ORIGINAL PAPER

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A computational analysis of ordering in ABCHN at the nematic–isotropic transition

Abstract A computational analysis of ordering in the nematogenic compound 4-alkenyl bicyclohexylnitrile has been carried out based on quantum mechanics and intermolecular forces. The evaluation of atomic charge and dipole moment at each atomic center has been carried out using the complete neglect differential overlap (CNDO/2) method. Modified Rayleigh–Schrodinger perturbation theory along with a multicentered- multipole expansion method has been employed to evaluate 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 (300 K), the nematic–isotropic transition temperature (364.7 K) and above transition temperature (450 K) using the Maxwell–Boltzmann formula. The various possible configurations during the different modes (i.e., stacking, in-plane and terminal) of interactions have been studied in terms of variation of probability due to small departures from the most probable configurations. An attempt has been made to analyze the characteristic features of liquid crystallinity in terms of their relative order with molecular parameters introduced in this paper.

Keywords ABCHN · Nematogen · CNDO/2 method · Quantum chemistry

Introduction

The study of liquid crystals draws together practitioners of a number of disciplines, most notably physicists, chemists and chemical engineers [1]. The progress of research in this material is so rapid due to the great variety of phenomena exhibited by liquid crystals and partly because of the enormous commercial interest and importance of liquid crystal displays [2]. In recent years, the focus has been laid on the investigation of new liquid crystal materials with differing molecular chemistry in order to study their viability in technological applications [3–5]. The proper understanding of liquid crystalline behavior requires an adequate theoretical background as a precursor to the application of new developments and to accounting for abnormal properties in the materials. The potential energy of interaction of two molecules is considered as a prime requirement in the theoretical investigation of molecular interactions. This interaction determines the positional and orientational order of the mesomorphic compounds, as well as the type of kinetics of physical and physicochemical process taking place in these substances. The cycle of mesomorphism (heating or cooling) and transition temperatures is governed by the intermolecular forces, which act between sides, planes and ends of a pair of molecules [6].

The key role of molecular interactions in mesomorphic compounds has attracted the attention of several workers [7–10] based on the Rayleigh–Schrodinger perturbation method. 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. Thus, the main emphasis was laid on finding out 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 the other depending on their energies, which are not directly related quantities. Hence, in order to obtain a qualitative measure for the relative preference, the author has evaluated the relative probability of occurrence of each configuration. These computations are able to provide information about the probability of dimer complexes, the relative freedom of a molecule in terms of variation in inclination, separation or sliding of one molecule over the other.

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The system 4-alkenyl bicyclohexylnitrile (ABCHN) chosen for the present investigation is quite interesting because the introduction of a double bond in specific positions along the terminal chain markedly affects the properties of the liquid crystalline homologous series, ABCHN [11]. The molecular geometry is shown in Fig. 1.

The present work deals with the computation of pair energies and configurational probabilities between a pair of ABCHN molecules at an intermediate distance of 6 Å for stacking and 8 Å in-plane interactions. Similarly, a distance of 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. Further, instead of finding the exact minimum energy configuration, a step has been put forward to elucidate the general behavior of the molecules surrounding a fixed molecule in a particular frame of reference. The terms like stacking, in-plane and terminal interactions are used to maintain continuity with previous work [12].

The thermodynamic data indicates that ABCHN gives a nematic to isotropic transition at 364.7 K [11].

The basic formalism and computational details

The molecular geometry of ABCHN was constructed on the basis of the published crystallographic data with the standard values of bond lengths and bond angles [11]. In order to achieve the interaction picture of a pair of mesogenic molecules, the following computations were carried out.

Evaluation of charge and atomic dipole distribution

The simplified formula for interaction energy calculations requires the evaluation of atomic charges [13] and dipole-moment components at each atomic center through an all-valence electron method. In the present computation, the CNDO/2 method [13] has been used to compute the net atomic charge and dipole moment at each atomic center of the molecule. These are equivalent to Lowdin orthogonalized orbital charges [14, 15]. A revised version of QCPE program No. 142, 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 the simplified formula provided by Claverie [16] for the evaluation of the interaction energy between a molecular pair has been used to calculate the energy for fixed configurations. The computer program INTER, originally developed by Claverie and later modified at the Chemical Physics Group, Tata Institute of Fundamental Research, Bombay, India, by Govil and associates has been used for this purpose with further modifications. According to second order perturbation theory as modified for intermediate range interactions, [16] the total pair interaction energy of molecules (U_{pair}) is represented as the sum of various terms contributing to the total energy:

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

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

Again, the electrostatic term is expressed as

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

where U_{QQ}, U_{QMI} and 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 up to only the dipole–dipole term gives satisfactory results [17]. The computation of the electrostatic term has, therefore, been restricted up to only the dipole–dipole energy term.

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. Kitaigorodsky [18] introduced a Buckingham formula whose parameters were later modified by Kitaigorodsky and Mirskaya [18] for hydrocarbon molecules and several other molecules and finally gave the expression:

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

$$U(\lambda, v) = K_\lambda K_v \left(-\frac{A}{Z^6} + B e^{-\gamma Z} \right)$$

Fig. 1 Molecular geometry of ABCHN

where $Z = R_{\lambda\nu}/R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^w_\lambda)\,(2R^w_\nu)]^{1/2}$, where R^w_λ and R^w_ν are the van der Waals radii of atoms λ and ν, respectively. The parameters A, B and γ do not depend on the atomic species. However, $R^0_{\lambda\nu}$ and factor $K_\lambda K_\nu$ allow the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [18].

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 along a bond parallel to the long molecular axis while the y-axis perpendicular to it lies in the plane of the molecule and z-axis perpendicular to the x–y plane of 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 better insight:

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

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

Results and discussion

The computed atomic net charges and dipole moment components are listed in Table 1. These are CNDO charges [13] and are equivalent to Lowdin orthogonalized orbital charges [14, 15]. The results of probability distributions based on the interaction-energy calculations during the different modes of interactions are discussed below.

Stacking interactions

In a molecular pair, one of the interacting molecules is fixed in the x–y plane while the second is kept at a separation of 6 Å along the z-axis with respect to the fixed one. The variation of probability with respect to rotation about the z-axis is shown in Fig. 2 corresponding to configuration $x(0°)y(0°)$ at room temperature, transition temperature and above transition temperature. This figure reveals that the maximum probability corresponds to the ABCHN molecule at an equilibrium position. The minimum energy thus obtained is then taken as the starting point and the entire process is repeated for small intervals. The energy is

minimized with respect to translations and rotations about x, y and z-axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other was achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. The global search for the minimum-energy configuration or the study of variation of interaction energy under pre-selected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route.

A graphical representation of the probability distribution with respect to translation along the long molecular axis (x-axis) corresponding to configuration $y(0°)z(180°)$ is shown in Fig. 3. 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 -0.8 ± 0.2 Å, which shows that sliding one molecule over the other is energetically allowed for a small range that may be correlated with the fluidity of the compound maintaining its alignment in the mesophase.

Again, the variation of probability with respect to rotation about the x-axis corresponding to configuration $y(0°)z(0°)$ has been carried out as shown in Fig. 4 at room temperature, the transition temperature and above the transition temperature. The maximum probability corresponds to an equilibrium position indicating a slight preference for the aligned structure of this configuration. Further, it may be observed that the rotational rigidity about the long molecular axis is less at the nematic–isotropic transition temperature (364.7 K). However, at room temperature (300 K) strong binding is observed 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 was kept at a separation of 8 Å along the y-axis with respect to the fixed one. Similar calculations were performed for in-plane interactions. Figure 5 shows the results with respect to translation along the long molecular axis corresponding to configuration $y(0°)$ at room temperature, the transition temperature and above the transition temperature. It may be observed that the translation freedom is much more pronounced than the stacking interactions. Further, the rotation about x-axis was carried out as shown in Fig. 6 corresponding to configuration $y(180°)$.

Evidently, 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 the y-axis corresponding to configuration $x(180°)$ at room temperature, the transition temperature and above the transition temperature.

Table 1 Calculated atomic net charges and dipole moments for ABCHN molecule

S. no.	Atom	Charge	Atomic dipole components		
			μ_X	μ_Y	μ_Z
1	C	0.030	0.038	0.023	−0.007
2	C	0.012	−0.060	0.098	−0.015
3	C	0.013	−0.023	0.080	−0.135
4	C	0.042	−0.031	−0.012	0.045
5	C	0.020	0.061	−0.093	0.011
6	C	0.013	0.074	0.016	0.068
7	C	−0.006	0.036	−0.005	−0.042
8	C	−0.013	−0.035	−0.001	0.066
9	C	0.023	0.075	−0.052	−0.026
10	C	0.027	−0.068	0.089	0.018
11	C	−0.009	−0.056	−0.146	0.003
12	C	0.031	−0.029	−0.049	0.022
13	C	0.012	−0.090	−0.053	−0.064
14	C	0.021	−0.139	0.086	−0.001
15	C	0.044	−0.060	−0.093	−0.034
16	C	0.021	0.120	−0.048	0.131
17	C	0.005	0.067	−0.065	0.010
18	C	0.077	−0.003	−0.067	−0.070
19	N	−0.172	0.580	1.682	0.266
20	H	−0.015	0.000	0.000	0.000
21	H	−0.011	0.000	0.000	0.000
22	H	−0.001	0.000	0.000	0.000
23	H	−0.018	0.000	0.000	0.000
24	H	−0.001	0.000	0.000	0.000
25	H	−0.018	0.000	0.000	0.000
26	H	−0.013	0.000	0.000	0.000
27	H	−0.005	0.000	0.000	0.000
28	H	−0.013	0.000	0.000	0.000
29	H	−0.005	0.000	0.000	0.000
30	H	−0.009	0.000	0.000	0.000
31	H	−0.008	0.000	0.000	0.000
32	H	−0.003	0.000	0.000	0.000
33	H	−0.007	0.000	0.000	0.000
34	H	−0.008	0.000	0.000	0.000
35	H	−0.008	0.000	0.000	0.000
36	H	0.001	0.000	0.000	0.000
37	H	−0.003	0.000	0.000	0.000
38	H	0.001	0.000	0.000	0.000
39	H	−0.015	0.000	0.000	0.000
40	H	−0.010	0.000	0.000	0.000
41	H	−0.004	0.000	0.000	0.000
42	H	−0.006	0.000	0.000	0.000
43	H	0.000	0.000	0.000	0.000
44	H	0.002	0.000	0.000	0.000
45	H	−0.004	0.000	0.000	0.000
46	H	0.000	0.000	0.000	0.000
47	H	−0.008	0.000	0.000	0.000
48	H	−0.000	0.000	0.000	0.000

These are CNDO charges and are equivalent to Lowdin orthogonalized orbital charges

It is evident from the figure that rotation about the y-axis does not alter the configuration probability drastically.

Terminal interactions

To investigate the terminal interactions away from the van der Waals contacts, the interacting molecule was shifted along the x-axis by 22 Å. The terminal interactions are much weaker as compared to stacking or in-plane interactions. Figure 8 shows the results of rotations about the x-axis corresponding to configuration $y(0°)$. In this case, molecules are completely free to rotate about their long molecular axis. The various possible geometrical arrangements between a molecular pair during the different modes of interactions were considered that provide information about the molecular arrangements inside the bulk materials.

Further, it is clear from the above discussion (at different modes of interactions) that in a molecular assembly, a number of local minimum-energy configurations exist. Each of them has their own importance as in the case of close molecular packing. Any molecule, depending on
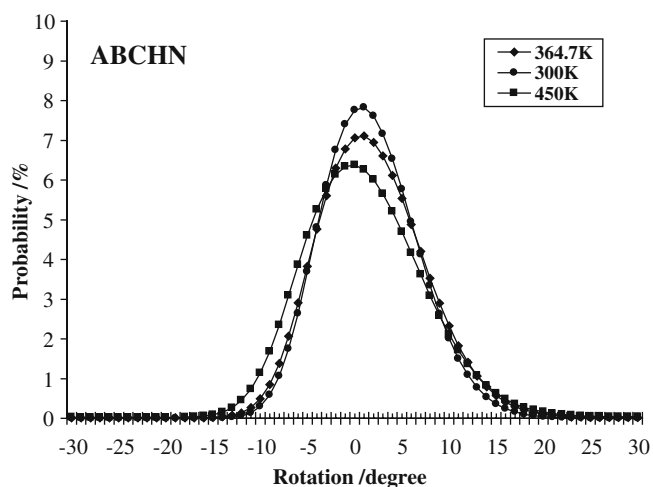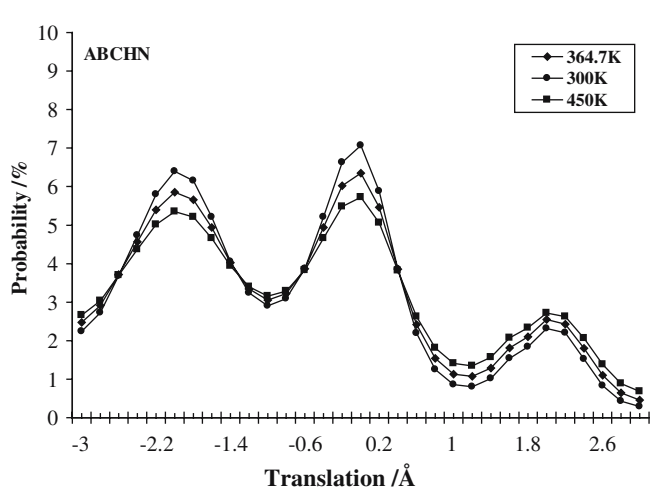
Fig. 2 Variation of probability with respect to rotation about *z*-axis corresponding to configuration $x(0°)y(0°)$ during stacking interactions at nematic–isotropic transition temperature (364.7 K), room temperature (300 K) and above transition temperature (450 K)
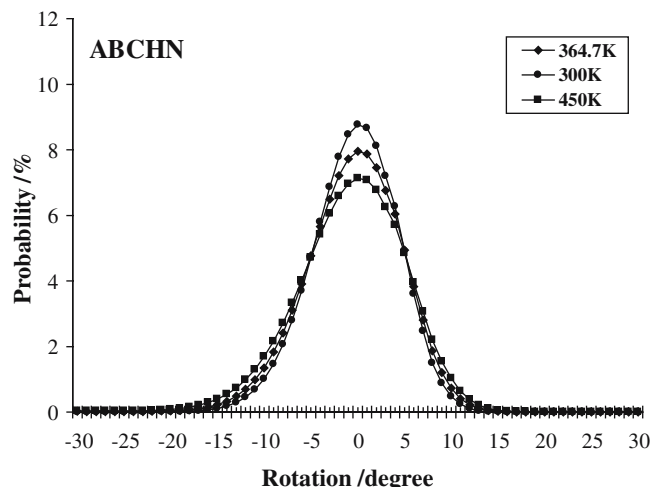
Fig. 4 Variation of probability with respect to rotation about *x*-axis corresponding to configuration $x(0°)z(0°)$ during stacking interactions at nematic–isotropic transition temperature (364.7 K), room temperature (300 K) and above transition temperature (450 K)
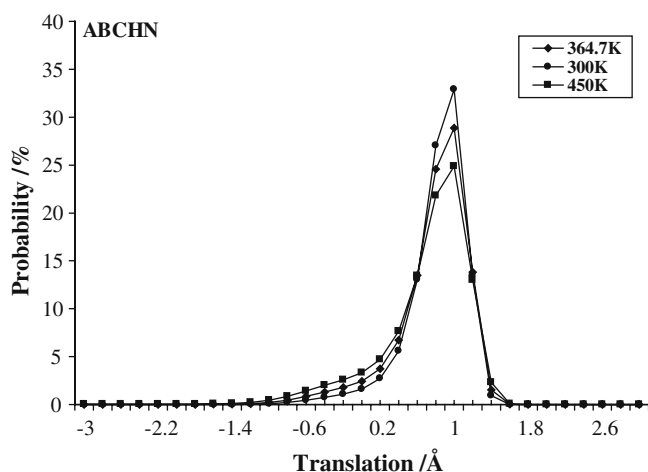
Fig. 3 A graphical representation of probability distribution with respect to translation along *x*-axis corresponding to configuration $y(0°)z(180°)$ during stacking interactions at nematic-isotropic transition temperature (364.7 K), room temperature (300 K) and above transition temperature (450 K)

Fig. 5 Variation of probability with respect to translation along *x*-axis corresponding to configuration $y(0°)$ during in-plane interactions at nematic–isotropic transition temperature (364.7 K), room temperature (300 K) and above transition temperature (450 K)

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 down from a very high temperature where the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy and the other minima have sequential preference depending on their individual relative probabilities.

Correlation of results with nematic character

In order to examine the results more closely, the translational rigidity parameter was calculated and an attempt made to understand the molecular behavior in terms of their relative order. The nematic character of liquid crystals is generally manifested by their translational freedom along the long molecular axis. Therefore, for stacking and in-plane interactions, translations were allowed at an interval of 0.2 Å and the corresponding change in probabilities reported.

Figure 9 shows the translational rigidity parameter [19] as a function of temperature during stacking and in-plane interactions. Evidently, the translational rigidity along the long molecular axis is 0.75 at the nematic–isotropic transition temperature (364.7 K). However, at room temperature (300 K), the value is 0.81, indicating strong binding at low temperatures.
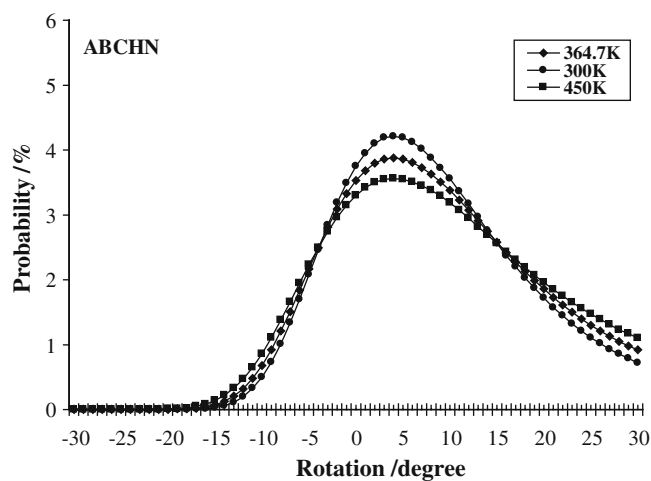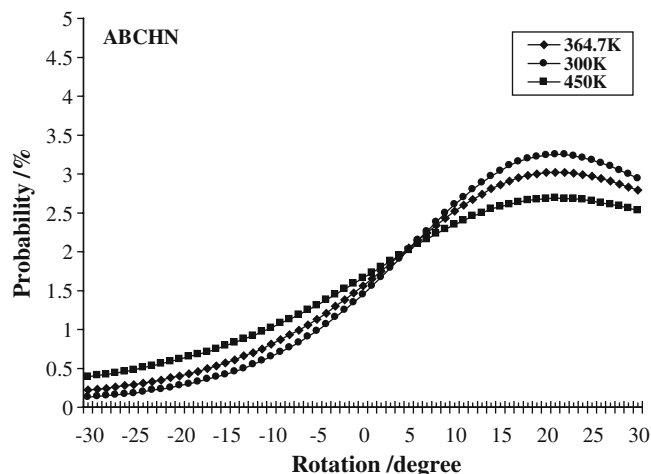
Fig. 6 Variation of probability with respect to rotation about *x*-axis corresponding to configuration *y*(180°) during in-plane interactions at nematic–isotropic transition temperature (364.7 K), room temperature (300 K) and above transition temperature (450 K)
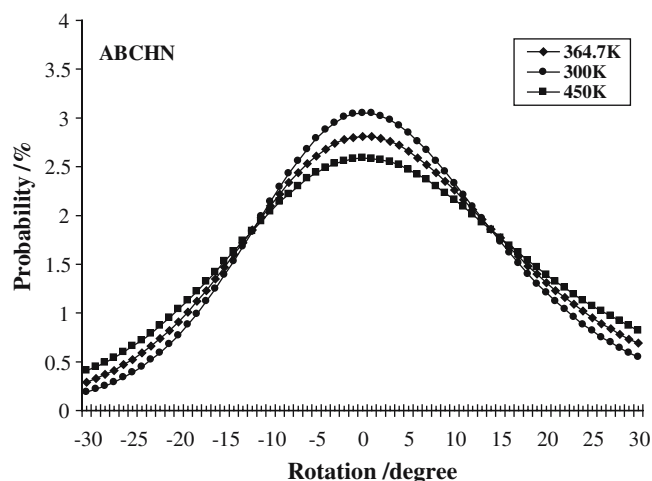
Fig. 8 Variation of probability with respect to rotation about *x*-axis corresponding to configuration *y*(0°) during terminal interactions at nematic–isotropic transition temperature (364.7 K), room temperature (300 K) and above transition temperature (450 K)

Fig. 7 Variation of probability with respect to rotation about *y*-axis corresponding to configuration *x*(180°) during in-plane interactions at nematic–isotropic transition temperature (364.7 K), room temperature (300 K) and above transition temperature (450 K)
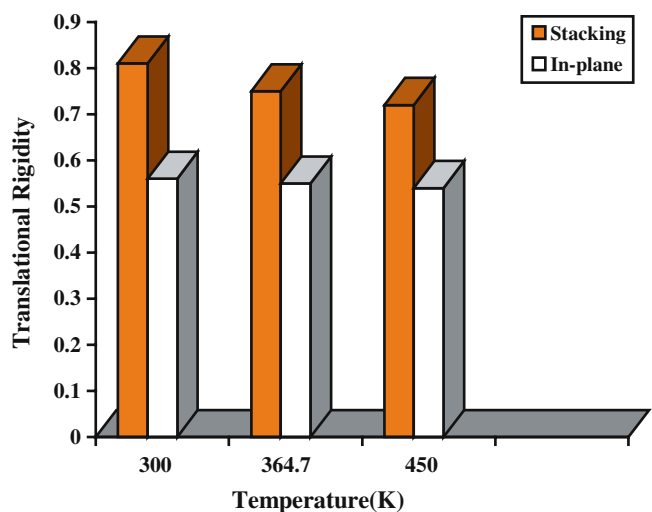
Fig. 9 Translational rigidity parameter as a function of temperature during stacking and in-plane interactions at room temperature, transition temperature and above-transition temperature

However, with 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 0.56, which reduced to 0.55 at the nematic–isotropic transition temperature (364.7 K). It may be noted that, though the freedom is considerable for smaller translation, longer translations are not permitted in general. Thus, small movements of molecules are only possible in the mesomorphic range. However, the comparable values in the two cases (*i.e.,* *stacking and in-plane interactions*) show that the molecule ABCHN does not show extraordinary preference

in forming the stacked layers, hence justifying the nematic character.

Conclusion

The present computations are able to provide information about the probability of dimer complexes, the relative freedom of a molecule in terms of variation in inclination, separation or sliding of one molecule over the other. Further, the translation effect shows the flexibility of configuration at a particular temperature, which has an indirect relation with the phase-transition property.

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