

Nematogenic Behaviour of a Cyano-Compound Using Quantum Mechanics and Computer Simulations

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Using quantum mechanics and intermolecular forces, the molecular ordering of a nematogenic cyano-compound, 5-(*trans*-4-ethylcyclohexyl)-2-(4-cyanophenyl)-pyrimidine (**ECCPP**), has been examined. The **CNDO/2** method has been employed to evaluate the net atomic charge and the dipole moment components at each atomic centre of the molecule. The configuration energy has been computed using the modified Rayleigh-Schrödinger perturbation method at intervals of 1 Å in translation and 10^0 in rotations, and corresponding probabilities have been calculated using Maxwell-Boltzmann statistics. The flexibility of various configurations has been studied in terms of the variation of the probability due to small departures from the most probable configuration. All possible geometrical arrangements between a molecular pair have been considered during stacking, in-plane and terminal interactions, and the most favourable configuration of pairing has been obtained. An attempt has been made to understand the behaviour of the molecules in terms of their relative order. The results have been compared with those obtained for other nematogens like **DPAB** [4,4'-di-n-propoxy-azoxybenzene] and **EMBAC** [ethyl 4-(4'-methoxybenzylidene amino) cinnamate].

Key words: ECCPP; CNDO/2 Method; Intermolecular Forces; Computer Simulation.

Introduction

Mesogenic compounds and their properties treated in the monographs [1, 2], are of great interest because of their use in display devices. Knowledge of the molecular arrangement in the crystalline state is needed for a proper understanding of several physical properties of liquid crystals [3, 4]. The nature of mesomorphism is determined by the extent to which forces like dipole-dipole, induced-dipole and van der Waals forces, operate to maintain a regular arrangement against the disturbing influence of thermal agitation [5, 6]. There have been many attempts to measure the long-range orientational order of liquid crystals and to explain it [7]. It is generally agreed that the prime requirement for the formation of a thermotropic crystal is anisotropy in the molecular interaction [8].

It is, therefore, necessary to compute the interaction energy for various configurations by changing the relative positions and orientations of the interacting molecules. With the values so obtained, and employing a suitable statistical method, one can determine the relative probability of the occurrence of each configuration. Through these computations one is able to obtain information about the probability of the formation of a dimer complex, the relative freedom of a molecule in terms of

variations in inclination, separation or sliding of one molecule over the other, etc.

The system chosen for the present investigation, **ECCPP**, has a structure which is common for a nematogen, and its transition to the mesophase is of a simple displacive type [9]. The pairing of molecules resulting from the interaction between opposed dipoles of cyano-groups exists both in the crystalline and the nematic state [9].

In the present paper, an attempt is made to interpret the results of intermolecular interaction energy calculations between two **ECCPP** molecules at a distance of 6 Å for stacking and 10 Å for in-plane interactions. Similarly, a distance 24 Å has been kept for terminal interactions. The choice of the distance has been made to eliminate the possibility of van der Waals contacts and to keep the molecule within the range of short and medium-range interactions. Also, instead of finding the exact minimum energy configuration, an attempt has been made to elucidate the general behaviour of a molecule near a fixed molecule in a particular frame of reference. Results have been discussed in the light of those obtained for the nematogens **DPAB** [6] and **EMBAC** [10].

The thermodynamic data show that **ECCPP** goes to the nematic phase at 373.6 K and to the isotropic melt at 507.9 K [9]. The length of the full-extended **ECCPP**

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molecule is 21.2 Å, whereas the length of the molecule in the crystalline state is 20.7 Å. This indicates that in the crystalline state the molecule is almost in its most extended form [9].

Method of Calculation

The molecular geometry of **ECCPP** has been constructed on the basis of the published crystallographic data with standard values of the bond lengths and bond angles. The phenyl and pyrimidine rings are highly planar and lie almost in the ac plane [9].

The computations have been carried out in two parts:

(A) Evaluation of the intermolecular interaction energy has been carried out using a modified second order perturbation method [11]. The total interaction energy, E_{total} , between a pair of interacting **ECCPP** molecules has been computed as the sum of various contributing terms:

$$E_{\text{total}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}}, \quad (1)$$

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

Electrostatic Energy

According to the multicentered-multipole expansion method as developed by Rein [12], the electrostatic energy may be expressed as the sum of interaction terms between atomic multipoles of successively higher orders:

$$E_{\text{el}} = E_{\text{QQ}} + E_{\text{QMI}} + E_{\text{MIMI}} + E_{\text{Qq}} + E_{\text{Mq}}, \quad (2)$$

where E_{QQ} , E_{QMI} , E_{MIMI} , E_{Qq} , and E_{Mq} are the mono-pole-mono-pole, mono-pole-dipole, dipole-dipole, mono-pole-quadrupole, and dipole-quadrupole terms, respectively. In general, for most molecular systems the first three terms have been found to be adequate [13]. The expressions for these terms are given below. The mono-pole-mono-pole interaction term E_{QQ} is given by

$$E_{\text{QQ}} = C \sum_{i,j} q_i \cdot q_j / r_{ij}, \quad (3)$$

where q_i , q_j are the monopoles on the atomic centres of the interacting molecules i and j , r_{ij} is the interatomic distance and C is a conversion factor (≈ 332) which expresses the energy in kcal/mole of the dimer.

The mono-pole-dipole interaction term is

$$E_{\text{QMI}} = C \sum_{i,j} q_i \mu_j r / r^3, \quad (4)$$

while the dipole-dipole interaction term is given by

$$E_{\text{MIMI}} = C \sum_{i,j} 1/r^3 \cdot [\mu_i \cdot \mu_j - 3(\mu_i \cdot r/r)(\mu_j \cdot r/r)], \quad (5)$$

where μ_i and μ_j represent the atomic dipoles, the subscript of r has been removed for simplicity and the other notations have the same meaning as in (3). The atomic net charges and dipole moments may be evaluated by using usual quantum mechanical [all valence electron] methods. In these computations, the **CNDO/2** method has been used [14].

Polarization Energy

The polarization energy of a molecule (s) is obtained as the sum of the polarization energies of the various bonds:

$$E_{\text{pol}}^{(s)} = C (-1/2) \sum_u^{(s)} \xi_u^{(s)} \bar{A}_u^{(s)} \xi_u^{(s)}, \quad (6)$$

where \bar{A}_u is the polarizability tensor of the bond u and $\xi_u^{(s)}$ the electric field created at this bond by the surrounding molecules. If the molecular charge distributions are represented by the atomic charges, it is found that

$$\xi_u^{(s)} = \sum_{t \neq s} \sum_{\lambda}^{(t)} q_{\lambda}^{(t)} R_{\lambda\mu} / R_{\lambda\mu}^3, \quad (7)$$

where $R_{\lambda\mu}$ is the vector joining the atom λ in molecule t to the 'centre of polarizable' charge on the bond u of molecule s .

Dispersion and Short-range Repulsion Energies

These two terms are considered together because several semiempirical expressions, viz. the Lennard-Jones or Buckingham type approach actually proceed in this way. Kitaigorodskii [15] introduced a Buckingham formula whose parameters were later modified by Kitaigorodskii and Mirskaya [16] for hydrocarbon molecules and several other molecules, and finally gave the expression

$$E_{\text{disp}} + E_{\text{rep}} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} E(\lambda, \nu), \quad (8)$$

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

where $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$; $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$. R_{λ}^w and R_{ν}^w are the van der Waals radii of atoms λ and ν , respective-

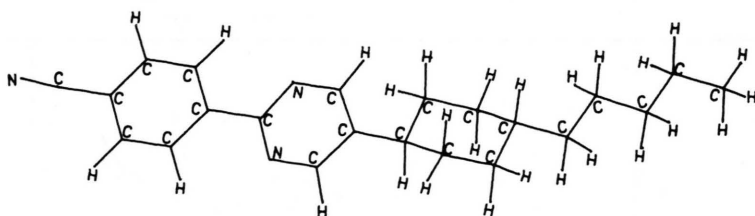


Fig. 1. Molecular geometry of 5-(trans-4-ethylcyclohexyl)-2-(4-cyanophenyl)-pyrimidine.

ly. The parameters A , B and γ do not depend on the atomic species. But $R_{\lambda\nu}^0$ and the factors K_{λ} and K_{ν} allow the energy minima to have different values according to the species involved. The recent values of these parameters may be found in [17, 18].

Energy minimization is carried out by keeping one of the molecules as fixed while the other one is rotated at intervals of 10° and the minimum energy point is obtained. The molecule is then translated along the long molecular axis at intervals of 2 \AA , and the corresponding energies are calculated. The minimum energy so obtained is then taken as starting point and the entire process is repeated at smaller intervals. The association energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 \AA in translation and 1° in rotation of one molecule with respect to the other has been achieved.

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

(B) 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 [19]

$$P_i = \exp(-\beta \epsilon_i) / \sum_i \exp(-\beta \epsilon_i); \beta = 1/kT,$$

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

Results and Discussion

The molecular geometry of **ECCPP** is shown in Figure 1. Table 1 represents a comparative picture of the to-

Table 1. Total energy*, binding energy** and total dipole moment of **ECCPP**, **DPAB** and **EMBAC** molecules.

Molecule	Total energy (A.U.)	Binding energy (A.U.)	Total dipole moment (Debyes)
ECCPP	-247.14	-24.79	2.13
DPAB	-223.57	-22.15	1.46
EMBAC	-232.62	-23.93	2.26

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

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

tal energy, the binding energy and the total dipole moments of the molecules **ECCPP**, **DPAB** and **EMBAC**. As evident from Table 1, the total energy, binding energy and total dipole moment, of these molecules exhibit the order:

$$\mathbf{ECCPP} > \mathbf{EMBAC} > \mathbf{DPAB}.$$

The results of the intermolecular interaction energy calculations and the configurational probability distribution are discussed below. The terms stacking, in-plane and terminal interactions have been used to maintain continuity with the previous works.

Stacking Interactions

The variation of the interaction energy components with respect to the configuration $X(0^\circ)Y(0^\circ)$ on the rotation about the X -axis is shown in Fig. 2a. The interacting molecule has been placed at a separation of 6 \AA along the Z -axis with respect to the fixed molecule. This distance has been chosen to eliminate van der Waals contacts and to keep the molecule within the range of short and medium-range interactions. The rotation about the X -axis has been made at intervals of 10° .

Figure 2a reveals that the dominant component of the total energy is the dispersion energy. The contribution of

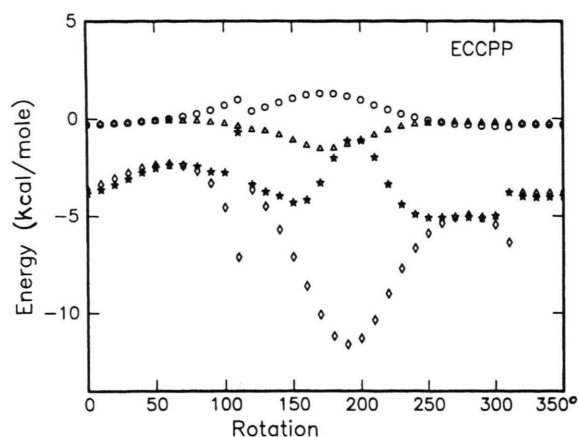


Fig. 2a. Variation of the stacking interaction energy components with respect to rotation about the X-axis. (○ – electrostatic; △ – polarization; ◇ – dispersion; * – total energy)

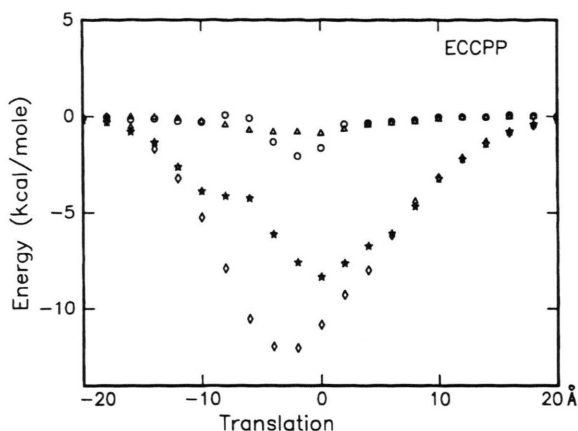


Fig. 3a. Variation of the stacking interaction energy components with respect to translation along the long molecular axis. Notations are as in Fig. 2a.

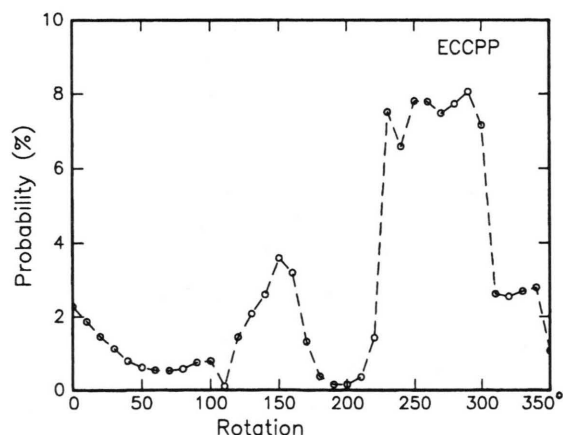


Fig. 2b. Variation of the probability with respect to rotation about the X-axis during stacking interactions at the nematic-isotropic transition temperature (507.9 K).

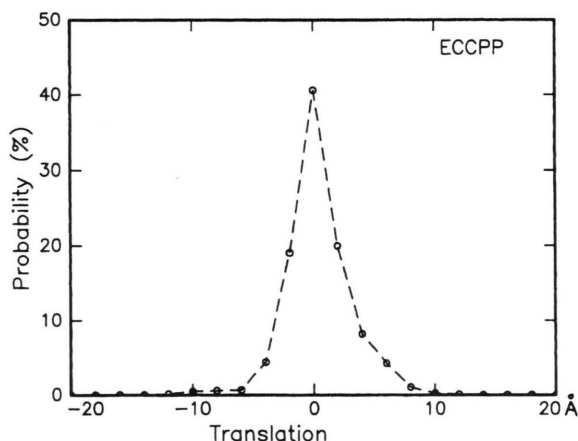


Fig. 3b. Variation of the probability with respect to translation along the long molecular axis during stacking interactions at nematic-isotropic transition temperature (507.9 K).

the polarization energy is negligible. The electrostatic energy term is much smaller than the dispersion term, but its symmetric fluctuation reflects the variation in the total energy curve. The repulsion energy component has not been plotted as it can easily be obtained with the help of the dispersion and Kitaigorodskii curves. The variation of the probability with respect to rotation about the X-axis is shown in Figure 2b. Evidently the maximum probability occurs at 290° rotation.

The variation of the intermolecular interaction energy components with respect to translation along the long molecular axis is shown in Fig. 3a, while their

probabilities are shown in Fig. 3b. All components increase with increased overlapping, the increase being small for electrostatic and polarization energy terms. The dispersion energy component is mainly responsible for the attraction between the planes of the **ECCPP** molecules, though the exact optimum results always from the Kitaigorodskii energy curve, which has a gross similarity with the total energy curve. Evidently the stacked pair of **ECCPP** molecules can slide one above the other in the range of $15 \text{ Å} \pm 5 \text{ Å}$ without any significant change in the energy and, hence, is capable of retaining molecular order upto 20 Å against increased thermal agitation.

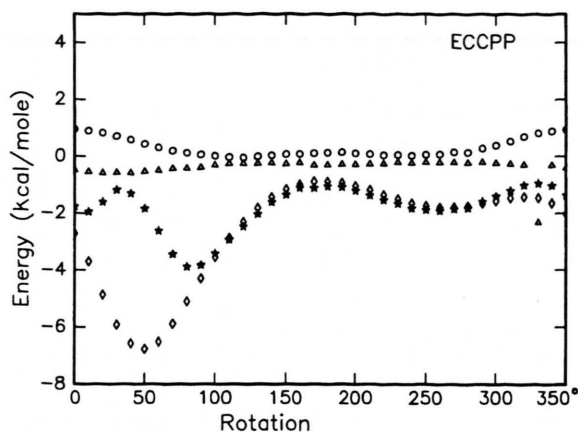


Fig. 4a. The angular dependence of the in-plane interaction energy components with respect to rotation about X-axis. Notations are as in Fig. 2a.

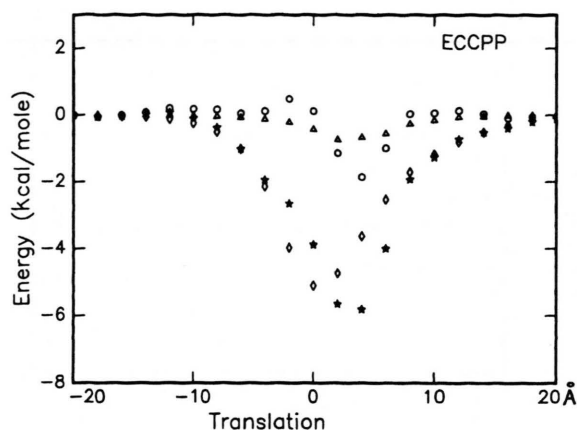


Fig. 5a. Variation of the in-plane interaction energy components with respect to translation along the long molecular axis. Notations are as in Fig. 2a.

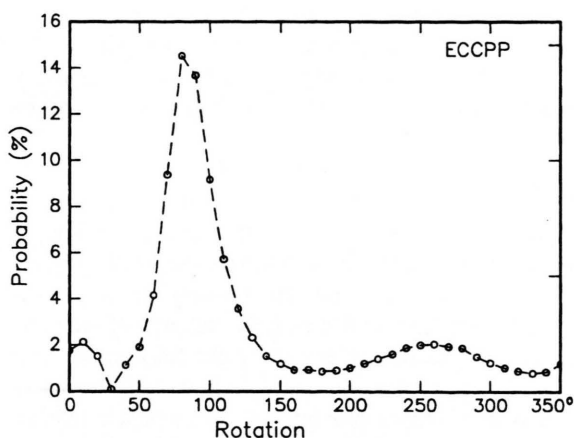


Fig. 4b. Variation of the probability with respect to rotation about the X-axis during in-plane interactions at nematic-isotropic transition temperature (507.6 K).

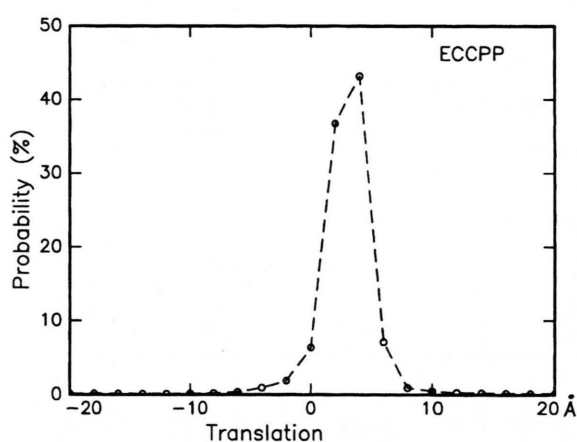


Fig. 5b. Variation of the probability.

In-plane Interactions

Figures 4a and b show the angular dependence of the interaction energy components with respect to rotation about the X-axis for the configuration $Y(0^\circ)$. Again the main attractive part of the energy comes through the dispersion term. In this case, the variation in the dispersion energy is asymmetrical, and hence several minima are observed corresponding to various inclinations. The probability is almost constant for a region of $180^\circ \pm 30^\circ$, which shows that sliding of one molecule over the other is energetically allowed to a large extent, which may be correlated with the fluidity of compounds maintaining their alignment in the mesophase.

The variation of interaction energy components on translation along the long molecular axis (X-axis) is shown in Fig. 5a and b. Since, the in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. The maximum probability occurs at 4 Å separation. Translation along the Y-axis has also been studied. It has been found that minor translations along the Y-axis do not alter the total energy very drastically.

Terminal Interactions

Since the length of the molecule is approximately 21 Å, to investigate the terminal interactions apart from

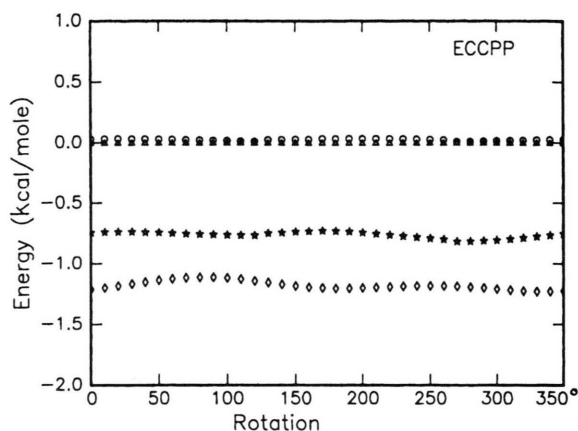


Fig. 6. Variation of the terminal interaction energy components with respect to rotation about the X-axis. Notations are as in Fig. 2a.

Table 2. Minimum energy values obtained after refinement during stacking, in-plane and terminal interactions. The energy is expressed in kcal/mole.

Energy terms	Stacking energy	In-plane energy	Terminal energy
E_{QQ}	0.27	-0.71	-0.01
E_{QMI}	-3.08	-1.29	-0.04
E_{MIMI}	-0.39	0.25	0.02
E_{el}	-3.19	-1.75	-0.03
E_{pol}	-0.99	-0.91	-0.01
E_{disp}	-10.13	-4.48	-1.17
E_{rep}	4.12	0.59	0.14
E_{total}	-10.19	-6.56	-1.08

van der Waals contacts, the interacting molecule has been shifted along the X-axis by 24 Å with respect to the fixed one and allowed to rotate about the X-axis. The interaction energy at such points has been examined. Rotation about the X-axis (Fig. 6) shows no preference for any angle, i.e. the molecules are completely free to rotate about their long molecular axis.

The most prominent energy minima of the interactions were further refined, and the values thus obtained are listed in Table 2. The results indicate that due to the planarity of the molecule stacking energies are much larger than in-plane and terminal interaction energies. This supports the earlier observations [5–7] and also the basic assumption of the molecular field theory [20–22].

The present calculation may be reasonably correlated with the mesomorphic behaviour of the system. The nematic character of liquid crystals is generally manifested by their translational freedom along the long molec-

Table 3. Comparative picture of translational and rotational rigidities during stacking, in-plane and terminal interactions between a pair of ECCPP molecules.

Temp. (K)	Translational rigidities* along X-axis		Rotational rigidities** about X-axis	
	Stacking interactions	In-plane interactions	In-plane interactions	Terminal interactions
300	1.73	1.24	0.72	0.52
373.6	1.35	1.12	0.68	0.51
507.9 N-I	1.04	0.98	0.63	0.50
550	0.89	0.95	0.62	0.50

* This has been defined as the ratio of the probability of being at the most probable point to that having ± 2 Å displacement along the long molecular axis.

** This has been defined as the ratio of the probability of being in the most probable position having $\pm 10^\circ$ rotation about the long molecular axis.

ular axis. Therefore, for stacking and in-plane interactions translations have been allowed at intervals of 2 Å and a corresponding change in interaction energies together with the probability distribution has been reported.

Table 3 shows that the ratio of the probability of being at the most probable point to that of being by ± 2 Å displaced along the long molecular axis is 1.04 at the nematic-isotropic transition temperature, while at room temperature it is 1.73, indicating a very strong binding at lower temperature. 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 for in-planar interactions. Thus, even at room temperature this ratio is 1.24, which reduces to 0.98 at the transition temperature (see Figs. 3b and 5b). Though considerable freedom exists for small translations, long translations are in general not permitted. Further, it may be observed that during terminal interactions, the molecule can rotate freely about its long molecular axis and shows 1.01 rotational rigidity at the nematic-isotropic transition temperature. Also, in-plane rotation is less restricted about the Y-axis than rotation about the Z-axis during stacking. These observations comply with the nematic character of the molecule.

Acknowledgement

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