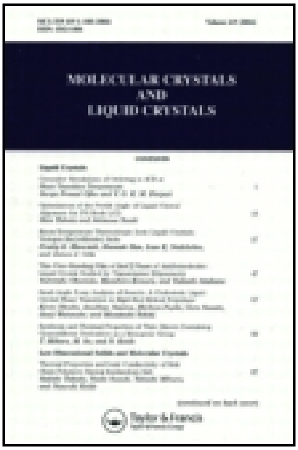

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Computer Simulations of Ordering in 4Cb at Phase Transition Temperature

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COMPUTER SIMULATIONS OF ORDERING IN 4CB AT PHASE TRANSITION TEMPERATURE

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The molecular ordering of 4′-n-butyl-4-cyanobiphenyl (4CB), a monotropic nematic liquid crystal, has been carried out at phase transition temperature with respect to translatory and orientational motions. The CNDO/2 method has been employed to compute the net atomic charge and atomic dipole moment at each atomic center. The modified Rayleigh-Schrodinger perturbation theory along with multicentered-multipole expansion method have been employed to evaluate long-range intermolecular interactions, while a 6-exp *potential function has been assumed for short-range interactions. The interaction energy values obtained through these computations were used to calculate the probability of each configuration at phase transition temperature using the Maxwell-Boltzmann formula. 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 correlated with molecular parameter introduced in this article, and an attempt has been made to explain the nematic behavior of the compounds in terms of their relative order.*

Keywords: 4CB; computer simulations; interaction energy; MB-statistics; nematogen

INTRODUCTION

The subject of phase transition is of vital interest to physicists, chemists, metallurgists, and others. This cross-disciplinary subject is not only of academic importance but is also of technological relevance [1,2]. The proper understanding of liquid crystalline behavior requires an adequate theoretical background as a precursor to application of new developments and to accounting for abnormal properties in the materials [3]. The potential

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energy of interaction of two molecules is considered as a prime requirement in the theoretical investigation of molecular interactions. This interaction determines the physical properties of liquid crystals, as well as the type of kinetics of physical and physicochemical processes taking place in these substances [4]. Furthermore, the simulation of liquid crystal phase behavior represents a major challenge despite the substantial increase in the availability of computer processing time [5–7].

The role of molecular interactions in mesogenic compounds has attracted the attention of several workers based on the Rayleigh-Schrodinger perturbation method [8,9]. These studies were aimed to compute interaction energy between a molecular pair to study the variation of interaction energy with respect to angle and distance between two molecules, but their attempts were directed towards explaining the aligned structure or, at best, correlating the minimum energy with observed crystal structure. It has been observed that the interaction energies for a pair of mesogens indicate the preference of a particular configuration over others depending on their energies, which are not directly related quantities. Hence, in order to obtain a quantitative measure for the relative preference, authors have evaluated the relative probability of occurrence of each configuration. These computations are able to provide information about the probability of the formation 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 article, we report the characteristic features of nematogenic compounds in terms of their energy and configurational probabilities between a molecular pair of 4CB molecules at an intermediate distance of 7 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 20 Å has been kept 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 range of short- and medium-range interactions. A possible explanation of liquid crystallinity of 4CB has been furnished. Furthermore, instead of finding the exact minimum energy configuration, an attempt has been made to elucidate the general behavior of the molecules surrounding a fixed molecule in a particular frame of reference.

An examination of thermodynamic data indicates that 4CB shows nematic–isotropic melt at 389.5 K [10].

SIMPLIFIED FORMULA AND COMPUTATIONAL TECHNIQUE

The molecular geometry of 4CB has been constructed on the basis of the published crystallographic data with the standard values of bond lengths and bond angles [10]. The terminal part of the butyl chain is disordered. The 4CB molecules pack in a sheetlike arrangement, with nearest neighbors oriented antiparallel to each other. The angle between the phenyl rings is $40'30'$ [10]. The calculations have been carried out in the three stages outlined below.

Evaluation of Charge and Atomic Dipole Distribution

The simplified formula for interaction energy calculations requires the evaluation of atomic charges and dipole moment components at each atomic center through an all-valence electron method. In the present computation, the CNDO/2 method [11] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule. A revised version QCPE No. 142 of program, which is an extension of the original program QCPE No. 141 for the third-row elements of the periodic table, has been used. The program language is FORTRAN IV.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [12] for the evaluation of interaction energy between a molecular pair has been used to calculate the energy for fixed configuration. The computer program INTER, originally developed by Claverie and later modified at Chemical Physics Group, Tata Institute of Fundamental Research, Bombay, India by Govil and associates has been used for this purpose, with further modification. According to the second-order perturbation theory as modified for intermediate-range interactions [12], 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 significantly affect the electrostatic interaction energy, and the calculation only up to dipole–dipole term gives satisfactory result [13]. 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 semiemperical approaches, *viz*. the Lennard-Jones or Buckingham-type approach, actually proceed in this way. Kitaigorodskii [14] introduced a Buckingham formula whose parameters were later modified by Kitaigorodskii and Mirskaya for hydrocarbon molecules and several other molecules, and finally gave the expression [15]

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

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

where $Z = R_{\lambda\nu}/R^0{}_{\lambda\nu}$; and $R^0{}_{\lambda\nu} = [(2R^w{}_\lambda)(2R^w{}_\nu)]^{1/2}$, where $R^w{}_\lambda$ and $R^w{}_\nu$ are the van der Waals radii of atom λ and ν, respectively. The parameters A, B, and γ do not depend on the atomic species. But $R^0{}_{\lambda\nu}$ and factor $K_\lambda K_\nu$ allows the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [16,17].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin on an atom has been chosen close to the center of mass of the molecule. The x axis is along a bond parallel to the long molecular axis, while the y axis perpendicular to it lies in the plane of the molecule and the z axis is perpendicular to the x–y plane of the molecule.

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:

$$P_i = exp(-\beta\varepsilon_i) / \sum_i exp(-\beta\varepsilon_i),$$

where P_i stands for probability; $\beta = 1/kT$, k is the Boltzman 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

The molecular geometry is shown in Figure 1. Computed atomic net charges and dipole moment components are listed in Table 1. The results of probability distribution based on interaction energy calculations at different modes of interactions are discussed below.

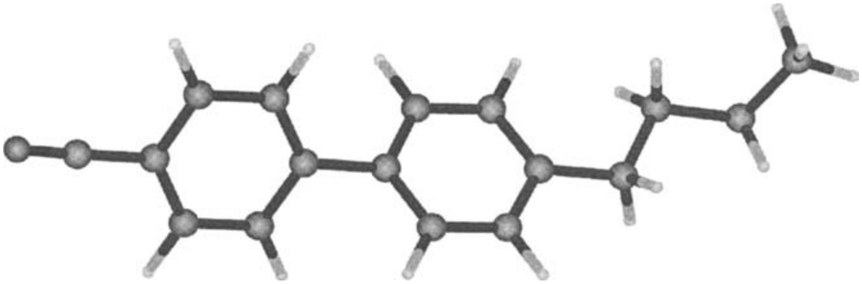

FIGURE 1 Molecular geometry of 4′-n-butyl-4-cyanobiphenyl (**4CB**).

Stacking Interactions

One of the interacting molecules is fixed in x–y plane, while the second molecule has been kept at separation of 7 Å along the z axis with respect to the fixed one. 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 range of short- and medium-range interactions.

The variation of stacking interaction energy with respect to rotation about z axis corresponding to configuration X(0°)Y(0°) has been carried out at an interval of 10°, and interaction energy at each point has been calculated. The minimum energy so obtained is then taken as starting point, and the entire process is repeated at smaller intervals. The energy has been minimized with respect to translation and rotation about x, y, and z axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to other has been achieved. The final lowest stacked geometry thus obtained at an interplanar separation of 4.06 Å with energy −9.64 kcal/mole (Fig. 2). This configuration agrees with those obtained from crystallographic studies [10]. It is important to note here that the path of minimization strictly depends on the objective of computation. The global search for minimum energy configuration or the study of variation of interaction energy under preselected conditions will have completely different paths and, therefore, one has to careful in choosing the specific route.

The variation of stacking interaction energy components with respect to rotation about x axis corresponding to configuration Y(0°)Z(180°) 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 is much smaller than the dispersion energy term.

The nematic character of liquid crystal is generally manifested by its translational freedom along the long molecular axis. Therefore, translations

TABLE 1 Calculated Atomic Net Charges and Dipole Moments Using the CNDO/2 Method for the Molecule 4CB

			Atomic dipole components		
S. No.	Atom	Charge	μ_X	μ_Y	μ_Z
1	C	0.022	0.022	0.035	0.062
2	C	− 0.001	−0.001	0.101	0.004
3	C	− 0.003	−0.003	0.001	0.012
4	C	0.026	0.026	−0.072	−0.043
5	C	− 0.012	−0.012	−0.105	0.010
6	C	− 0.005	−0.005	−0.013	−0.030
7	C	0.013	0.013	0.023	0.007
8	C	0.015	0.015	−0.007	−0.016
9	C	0.024	0.024	0.049	0.048
10	C	0.000	0.000	−0.146	−0.105
11	C	0.035	0.035	−0.062	−0.007
12	C	− 0.007	−0.007	−0.006	0.093
13	C	0.011	0.011	0.091	0.088
14	C	0.030	0.030	−0.054	0.044
15	C	0.009	0.009	−0.039	−0.123
16	C	− 0.010	−0.010	−0.105	−0.055
17	C	0.078	0.078	−0.078	0.016
18	N	− 0.163	−0.163	1.520	−0.246
19	H	0.000	0.000	0.000	0.000
20	H	− 0.001	0.000	0.000	0.000
21	H	− 0.004	0.000	0.000	0.000
22	H	0.009	0.000	0.000	0.000
23	H	− 0.008	0.000	0.000	0.000
24	H	− 0.010	0.000	0.000	0.000
25	H	− 0.004	0.000	0.000	0.000
26	H	− 0.003	0.000	0.000	0.000
27	H	0.001	0.000	0.000	0.000
28	H	0.000	0.000	0.000	0.000
29	H	− 0.008	0.000	0.000	0.000
30	H	− 0.005	0.000	0.000	0.000
31	H	− 0.009	0.000	0.000	0.000
32	H	− 0.013	0.000	0.000	0.000
33	H	− 0.002	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

have been allowed at intervals of 0.2 Å, and corresponding change in probabilities distribution are shown in Figure 3. It is evident that the stacked pair of 4CB molecules can slide one above the other in the range of $-1.8\,\text{Å} \pm 0.2\,\text{Å}$ without any significant change in the energy and thus is capable of retaining molecular order up to $-1.2\,\text{Å}$ against increased thermal agitation.

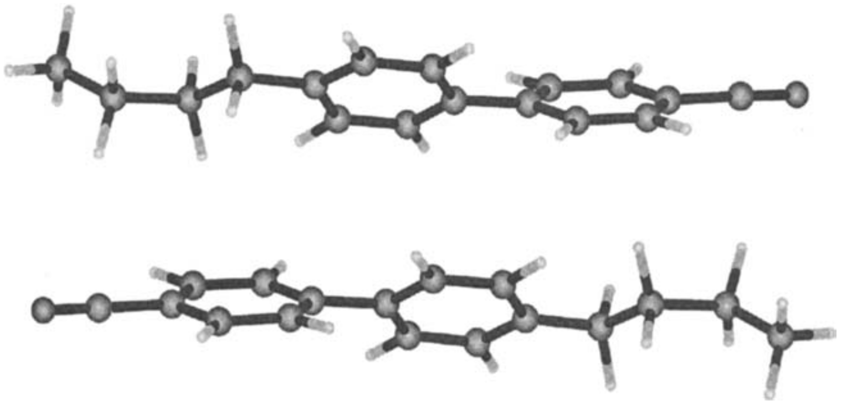

FIGURE 2 The lowest stacking energy configuration obtained with energy −9.642 kcal/mole at intermolecular separation of 4.06 Å.

In-plane Interactions

Similar calculations have been performed for in-plane interactions. The interacting molecule has been kept at separation of 8 Å along y axis with

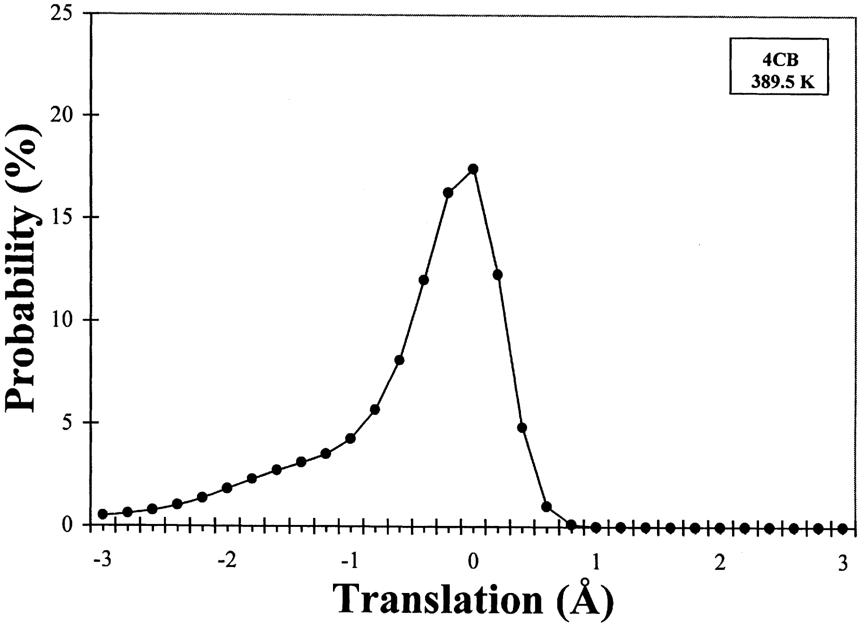

FIGURE 3 Variation of probability with respect to translation along x axis during stacking interactions at nematic–isotropic transition temperature.

respect to fixed one to avoid the possibility of van der Waals contacts completely. Again, rotations about y and x axis have been obtained, and corresponding energies have been calculated. The energy has been minimized with respect to translation and rotation about all axes. The lowest in-plane geometry thus obtained at separation of 3.87 Å with energy −4.618 kcal/mole (Fig. 4). The study of variation of in-plane interaction energy with respect to rotation about x axis corresponding to configuration Y(0°) has been carried out. 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 x axis corresponding to configuration Y(180°) is shown in Figure 5. Since the in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. Evidently, the maximum probability occurs at 1.2 Å separation. The variation of probability is almost constant for a region of −1.6 Å ± 0.6 Å, which may be correlated with the fluidity of compound maintaining their alignment in mesophase.

Terminal Interactions

The end-to-end interactions are weakest but become important when the molecule possesses polar group at either or both of the ends or if there is a possibility of hydrogen bonding. Terminal interactions are much weaker as compared to stacking or in-plane interactions. To investigate the terminal interactions apart from van der Waals contacts, the

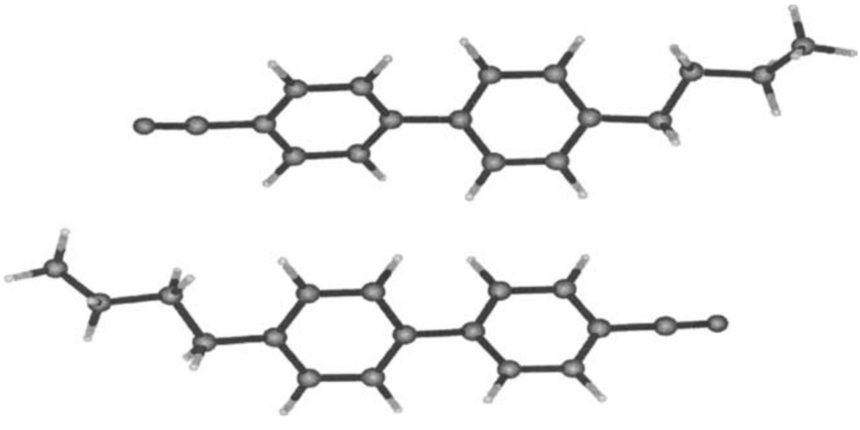

FIGURE 4 The lowest in-plane energy configuration obtained with energy −4.618 kcal/mole at intermolecular separation of 3.87 Å.

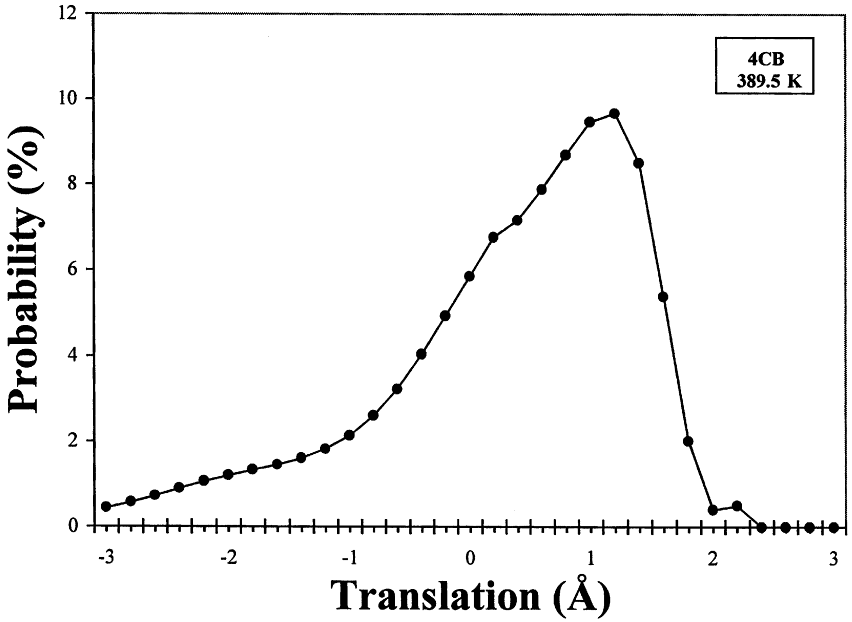

FIGURE 5 Variation of probability with respect to translation along x axis during in-plane interactions at nematic–isotropic transition temperature.

interacting molecule has shifted along the x axis by 20 Å with respect to the fixed one and rotations are allowed about x axis. The variation of probability with fixed one and rotations are allowed about x axis (Fig. 6) corresponding to configuration Y(0°) shows no preference for any angle, i.e., molecules are completely free to rotate about their long molecular axis.

The most prominent energy minima of the above-mentioned interactions are refined, and the values obtained are listed in Table 2 with all the contributory terms to enable comparison. These results indicate that the refinement corresponding to stacking energy is maximum, and the magnitude of stacking is larger than in-plane and terminal interactions.

CORRELATION OF THE RESULTS

The results may be closely examined with the translational rigidity parameter* to understand the molecular behavior in terms of their relative

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*This has been defined as the ratio of probability being at maximum probable point to having ±0.2 Å displacement along the long molecular axis.

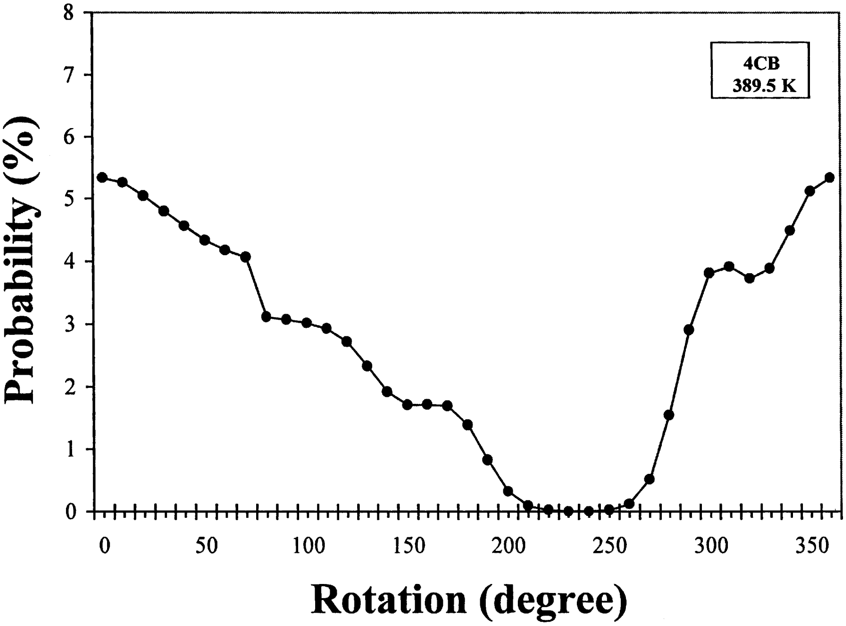

FIGURE 6 Variation of probability with respect to rotation about x axis during terminal interactions at nematic–isotropic transition temperature.

order. Figure 7 shows the translational rigidity as a function of temperature during stacking and in-plane interactions. Evidently, the translational rigidity along the long molecular axis during stacking interactions is 0.66 at nematic-isotropic transition temperature (389.5 K). However, at room temperature (300 K) the value is 0.68, indicating a strong binding, but with

TABLE 2 Stacking, In-plane, and Terminal Interaction Energy Values Between a Pair of 4CB Molecules After Refinement

Interaction energy terms	Stacking energy	In-plane energy	Terminal energy
U_{QQ}	0.131	−0.010	−0.030
U_{QMI}	−0.001	−0.003	−0.125
U_{MIMI}	−0.062	0.036	0.019
U_{el}	0.067	0.023	−0.135
U_{pol}	−0.095	−0.064	−0.343
U_{disp}	−15.469	−6.597	−1.326
U_{rep}	5.854	2.020	0.580
U_{total}	−9.642	−4.618	−1.224

Energy is expressed in kcal/mole.

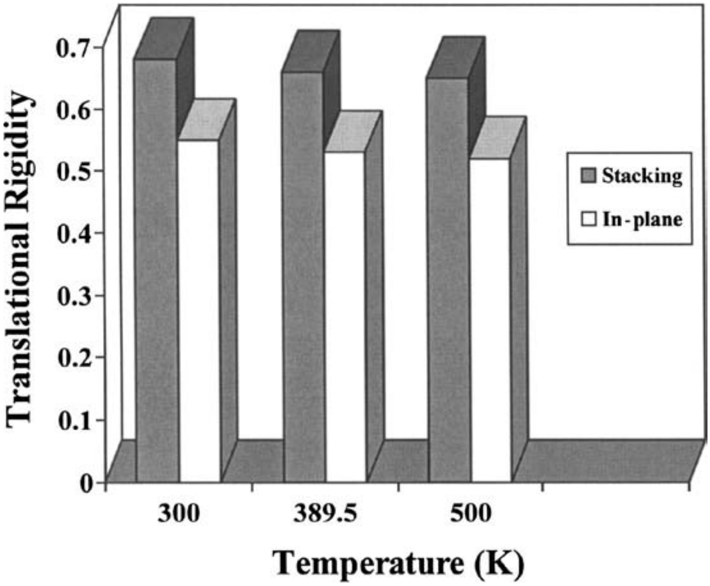

FIGURE 7 Translational rigidity parameter as a function of temperature for 4CB molecule during stacking and in-plane interactions.

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. Thus, even at room temperature this value is 0.55, which reduced to 0.53 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 the cases (i.e., stacking and in-plane interactions) indicate that the molecule 4CB does not show extraordinary preference in forming the stacked layers, hence justifying the nematic character. A comparative study on the other systems may lead to more general conclusion.

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