENYLCYCLOHEXANES (BCHs) AT PHASE TRANSITION TEMPERATURE

*Durga Prasad Ojha, N. Ajeetha, and V. G. K. M. Pisipati**
Centre for Liquid Crystal Research and Education (CLCRE),
Faculty of Physical Sciences, Nagarjuna University,
Nagarjuna Nagar-522 510, A.P., India

A comparative computer simulation on two liquid crystalline disubstituted biphenylcyclohexanes ***(BCHs)*** *of general formula R-C_6H_{10}-C_6H_4-X with R: C_3H_7; X: H* ***(BCH30)*** *and R: C_5H_{11}; X: CN* ***(BCH5CN)*** *has been carried out on the basis of quantum mechanics and intermolecular forces. The net atomic charge and atomic dipole moment at each atomic center has been evaluated using the* ***CNDO/2*** *method. The configurational energy has been computed using the Rayleigh-Schrodinger perturbation method. The obtained energies were used to calculate the probability of each configuration at phase transition temperature, using the Maxwell-Boltzmann's formula. The flexibility of various configurations has been studied in terms of variation of probability due to small departures from the most probable configurations. Further, the various possible geometrical arrangements between a molecular pair during the different modes of interactions have been considered. An attempt has been made to explain the mesogenic behavior of these compounds in terms of their relative order.*

Keywords: BCHs; CNDO/2 method; quantum chemistry; computer simulations

INTRODUCTION

The link between the design of liquid molecules and the simulation of liquid crystal phase behavior represents a major challenge despite the substantial increase in the availability of computer processing time [1–3].

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*Corresponding author. E-mail: venkata_pisipati@hotmail.com

Further, interest has focused on stable phases mediating the transition between different liquid crystalline phases in which the degree of order within the layers changes, quite often very subtly, from one phase to another [4–7]. The majority of mesogenic molecules are composed of an aromatic core to which is attached one or two alkyl chains. The liquid crystal properties, such as the nematic-isotropic transition temperature and the entropy of transitions, are influenced by the presence of the alkyl chain [8]. It is well known that the prime requirements for the formation of a thermotropic liquid crystal is the molecular interaction. This interaction determines the physical properties of liquid crystals, as well as the type of physical and physicochemical process taking place in these substances [9].

Recently, the role of intermolecular forces in mesomorphic behavior has attracted attention of several workers based on the Rayleigh-Schrodinger perturbation method [10–12]. These studies were aimed at establishing the anisotropic nature of the pair-potential, and subsequently finding out the minimum energy configuration of a pair of liquid crystalline molecules. One of the limitations of the works was that the relative preference of different configurations was estimated on the basis of interaction energy. These values, however, do not reflect the actual relative preference. Since mesogenic properties are related to molecular aggregation in a specific manner, probability calculation based on interaction energy results will provide valuable information in this respect.

It is therefore necessary to compute the interaction energy for various configurations by changing the relative positions and orientations of the interacting molecules at different modes of interactions. With the values so obtained and by employing a suitable statistical method—one can determine the relative probability of occurrence of each configuration. 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 communication, an attempt has been made to identify the characteristic features of mesogens in terms of pair energy or configurational probabilities between a molecular pair of smectogenic (**BCH30**) and nematogenic (**BCH5CN**) compounds an intermediate distance of 6 Å for stacking and 8 Å in-plane interactions. Similarly, a distance 22 Å has been kept for terminal interactions. The choice of 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.

The thermodynamic data indicates that BCH30 gives smectic B to isotropic transition at 366 K, while BCH5CN shows nematic to isotropic transition at 494 K [13].

COMPUTATIONAL TECHNIQUE

The molecular geometry of **BCH30** and **BCH5CN** has been constructed on the basis of the published crystallographic data with standard values of bond lengths and bond angles [13]. In both the compounds, the molecules form layers in the crystalline state. The dihedral angles between the phenyl rings in the biphenyl unit are 2.4° (**BCH5CH**) and 23.8° (**BCH30**), respectively [13].

In order to find out the interaction energy between two molecules, it is necessary to compute the atomic net charges and dipole moments through an all-valence electron method. In the present computation, the **CNDO/2** method [14] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule. The calculations have been carried out in two stages as given below.

Computation of Interaction Energy at Various Configurations

A computer program based on simplified formula for the evaluation of interaction energy between a molecular pair has been used to calculate the energy for fixed configuration. According to the second-order perturbation theory as modified for intermediate range interactions [15], the total pair interaction energy of molecules (U_{pair}) is represented as sum of various terms contributing to the total energy:

$$U_{pair} = U_{el} + U_{pol} + U_{disp} + U_{rep}$$

where $U_{el}, U_{pol}, U_{disp}$, and U_{rep} are the electrostatic, polarization, dispersion, and repulsion energy terms, respectively.

Again, electrostatic term is expressed as

$$U_{el} = U_{QQ} + U_{QMI} + U_{MIMI} + \cdots$$

where $U_{QQ}, U_{QMI}, U_{MIMI}$, etc. are monopole-monopole, monopole-dipole, and dipole-dipole terms, respectively. In fact, the inclusion of higher order multipoles does not affect the electrostatic interaction energy significantly, and the calculation only up to dipole-dipole term gives satisfactory result [16]. The computation of electrostatic term has, therefore, been restricted only up to dipole-dipole energy term.

In the present computation, the dispersion and short-range repulsion terms are considered together because several semiempirical approaches, e.g., the Lennard-Jones or Buckingham type approach, actually proceed in this way. Kitaigorodskii introduced a Buckingham formula whose parameters were later modified by Kitaigorodskii and Mirskay for hydrocarbon molecules and several other molecules, and finally gave the expression:

$$U_{disp} + U_{rep} = \sum_{\lambda}^{(1)} \sum_{v}^{(2)} U(\lambda, v)$$

$$U(\lambda, v) = K_\lambda K_v(-A/Z^6 + Be^{-\gamma Z})$$

where $Z = R_{\lambda v}/R^0{}_{\lambda v}; R^0{}_{\lambda v} = [(2R^w{}_\lambda)(2R^w{}_v)]^{1/2}$, where R_λ^w and R_v^w are the van der Waals radii of atom λ and v, respectively. The parameters A, B, and γ do not depend on the atomic species. However, $R_{\lambda v}^0$ and factor $K_\lambda K_v$ allows the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [17].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin of 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 is perpendicular to the molecular plane.

Computation of Configurational Probabilities

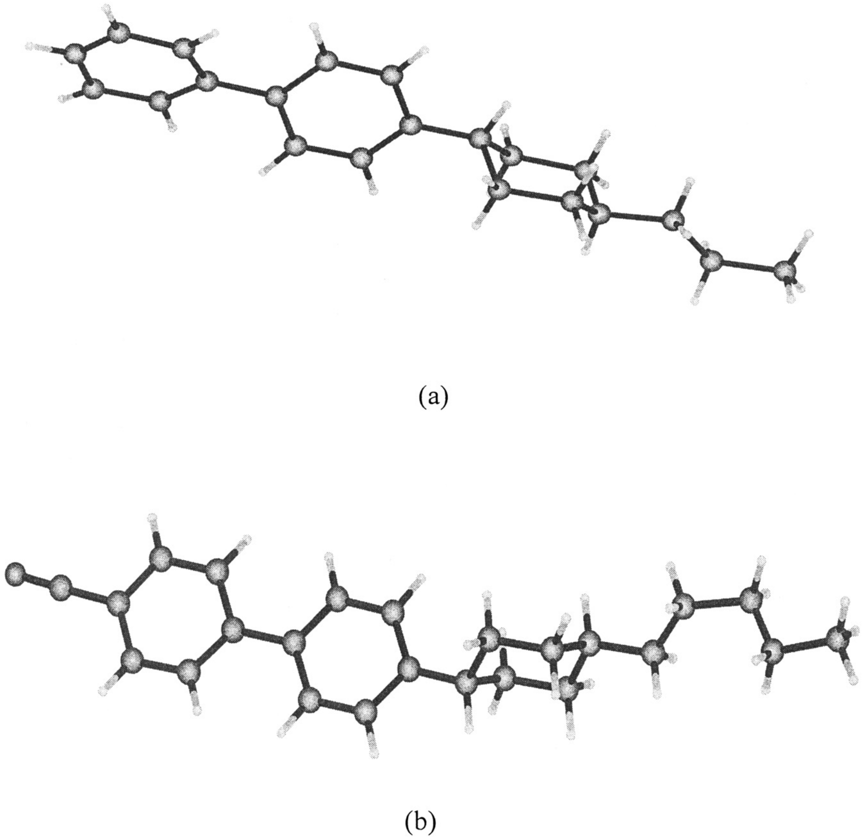
The total interaction energy values obtained through these computations were used as input to calculate the probability of occurrence of a particular configuration i using the Maxwell-Boltzmann formula [18] in order to obtain a better insight:

$$P_i = \frac{exp(-\beta\varepsilon_i)}{\sum_i exp(-\beta\varepsilon_i)}$$

where P_i stands for probability. $\beta = 1/kT$ where k is the Boltzmann constant, T is the absolute temperature, and ε_i represents the energy of the configuration i relative to the minimum energy value in a particular set for which the probability distribution is computed.

RESULTS AND DISCUSSION

Molecular geometry of **BCHs** is shown in Figure 1. The results of probability distribution based on interaction energy calculations at different modes of interactions are discussed below.


(a)

(b)

FIGURE 1 Molecular geometry of BCHs: (a) BCH30, (b) BCH5CN.

Stacking Interactions

In a molecular pair, one of the interacting molecules is fixed in x-y plane, while the second has been kept at a separation of 6 Å along z-axis with respect to fixed one. The variation of probability with respect to rotation about z-axis is shown in Figure 2 corresponding to configuration X(0°)Y(0°)* at its phase transition temperature. An observation of this figure reveals that the maximum probability corresponds to **BCH30** at −7° rotations while for **BCH5CN** at 2° rotations. The flexibility of rotation is sufficiently small for **BCH30**, which accounts for the smectic character of

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*Rotational set $X(\theta_1{}^0)Y(\theta_2{}^0)$ means that the molecule has been rotated from its initial position by θ_1^0 about x-axis and by θ_2^0 about the y-axis. Interaction energy has been calculated after displacing the molecule to specified distance with molecule in initial position.

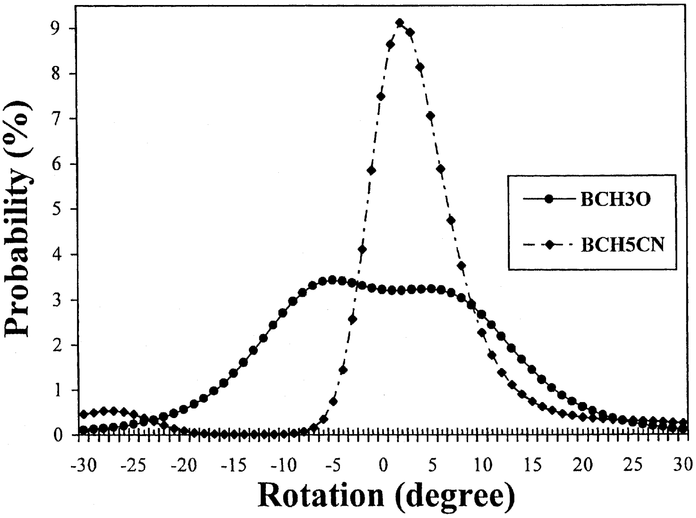

FIGURE 2 Variation of probability with respect to rotation about z-axis during stacking interactions at phase transition temperature (BCH30 at 366 K and BCH5CN at 494 K).

the molecule. Further, it indicates that a finite probability for alignment at low temperature exists when the thermal vibration does not drastically disturb the molecular alignments.

Having refined the interacting configuration with respect to rotation about z-axis at the equilibrium, the energy is brought down and the probability is further investigated with respect to translation along the long molecular axis (x-axis) corresponding to configuration Y(0°)Z(180°), as shown in Figure 3. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other has been achieved. It may be observed that the configuration shows a sharp preference towards the minimum energy point. The variation of probability is almost constant in the region of $-0.6\,\text{Å} \pm 0.4\,\text{Å}$ for **BCH5CN** without any significant change in the energy; hence it is capable of retaining molecular order upto 0.1 Å against increased thermal agitation.

The variation of probability with respect to rotation about x-axis corresponding to configuration Y(0°) is shown in Figure 4 at its phase transition temperature. The maximum probability corresponds to **BCH30** at $-2°$ rotations while the maximum probability for **BCH5CN** is at an equilibrium position, indicating a slight preference for aligned structure of this configuration. Further, it may be observed that the rotational rigidity about the long molecular axis is less at nematic-isotropic transition temperature

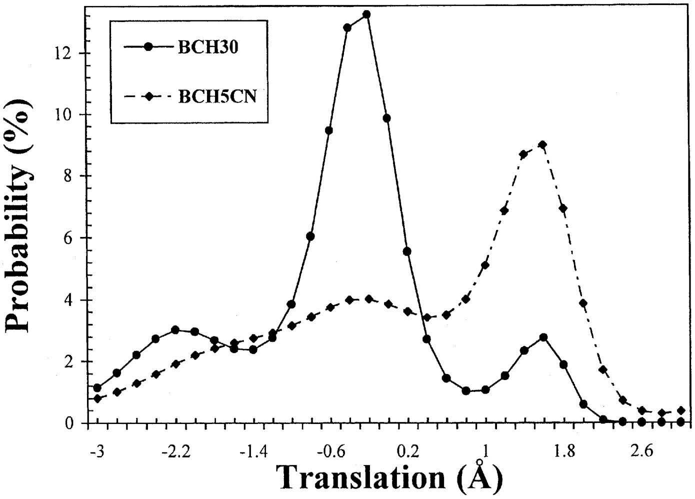

FIGURE 3 Variation of probability with respect to translation along x-axis during stacking interactions at phase transition temperature (BCH30 at 366 K and BCH5CN at 494 K).

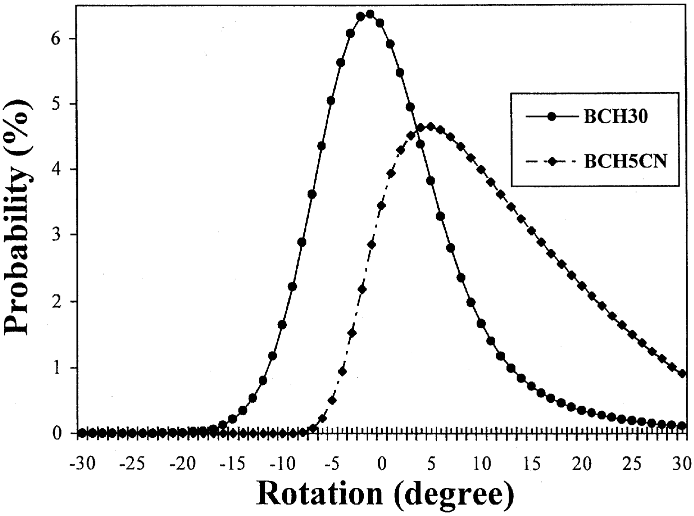

FIGURE 4 Variation of probability with respect to rotation about x-axis during stacking interactions at phase transition temperature (BCH30 at 366 K and BCH5CN at 494 K).

for **BCH5CN** molecule. However, at room temperature (300 K) the value indicates a strong binding, but with the increase of temperature the molecules obtain sufficient freedom to rotate about the long molecular axis.

In-plane Interactions

To avoid the possibility of van der Waals contacts completely, the interacting molecule has been kept at separation of 8 Å along y-axis with respect to fixed one. The similar calculations have been performed for in-plane interactions. Figure 5 shows the results with respect to translation along the long molecular axis corresponding to configuration Y(0°). It may be observed that the translation freedom is much more pronounced than of the stacking interactions. Figure 6 shows a graphical representation of probability distribution with respect to the rotation about x-axis corresponding to configuration Y(180°). 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 7 shows the variation of probability with respect to rotation about y-axis corresponding to configuration X(180°). Evidently the probability changes drastically in the range of 21° ± 4° for **BCH30**, which restricts the

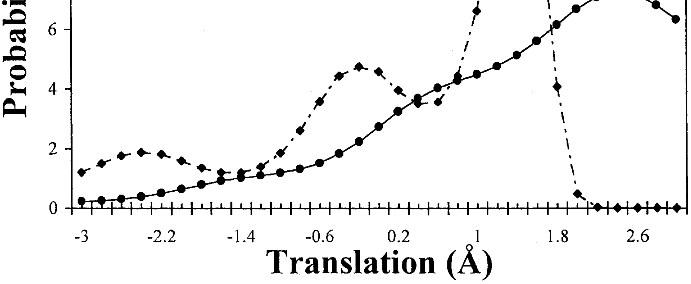

FIGURE 5 Variation of probability with respect to translation along x-axis during in-plane interactions at phase transition temperature (BCH30 at 366 K and BCH5CN at 494 K).

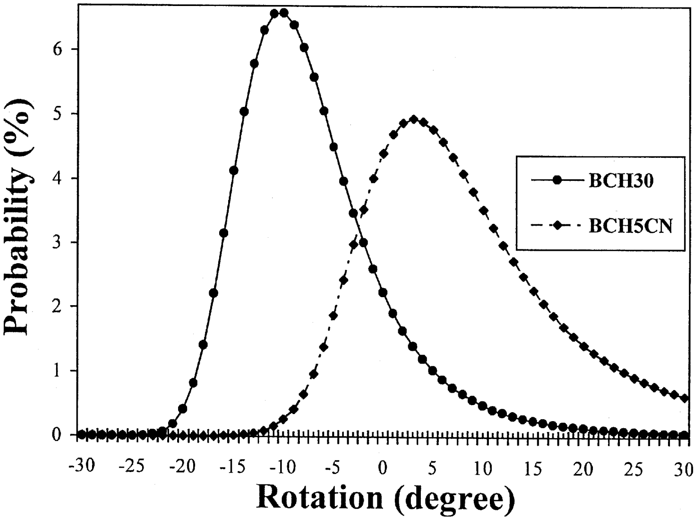

FIGURE 6 A graphical representation of probability distribution with respect to rotation about x-axis during in-plane interactions at phase transition temperature (BCH30 at 366 K and BCH5CN at 494 K).

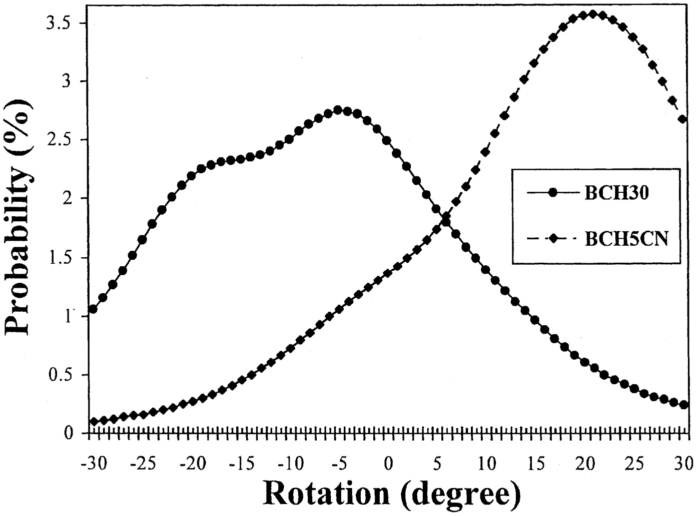

FIGURE 7 Variation of probability with respect to rotation about y-axis during in-plane interactions at phase transition temperature (BCH30 at 366 K and BCH5CN at 494 K).

rotational freedom of the molecule along y-axis and favored structure in mesophase.

Terminal Interactions

To investigate the terminal interactions away from the van der Waals contacts, the interacting molecule has been shifted along the x-axis by 22 Å. Terminal interactions are much weaker as compared to stacking or in-plane interactions. Figure 8 shows the results of probability distribution with respect to rotations about x-axis. In this case molecules are completely free to rotate about their long molecular axis. Further, maxima of probability is observed corresponding to various inclinations.

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 and are listed in Table 1 with all the contributing terms to enable comparison. It seems important to note that the largest attractive contribution in stabilizing the stacked, in-plane, and terminal interacting pair of **BCH30** and **BCH5CN** molecules comes from the dispersion forces. This supports the earlier observations [10–12]. Further, all possible geometrical arrangements between a molecular pair during the different modes of interactions have been considered and provide information about molecular arrangements inside the bulk materials.

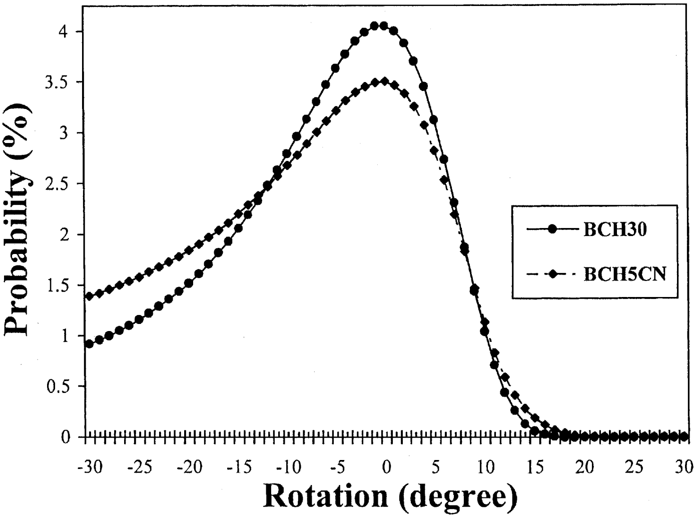

FIGURE 8 Variation of probability with respect to rotation about x-axis during terminal interactions at phase transition temperature (BCH30 at 366 K and BCH5CN at 494 K).

TABLE 1 Stacking, In-plane, and Terminal Interaction Energy Values Between a Pair of **BCH30** and **BCH5CN** Molecules After Refinement

Interaction	U_{total}	U_{el}	U_{pol}	U_{disp}	U_{rep}
BCH30					
Stacking	−9.681	−0.009	−0.012	−15.215	5.555
In-plane	−6.046	0.0011	−0.005	−10.069	4.016
Terminal	−4.275	0.010	−0.009	−8.993	3.717
BCH5CN					
Stacking	−11.892	0.087	−0.042	−16.337	4.401
In-plane	−8.802	0.062	−0.016	−13.890	5.802
Terminal	−3.389	−0.249	−0.423	−4.552	1.837

Energy is expressed in kcal/mole.

It may, therefore, be concluded from the above discussion that in a molecular assembly, a number of local minimum energy configuration exists. All of them have their own importance as in 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 disordered distribution, the global minimum has the maximum probability of occupancy. The other minima have sequential preference depending on their individual relative probability.

CORRELATION OF THE RESULTS

The results may be more closely examined with the parameters detailed below (*viz.* translational rigidities and rotational rigidities), and an attempt has been made to understand the molecular behavior in terms of their relative order.

Translational Rigidities

This has been defined as the ratio of probability being at the maximum probable point to having ±0.1 Å displacement along the long molecular axis. Table 2 shows the ratio of probability along the long molecular axis during stacking interactions is 0.62 at nematic-isotropic transition temperature (494 K) for **BCH5CN**. However, at room temperature (300 K) the value is 0.72, indicating a strong binding but with increase of temperature, the molecules obtain sufficient freedom to slide along the long molecular

TABLE 2 Translational Rigidities Along the Long Molecular Axis (x-axis) During Stacking and In-plane Interactions Between a Molecular Pair of **BCH30** and **BCH5CN** Molecules

	Probability ratio	
Temperature (K)	Stacking interactions	In-plane interactions
BCH30		
300	0.60	0.51
366 S_A-I	0.58	0.50
550	0.55	0.50
BCH5CN		
300	0.72	0.62
494 N-I	0.62	0.57
550	0.61	0.56

axis. Such translational freedom is much more pronounced in planar interactions. Thus, even at room temperature this value is 0.62 for **BCH5CN**, which reduced to 0.57 at nematic-isotropic transition temperature. It may be noted that although the freedom is considerable for smaller translation, in general longer translations are not permitted. Thus, small movements of molecules are only possible in the mesomorphic range. However, the comparable values in both cases i.e., stacking and in-plane interactions indicate that the molecule **BCH5CN** does not show extraordinary preference in forming the stacked layers and hence justifies the nematic character.

TABLE 3 Comparative Pictures of Rotational Rigidities During Stacking About z-axis

	Rotational rigidities		
Temperature (K)	Stacking interactions	In-plane interactions	Terminal interactions
BCH30			
300	0.53	0.51	0.50
366 S_A-I	0.51	0.50	0.50
550	0.50	0.50	0.50
BCH5CN			
300	0.54	0.52	0.50
494 N-I	0.52	0.51	0.50
550	0.51	0.51	0.50

In-plane about y-axis and terminal about x-axis between a molecular pair of **BCH30** and **BCH5CN** molecules.

It is clear that the rigidities decrease with the increase of temperature. Further, the nature of the curve in Figure 5 shows the tendency of **BCH30** molecules to form a layered structure at smectic *B* to isotropic transition temperature (366 K).

Rotational Rigidities

This has been defined as the ratio of probability being at maximum probable point to having $\pm 1^\circ$ rotation about z-axis during stacking interactions, while the rotation is extended about the y-axis for in-plane and x-axis for terminal interactions (Table 3). It may, therefore, be concluded that the flexibility of rotation about the z-axis is sufficiently small (see Figure 2), which accounts for the smectic character of the **BCH30** molecule. Table 3 clearly shows that during terminal interactions the molecules can rotate freely about its long molecular axis.

These two parameters may be help to understand the mesogenic character of the molecule. A comparative study of other systems may lead to a more general conclusion.

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