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# Molecular ordering of a cyano compound at a displacive transition temperature: a statistical analysis based on quantum mechanics and computer simulations

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A statistical analysis has been carried out to determine the configurational preference of a pair of 4-cyanophenyl 4-*n*-pentylbenzoate (CPPB) molecules 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 centre of the molecule. Configurational energy has been computed using the Rayleigh–Schrodinger perturbation method. The total interaction energy values obtained through these computations were used to calculate the probability of each configuration at the phase transition temperature using the Maxwell–Boltzmann formula. An attempt has been made to identify the most probable configuration at the phase transition temperature. Further, the flexibility of various configurations has been studied in terms of variation of probability due to small departures from the most probable configuration. On the basis of stacking, in-plane and terminal interaction energy calculations, all possible geometrical arrangements of the molecular pair have been considered. The results are discussed in the light of experimental as well as theoretical observations. The nature of the mesophase has been correlated with the parameter introduced in this paper.

## 1. Introduction

Liquid crystalline compounds and their properties are of great interest because of the widespread use of such materials in display devices [1–4]. Intermolecular interactions are extremely important in understanding the mesogenic behaviour of liquid crystals. The melting point (the temperature at which an ordered geometrical arrangement collapses and gives rise to the disordered isotropic melt) depends to a very large extent on the nature of the intermolecular interaction existing within the system. The cycle of mesomorphism (heating or cooling) and the transition temperature are governed by the intermolecular forces that act between the planes and ends of the molecule [5]. It is generally agreed that the prime requirement for the formation of a thermotropic liquid crystal is anisotropy in the molecular interaction [6]. There have been many attempts to measure and explore the long-range orientational order of liquid crystals [7, 8].

Recently computer simulation is finding an increasingly influential role in placing empirical structure–property relationships on firm theoretical foundations [9–11]. 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, complex structural anisotropy and electrostatic forces.

One of the limitations of previous work [7, 8] was that the relative preferences for different configurations were estimated on the basis of interaction energy values, which are not directly related quantities. Hence, in order to obtain a quantitative measure for the relative preference, we have extended the interaction energy calculations to a probability calculation. 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 aggregation. It therefore seems important to investigate the relative freedom of the molecules to depart from the minimum energy configuration in terms of (a) variation in orientation, and (b) translation along the molecular long axis. Through these computations one is able to obtain information on dimer complexes, 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 liquid crystallinity in terms of pair energy or configuration probabilities

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between a pair of CPPB molecules at an intermediate distance of 4.5 Å for stacking and 5 Å for in-plane interactions. Similarly, a distance of 20 Å has been used for terminal interactions. The choice of distance has been made to eliminate the possibility of van der Waals contacts and to keep the molecule within the short- and medium-range interactions.

Thermodynamic data has revealed that CPPB shows a monotropic nematic phase at 329 K [12]. The molecule adopts a widely stretched and nearly linear form, so that the general geometric condition required for molecules forming liquid crystals is fulfilled by CPPB. The molecules are packed in an approximate parallel-imbriated mode, the molecular long axes making an angle 5° with the crystal *c* axis [12].

## 2. Simplified formula and computational details

The molecular geometry of CPPB has been constructed on the basis of the published crystallographic data with standard values of bond lengths and bond angles [12]. In order to determine the interaction energy between two molecules, it is necessary to compute atomic net charges and dipole moments through an all valence electron method. In the present work, the CNDO/2 method [13] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule. The computations have been carried out in two parts, as follows.

### 2.1. Computation of interaction energy at various configurations

A computer program based on a 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 [14], the total interaction energy ( $E_{\text{total}}$ ) between a pair molecules is given by

$$E_{\text{total}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}}$$

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

Again, the electrostatic term is expressed as

$$E_{\text{el}} = E_{\text{QO}} + E_{\text{QMI}} + E_{\text{MIMI}} + \dots$$

where  $E_{\text{QO}}$ ,  $E_{\text{QMI}}$  and  $E_{\text{MIMI}}$ , 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 up to only the dipole–dipole term gives a satisfactory result [15]; the computation of the electrostatic term has been accordingly restricted.

In the present computation the dispersion and short-range repulsion terms are considered together because several semiempirical approaches (viz. the Lennard–Jones or Buckingham-type approach) actually proceed in this way [15]. 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 [16].

$$E_{\text{disp}} + E_{\text{rep}} = \sum_{\lambda} \sum_{\nu}^{(1) (2)} E(\lambda, \nu)$$

$$E(\lambda, \nu) = K_{\lambda} K_{\nu} [-A/Z^6 + B \exp(-\gamma Z)]$$

where  $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$ ;  $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$  where  $R_{\lambda}^w$  and  $R_{\nu}^w$  are the van der Waals radii of atoms  $\lambda$  and  $\nu$  respectively. The parameters  $A$ ,  $B$  and  $\gamma$  do not depend on the atomic species. But  $R_{\lambda\nu}^0$  and factors  $K_{\lambda}$ ,  $K_{\nu}$  allow the energy minima to have different values according to the atomic species involved.

As mentioned earlier, the aim of the present investigation was to calculate the probability distribution of different configurations allowing free-rotation and translation of one molecule in the presence of another at a fixed position. Terms such as stacking, in-plane or terminal interactions will be used to maintain continuity with our previous studies [17–19].

To facilitate these calculations an orthogonal coordinate system is defined by taking the origin on an atom at the centre 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 the *Z*-axis is perpendicular to the molecular plane. All the calculations are done on an IBM Pentium PC, necessary codes are written in FORTRAN.

### 2.2. Computation of configurational probabilities

The total interaction energy values obtained through these calculations were used as input to calculate the intrinsic probability of each configuration with the help of the Maxwell–Boltzmann formula [17]:

$$P_i = \exp(-\beta \varepsilon_i) / \sum_i \exp(-\beta \varepsilon_i); \quad \beta = 1/kT$$

where  $P_i$  is the probability of a particular configuration, and  $\varepsilon_i$  the energy of configuration  $i$  relative to the minimum energy configuration.  $k$  is the Boltzmann Constant, and  $T$  the absolute temperature.

## 3. Results and discussion

The molecular geometry of CPPB is shown in figure 1. Computed net atomic charges and dipole moments at each atomic centre are listed in table 1. The total energy, binding energy and total dipole moment along with its

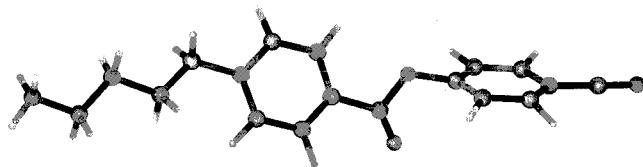


Figure 1. Molecular geometry of 4-cyanophenyl 4-*n*-pentylbenzoate (CPPB).

Table 1. Calculated atomic net charge and dipole moments using the CNDO/2 method for the molecule CPPB.

S. No.	Atom	Charge	Atomic dipole components		
			$\mu_x$	$\mu_y$	$\mu_z$
1	C	-0.061	-0.079	-0.024	0.019
2	C	0.442	0.339	0.011	0.013
3	O	-0.308	0.806	-0.920	0.029
4	C	0.192	-0.139	0.009	0.021
5	C	-0.043	0.180	-0.020	-0.183
6	C	0.033	-0.030	-0.067	-0.243
7	C	0.022	0.031	0.068	-0.001
8	C	0.035	-0.109	-0.042	0.148
9	C	-0.043	0.049	0.000	0.177
10	O	-0.272	-0.888	1.052	-0.022
11	C	0.080	0.081	0.053	0.012
12	N	-0.165	-1.700	-0.557	-0.105
13	C	0.036	-0.059	-0.153	-0.006
14	C	-0.018	0.029	-0.130	0.020
15	C	0.048	0.060	0.014	-0.017
16	C	-0.017	0.044	0.138	0.030
17	C	0.031	-0.028	0.151	-0.046
18	C	0.009	0.008	-0.043	0.013
19	C	0.020	-0.008	0.076	-0.027
20	C	0.018	0.108	-0.070	-0.074
21	C	0.030	-0.143	0.082	0.033
22	C	-0.016	0.206	0.005	0.035
23	H	-0.006	0.000	0.000	0.000
24	H	0.011	0.000	0.000	0.000
25	H	0.001	0.000	0.000	0.000
26	H	-0.002	0.000	0.000	0.000
27	H	-0.013	0.000	0.000	0.000
28	H	-0.003	0.000	0.000	0.000
29	H	-0.008	0.000	0.000	0.000
30	H	-0.009	0.000	0.000	0.000
31	H	-0.014	0.000	0.000	0.000
32	H	0.002	0.000	0.000	0.000
33	H	0.000	0.000	0.000	0.000
34	H	-0.004	0.000	0.000	0.000
35	H	-0.002	0.000	0.000	0.000
36	H	-0.002	0.000	0.000	0.000
37	H	-0.005	0.000	0.000	0.000
38	H	0.009	0.000	0.000	0.000
39	H	-0.011	0.000	0.000	0.000
40	H	-0.010	0.000	0.000	0.000
41	H	0.016	0.000	0.000	0.000

components are listed in table 2. The results of probability distribution based on interaction energy calculations are discussed below.

Table 2. Total energy<sup>a</sup>, binding energy<sup>b</sup>, total dipole moment and its components of the CPPB molecule. Total energy = -197.59 au, binding energy = -21.08 au, total dipole moment = 3.31 D.

Components	$\mu_x$	$\mu_y$	$\mu_z$
Densities <sup>c</sup>	-1.99	-0.29	-0.16
sp <sup>d</sup>	-1.24	-0.37	-0.17
pd <sup>e</sup>	0.00	0.00	0.00
Total <sup>f</sup>	-3.23	0.67	-0.33

<sup>a</sup> The total energy corresponds to the sum of the atomic and electronic energies of all the constituents of the molecule in the equilibrium geometry.

<sup>b</sup> The binding energy of a molecule is the difference between the energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms.

<sup>c</sup> Contribution to dipole moment components due to electron densities.

<sup>d</sup> sp hybridization moment.

<sup>e</sup> pd hybridization moment.

<sup>f</sup> Sum of electron density and hybridization contribution to the dipole moment component.

### 3.1. Stacking interactions

One of the interacting molecules is fixed in the XY-plane, while the second has been kept at a separation of 4.5 Å along the Z-axis with respect to the fixed molecule. The choice of distance has been made to eliminate the possibility of van der Waals contacts completely, and to keep the molecule within the range of short- and medium-range interactions.

The variation of stacking interaction energy with respect to rotation about the Z-axis has been carried out corresponding to configuration  $X(0^\circ) Y(0^\circ)$  at an interval of  $10^\circ$ , and interaction energy at each point has been calculated. The minimum energy so obtained is then taken as the starting point and the entire process repeated at smaller intervals. The energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 Å in translation and  $1^\circ$  in rotation of one molecule with respect to the other has been achieved. It is important to note here that the path of minimization strictly depends on the objective of the computation. The global search for minimum energy configuration or the study of variation of interaction energy under a pre-selected condition will have completely different paths and, therefore is needed in choosing the specific route.

The variation of stacking interaction energy components with respect to rotation about the X-axis corresponding to configuration  $Y(0^\circ) Z(0^\circ)$  has been carried out, and it has been observed that the dominant component of the total energy is the dispersion energy. The contribution of polarization energy is negligible. The electrostatic energy term is much smaller than the dispersion term.

Furthermore, the translational freedom along the molecular long axis corresponding to configuration  $Y(0^\circ)$   $Z(180^\circ)$  has been allowed at intervals of  $0.2 \text{ \AA}$ , and the corresponding change in probabilities distribution based on interaction energies is shown in figure 2. It is evident that the stacked pair of CPPB molecules can slide one above the other in the range  $-2 \pm 0.4 \text{ \AA}$  without any significant change in the energy, and hence is capable of retaining molecular order upto  $3 \text{ \AA}$  against increased thermal agitation.

### 3.2. In-plane interactions

Similar calculations have been performed for in-plane interactions. The interacting molecule has been kept at a separation of  $5 \text{ \AA}$  along the  $Y$ -axis with respect to the fixed molecule to avoid the possibility of van der Waals contacts. Again, rotation about the  $Y$ - and  $X$ -axes has been given and corresponding energy calculated. The energy has been minimized with respect to translation and rotation about all axes.

Figure 3 shows the variation of in-plane interaction energy with respect to rotation about the  $X$ -axis corresponding to configuration  $Y(0^\circ)$ . It has been observed that the main attractive part of the energy comes through the dispersion term. The variation in the dispersion energy is asymmetrical, and hence several minima are observed corresponding to various inclinations.

The variation of probability with respect to translation along the  $X$ -axis is shown in figure 4, corresponding to configuration  $Y(180^\circ)$ . The in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. The maximum probability occurs at an equilibrium position. The

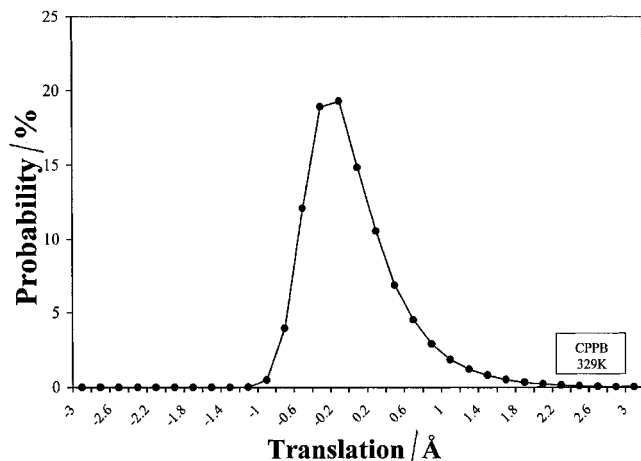


Figure 2. Variation of probability with respect to translation along the  $X$ -axis during stacking interactions at the nematic-isotropic transition temperature.

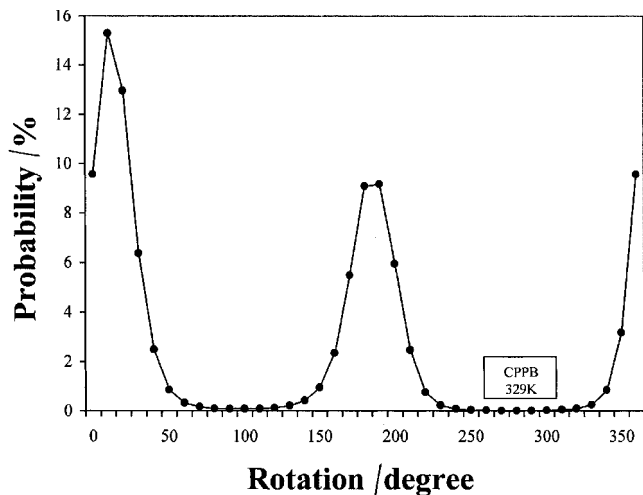


Figure 3. Variation of probability with respect to rotation about the  $X$ -axis during in-plane interactions at the nematic-isotropic transition temperature.

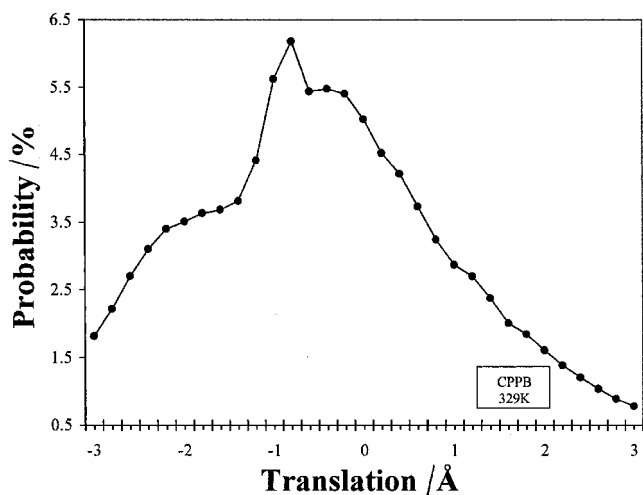


Figure 4. Variation of probability with respect to translation along the  $X$ -axis during in-plane interactions at the nematic-isotropic transition temperature.

variation of probability is almost constant for a region of  $-1.6 \pm 0.4 \text{ \AA}$ , which may be correlated with the fluidity of molecules maintaining their alignment in mesophase.

### 3.3. Terminal interactions

Terminal interactions are much weaker than stacking or in-plane interactions. To investigate the terminal interactions apart from van der Waals contacts, the interacting molecule was shifted along the  $X$ -axis by  $22 \text{ \AA}$  with respect to the fixed molecule and rotation allowed about the  $X$ -axis. The variation of probability with respect to rotation about the  $X$ -axis (figure 5) corresponding to configuration  $Y(0^\circ)$  shows no preference for any angle, i.e. molecules are completely free to rotate about their molecular long axis.

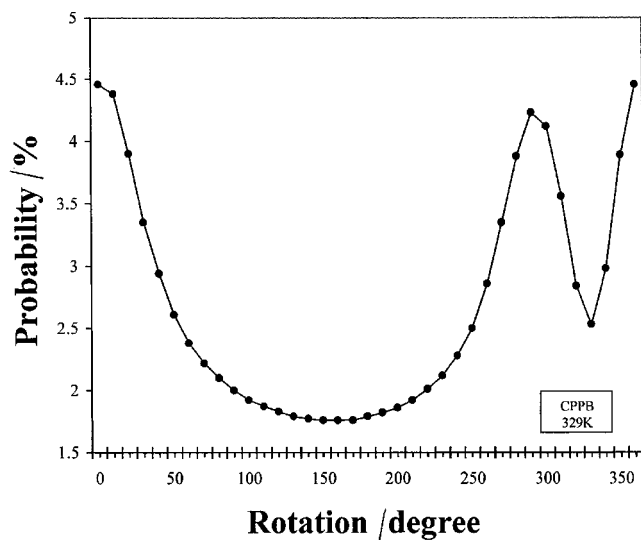


Figure 5. Variation of probability with respect to rotation about the *X*-axis during terminal interactions at the nematic–isotropic transition temperature.

The most prominent energy minima of the above-mentioned interactions are refined, and the values thus obtained are listed in table 3 with all the contributory terms to enable comparison. These results indicate that the refinement corresponding to stacking energy is maximum, and the ultimate magnitude of stacking energy is larger than in-plane and terminal interactions. This supports earlier observations [7, 8] and also the basic assumption of molecular field theory [20–22]. The final lowest stacked geometry (figure 6) is thus obtained at an interplanar separation of 4 Å with energy  $-11.04 \text{ kcal mol}^{-1}$ ; for in-plane geometry (figure 7) the separation is 4.5 Å with energy  $-7.76 \text{ kcal mol}^{-1}$ . These configurations agree with those obtained from crystallographic studies [12].

The calculations may be reasonably correlated with the mesomorphic behaviour of the system. When solid crystals of CPPB are heated, thermal vibrations disturb

Table 3. Minimum energy values obtained between a pair of CPPB molecules during stacking, in-plane and terminal interactions after refinement. Energy is expressed in  $\text{kcal mol}^{-1}$ .

Energy terms	Stacking energy	In-plane energy	Terminal energy
$E_{QQ}$	0.053	-0.072	-0.100
$E_{QM1}$	-0.001	-0.749	-0.055
$E_{M1M1}$	-0.372	-0.525	0.179
$E_{el}$	-0.319	1.346	0.024
$E_{pol}$	-0.184	-0.283	-0.403
$E_{disp}$	-15.740	-10.416	-1.038
$E_{rep}$	5.207	4.288	0.522
$E_{total}$	-11.036	-7.756	-0.895

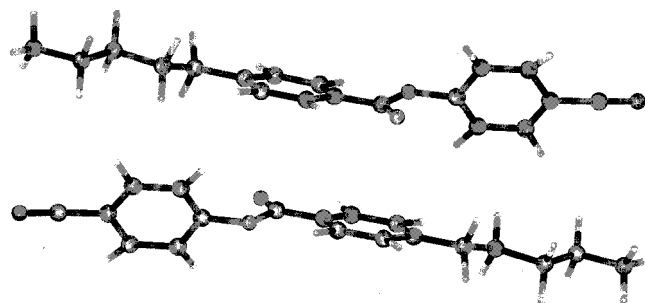


Figure 6. The lowest stacking energy configuration obtained with energy  $-11.04 \text{ kcal mol}^{-1}$  at an intermolecular separation of 4 Å.

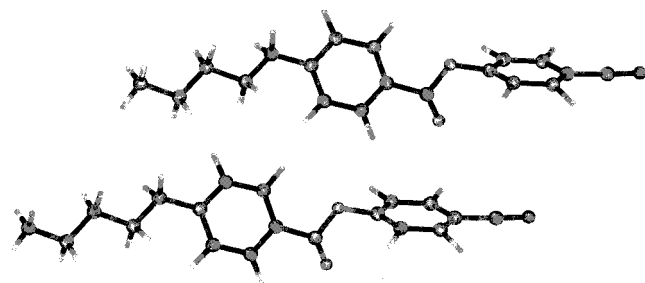


Figure 7. The lowest in-plane energy configuration obtained with energy  $-7.76 \text{ kcal mol}^{-1}$  at an intermolecular separation of 4.5 Å.

the molecular ordering of the strongly packed geometrical arrangement of molecules. Consequently, the attractions between a pair of molecules, which largely consist of dispersion forces, tend to weaken at higher temperature, and hence the possibility of movement within a molecular pair along the molecular long axis is considerably enhanced (figure 2). The freedom of a molecule in a stacked pair to slide along an axis perpendicular to the molecular long axis (*Y*-axis) is energetically restricted. These results favour the nematic behaviour of the system at high temperature because the molecules of CPPB are capable of sliding along the molecular long axis with simultaneous relative orientations. At very high temperature, an all round breaking of the dispersion forces results and all possible geometries (even perpendicular stacking) are equally favoured, which ultimately causes the system to pass into an isotropic melt state.

#### 3.4. Effect of translation and correlation of results

The nematic character of liquid crystal is generally manifested by its translational freedom along the molecular long axis. In order to examine the obtained results more closely, the translational rigidity parameter (similar to the order parameter) has been calculated and an attempt made to understand the molecular behaviour in terms of their relative order as given below.

Table 4. Translational rigidities along the molecular long axis ( $X$ -axis) during stacking and in-plane interactions between a pair of CPPB molecules.

Temperature (K)	Probability ratio	
	Stacking interactions	In-plane interactions
300	0.58	0.56
329 N-I	0.57	0.55
334	0.57	0.55

### 3.4.1. Translational rigidity

This has been defined as the probability ratio being at maximum probable point to having  $\pm 0.2 \text{ \AA}$  displacement along the long molecular axis. Table 4 shows that the probability ratio along the molecular long axis is 0.57 at the nematic–isotropic transition temperature (329 K). However, at room temperature (300 K) the value is 0.58, indicating a strong binding at lower temperature; with increase of temperature, the molecules obtain sufficient freedom to slide along the molecular long axis. Such translational freedom is much more pronounced in planar interaction. Thus, even at room temperature this value is 0.56, reducing to 0.55 at the transition temperature. It may be noted (figure 4) that although the freedom is considerable for smaller translation, longer translations are not in general permitted. Thus in the mesomorphic range, only small movements of the molecules are possible. However, the comparable values in both cases show that the molecules show no extraordinary preference in forming stacked layers, hence justifying the nematic character.

Furthermore, all possible geometrical arrangements between a molecular pair during stacking, in-plane and terminal interactions have been considered and provide an insight of molecular arrangements inside bulk material. A global search of minimum energy configuration is difficult and time consuming, since it would involve many non-physical configurations which could be avoided by choosing a suitable path for minimization.

It may therefore be concluded from the above discussion, that an isolated consideration for any particular degree of freedom manifests, in general, a preference for an aligned structure with some allowance of deviation from its minimum energy (or maximum probability) configuration. Also, each configuration has its own minimum energy structure for every degree of freedom. Thus in a molecular assembly, a number of local minimum energy configurations exist. 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 cooling from a very high temperature when the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy and the others have a sequential preference depending on their individual relative probabilities.

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