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Ordering of *p*-*n*-alkoxybenzoic acids at phase transition temperatures: a comparative computational analysis

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Abstract A comparative analysis of molecular ordering of nematogenic *p*-*n*-alkoxybenzoic acids has been carried out with respect to translatory and orientational motions for the acids with seven (7OBAC), eight (8OBAC), nine (9OBAC) and 10 (10OBAC) carbon atoms in the alkyl chain. The CNDO/2 method has been used to compute the net atomic charge and dipole moment components at each atomic center. Modified Rayleigh–Schrodinger perturbation theory with multicentered–multipole expansion method has been used 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 by these computations were used to calculate the probability of each configuration at the phase-transition temperature using the Maxwell–Boltzmann formula. The flexibility of various configurations has been studied in terms of variation of probability due to small departures from the most probable configuration. A comparative picture of molecular parameters like total energy, binding energy and total dipole moment has been given. An attempt has been made to explain the nematogenicity of these acids in terms of their relative order with the molecular parameter introduced in this paper.

Keywords OBAC · CNDO/2 method · Nematogens · Computer simulation

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Introduction

The alkoxybenzoic acids are of structural interest because some members of this series show liquid crystalline behavior on melting. This series represents thermodynamically, one of the groups of materials that form mesophases. The first two members of this series, the methoxy- and ethoxy-substituted benzoic acids, do not show any mesophase, neither in the heating nor in the cooling cycle. However, the propyl to hexyl derivatives of benzoic acids show only a nematic mesophase. Further, for the heptyl to tridecyl derivatives, both smectic and nematic mesophase are observed and solid–solid transitions appear in the case of molecules with even carbon numbers [1].

The majority of mesogenic molecules is composed of an aromatic core to which one or two alkyl chains are attached. 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 [2]. The proper understanding of liquid crystalline behavior requires an adequate theoretical background as a precursor to applications of new materials and to account for abnormal properties in the materials [3]. Further, the simulation of liquid–crystal phase behavior represents a major challenge despite the substantial increase in the availability of computer processing time [4–7]. The potential energy of interaction of two molecules is considered as a prime requirement in the theoretical investigation on molecular interactions. This interaction determines the physical properties of liquid crystals, as well as the type of physical and physicochemical process taking place in these substances [8].

The role of molecular interactions in mesogenic compounds has attracted the attention of several workers [8–10] based on Rayleigh–Schrodinger perturbation theory. These studies were designed to compute the interaction energy between a molecular pair to study the variation of the interaction energy with respect to angle and distance

between two molecules. This work was 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 a preference of a particular configuration over the other 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 dimers, the relative freedom of a molecule in terms of variation in inclination, separation or sliding of one molecule over the other, etc.

In the present paper, we report a comparative analysis of the characteristic features of *p*-*n*-alkoxybenzoic acids (7OBAC, 8OBAC, 9OBAC and 10OBAC) in terms of pair energies and complete configurational probabilities for a molecular pair at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions. This distance has been chosen to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the short- and medium-range interactions.

The general feature of all these molecules is that they possess a polarizable aromatic ring associated with two highly electronegative atoms at one end and the long-alkoxy chain at the other end. The thermodynamic parameters reveal that the molecules show nematic to isotropic transition temperature as given below [11]:

7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K, and 10OBAC at 416 K

Simplified formula and computational technique

The molecular geometries of 7OBAC, 8OBAC, 9OBAC and 10OBAC were constructed on the basis of published crystallographic data with standard values of bond lengths and bond angles [11]. Depending on the property of interest, a number of following methodologies were used in this work as described below.

Computation of atomic net charge and dipole moments

The simplified formula for interaction energy calculations requires the evaluation of atomic net charges and dipole moment components at each atomic center through an all-valence electron method. In the present computation, the CNDO/2 method [12] was used to compute the net atomic charge and dipole moment at each atomic center of the molecule. A revised version of the QCPE program 142, which is an extension of the original program QCPE No. 141 for the third row elements of periodic table, was used. The program language is FORTRAN IV.

Computation of interaction energy at various configurations

A detailed computational scheme based on a simplified formula provided by Claverie [13] for evaluating the interaction energy between a molecular pair was 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 was used for this purpose with further modification. According to the second order perturbation theory as modified by Caillet and Claverie [14] for intermediate range interactions, the total pair-interaction energy of molecules (U_{pair}) is represented as sum of various terms contributing to the total energy:

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

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

$$U_{\text{el}} = U_{\text{QQ}} + U_{\text{QMI}} + U_{\text{MIMI}} + \dots$$

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 results [15]. The computation of the electrostatic term has, therefore, been restricted only up to the dipole–dipole energy terms.

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 approaches, actually proceed in this way. Kitaygorodsky [16] introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [16] for hydrocarbon molecules and several other molecules and finally gave the expression:

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

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

where $Z = \frac{R_{\lambda\nu}}{R_{\lambda\nu}^0}$; $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$, where R_{λ}^w and R_{ν}^w 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. But $R_{\lambda\nu}^0$ 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 [16].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin on an atom has

been chosen at almost the midpoint of the molecule. The x -axis lies along a bond parallel to the long molecular axis while the y -axis lies in the plane of the molecule and the z -axis 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 [17] in order to obtain a better insight:

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

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.

Fig. 1 Molecular geometries of
a 7OBAC b 8OBAC c 9OBAC d
10OBAC

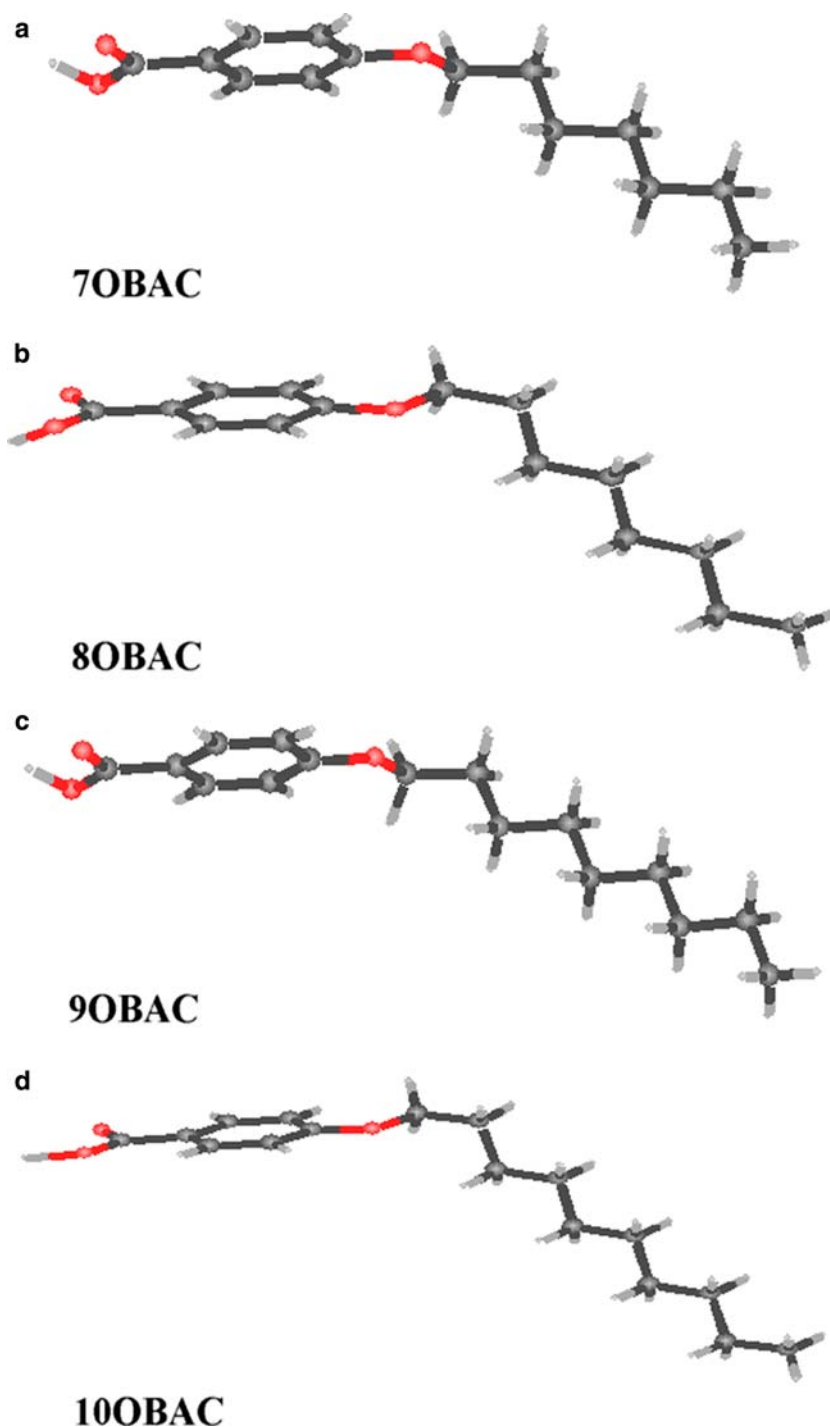
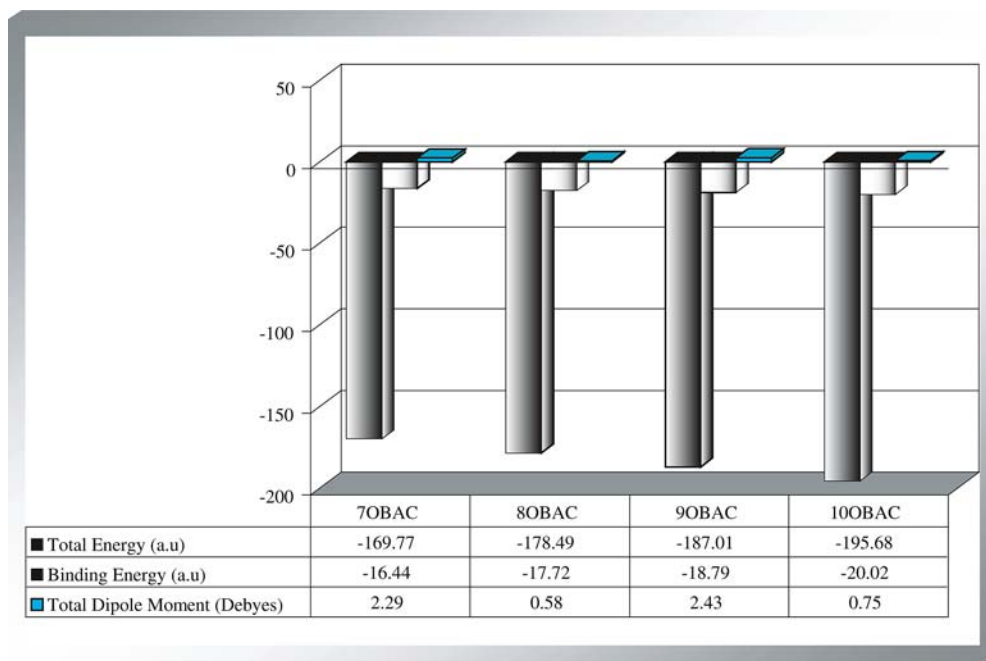


Fig. 2 A comparative picture of total energy, binding energy and total dipole moment of the 7OBAC, 8OBAC, 9OBAC and 10OBAC molecules



Results and discussion

The molecular geometries of 7OBAC, 8OBAC, 9OBAC and 10OBAC are shown in Fig. 1. Figure 2 shows a comparative picture of the total energy, binding energy and total dipole moments of *p*-*n*-alkoxybenzoic acids with 7, 8, 9, and 10 carbon atoms in the alkyl chain.

The results for the probability distributions based on interaction energy calculations at different modes of interactions are discussed below.

Stacking interactions

In a molecular pair, one of the interacting molecules was fixed in the *x*-*y* plane, while the second was 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 corresponding to configuration $x(0^\circ)y(0^\circ)$ at the nematic–isotropic transition temperature is shown in Fig. 3. It reveals that the maximum probability of the molecules corresponds to 9OBAC at 1° rotation. The minimum energy thus

Fig. 3 Variation of probability with respect to rotation about *z*-axis during stacking interactions at the nematic–isotropic transition temperature (7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K and 10OBAC at 416 K)

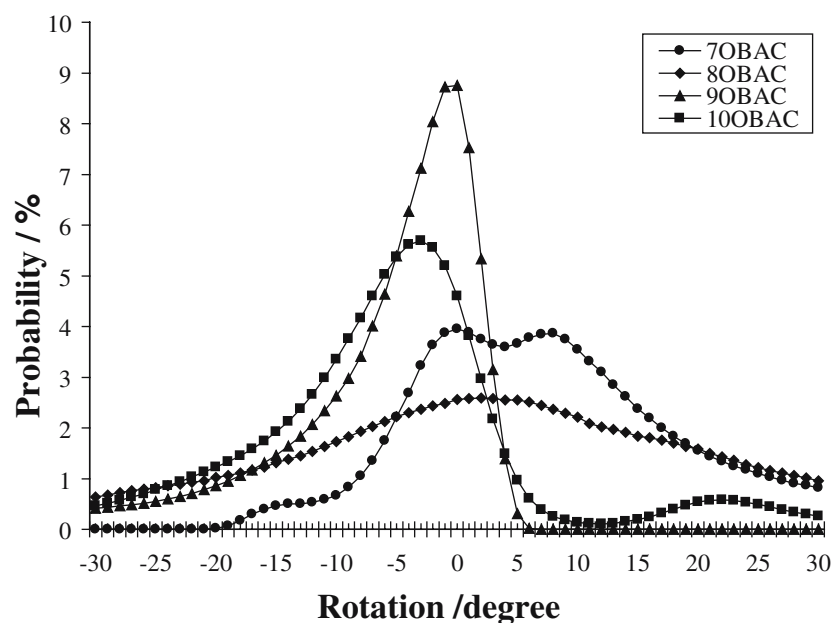
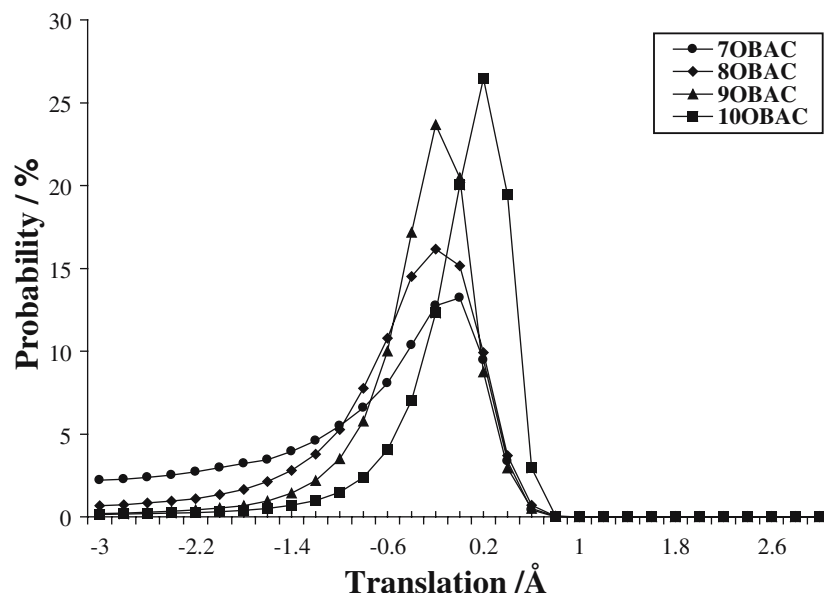


Fig. 4 Variation of probability with respect to translation along x -axis during stacking interactions at the nematic–isotropic transition temperature (7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K and 10OBAC at 416 K)



obtained in each molecule is then taken as starting point and the entire process is repeated for small intervals. The energy was minimized with respect to translation and rotation about all 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 that the path of minimization strictly depends on the objective of computation. The global search for the minimum energy configuration or the study of the variation of the interaction energy under pre-selected conditions have completely different paths and, therefore, one has to be careful in choosing the specific route.

The variation of probability with respect to translation along the long molecular axis (the x -axis) corresponding to configuration $y(0^\circ)z(180^\circ)$ is shown in Fig. 4

for the 7OBAC, 8OBAC, 9OBAC and 10OBAC molecules. It may be observed that the configurations show a sharp preference towards the minimum energy point at the nematic–isotropic transition temperature. The variation of probability is almost constant in the region of 1.8 ± 0.8 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 mesophase.

Figure 5 shows the variation of probability with respect to rotation about the x -axis corresponding to the configuration $y(0^\circ)z(0^\circ)$ at nematic–isotropic transition temperature. The maximum probability corresponds to 7OBAC and 9OBAC at their initial positions while the maximum probability for 8OBAC and 10OBAC is found at the equilibrium position, indicating a slight

Fig. 5 Variation of probability with respect to rotation about x -axis during stacking interactions at the nematic–isotropic transition temperature (7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K and 10OBAC at 416 K)

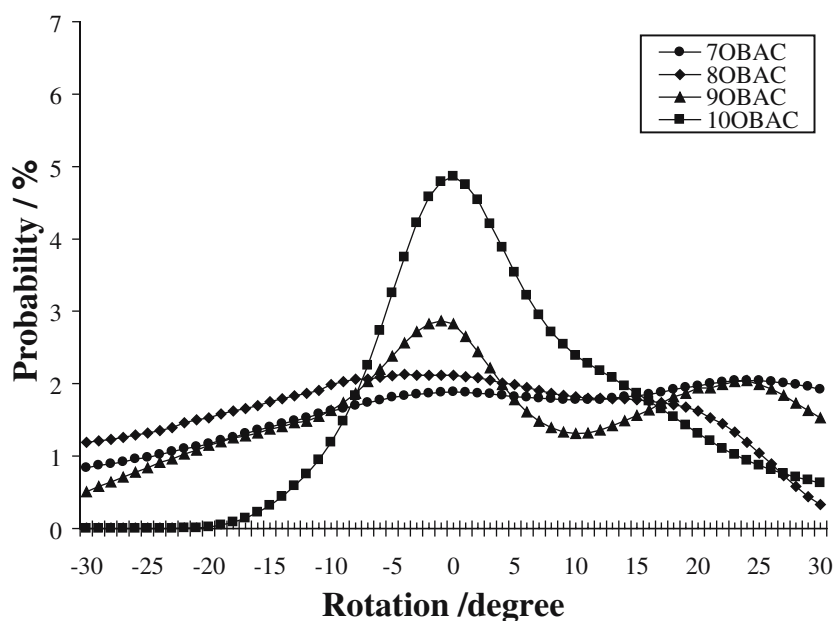
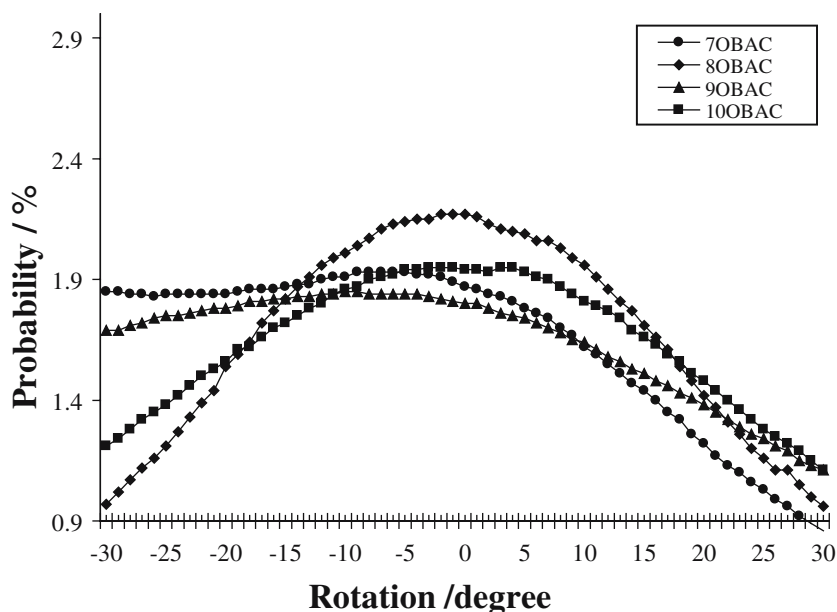


Fig. 6 Variation of probability with respect to rotation about x -axis during in-plane interactions at the nematic–isotropic transition temperature (7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K and 10OBAC at 416 K)



preference for the aligned structure in this configuration. Further, it may be observed that the rotational rigidity about the long molecular axis is lower at the nematic–isotropic transition temperature, whereas at room temperature (300 K) the observed value indicates a strong binding. However, with increasing 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 6 shows the variation of probability with respect to rotation about the x -axis, corresponding to configuration $y(0^\circ)$. Evidently, no pronounced peak exists at an equilibrium point and all the remaining regions have negligible probability as compared to this configuration. Further, it may be observed that the rotational freedom is much more pronounced as compared to the stacking interactions.

The effect of translation along the x -axis, corresponding to configuration $y(0^\circ)$ at the nematic–isotropic transition temperature is shown in Fig. 7. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. It is evident from the figure that the maximum probability occurs at an equilibrium position. Having refined the interacting configuration with respect to

Fig. 7 Variation of probability with respect to translation along x -axis during in-plane interactions at the nematic–isotropic transition temperature (7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K and 10OBAC at 416 K)

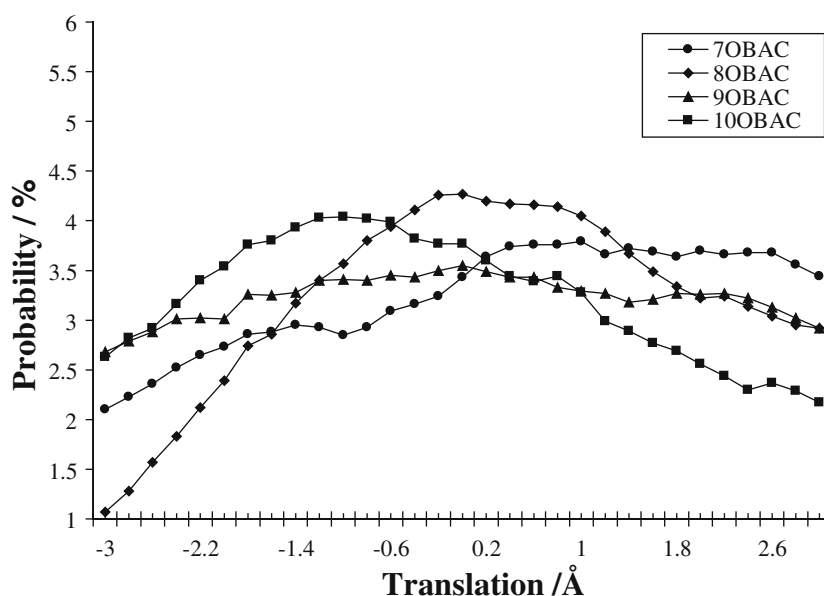
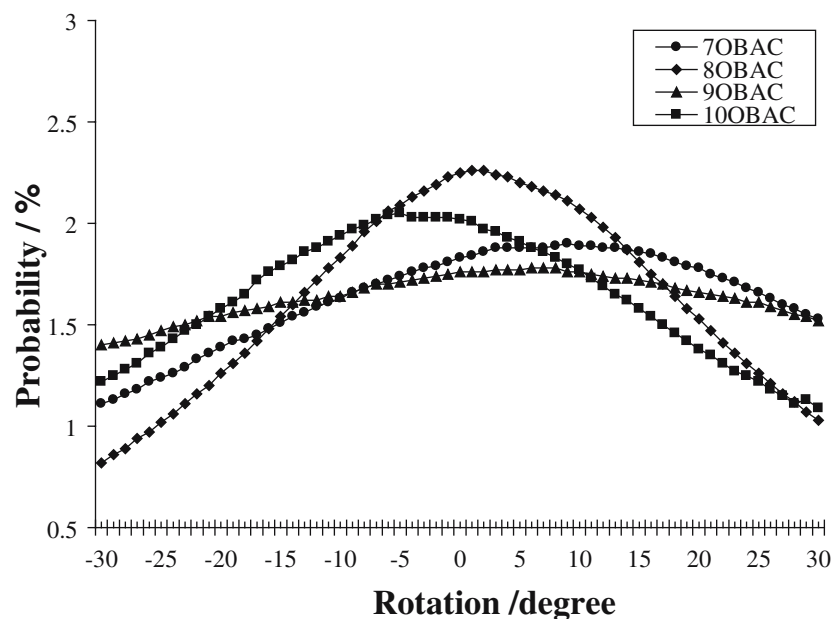


Fig. 8 A graphical representation of probability with respect to rotation about y -axis during in-plane interactions at the nematic–isotropic transition temperature (7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K and 10OBAC at 416 K)



translation along the x -axis at an equilibrium condition, the energy is brought down and the probability is further investigated with respect to rotation about the y -axis.

A graphical representation of the probability with respect to rotation about the y -axis corresponding to configuration $x(180^\circ)$ is shown in Fig. 8. Evidently, the rotation about the y -axis does not alter the total energy or configurational probability drastically.

Terminal interactions

The end-to-end interactions are weakest but become important when the molecules possess a polar group

either on both ends or if there is a possibility of hydrogen bonding. To investigate the terminal interactions away from van der Waals contacts, the interacting molecule was shifted along the x -axis by 22 Å. The terminal interactions are much weaker than the stacking and in-plane interactions. The rotation about the x -axis (Fig. 9) shows no preference for any angle. Further, it has been observed that the refined interaction energies corresponding to different modes of interactions in the interacting pairs of 7OBAC, 8OBAC, 9OBAC and 10OBAC molecules comes from dispersion forces. Further, the various possible geometrical arrangements between a molecular pair have been considered.

Fig. 9 Variation of probability with respect to rotation about x -axis during terminal interactions at the nematic–isotropic transition temperature (7OBAC at 420 K, 8OBAC at 419 K, 9OBAC at 416 K and 10OBAC at 416 K)

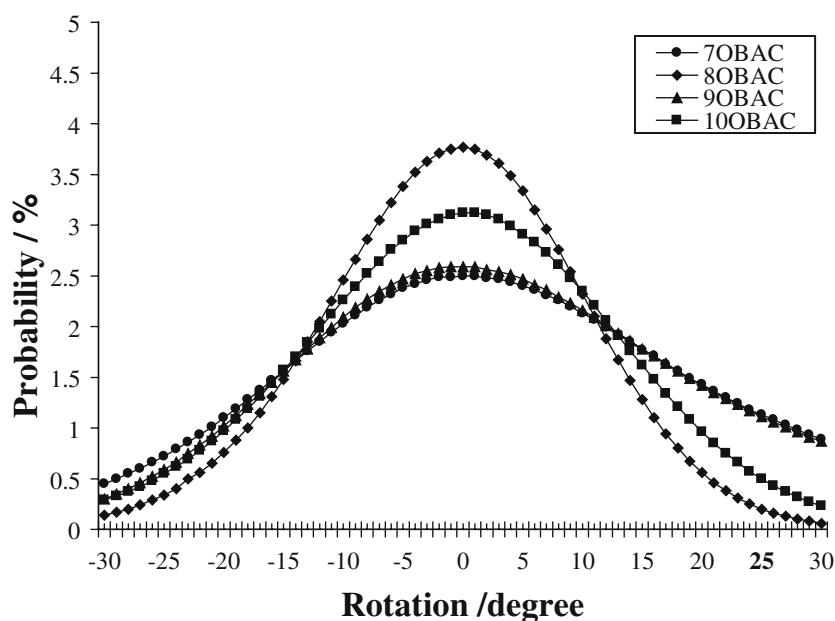
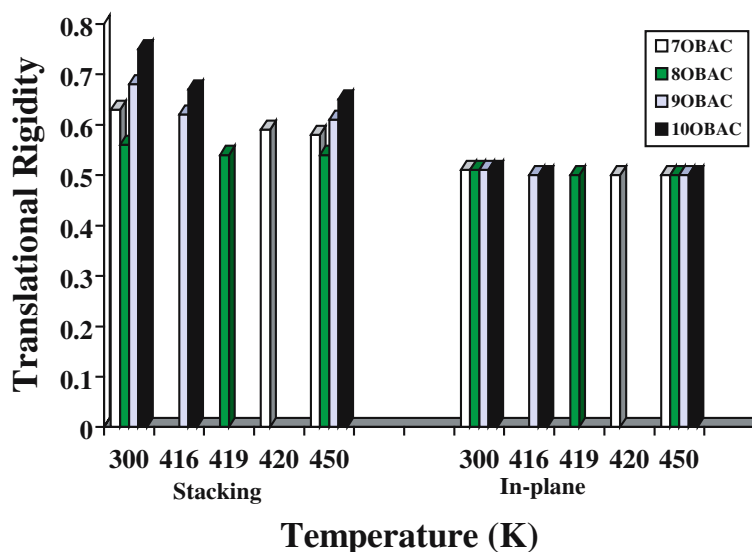


Fig. 10 Translational rigidity parameter as a function of temperature (i.e. room temperature, transition temperature and above transition temperature) during stacking and in-plane interactions



Translational effect

The nematic character of liquid crystals is generally manifested by their translational freedom along the long molecular axis. Therefore, translations were allowed in an interval of 0.2 Å and the corresponding change in probabilities reported.

Figure 10 shows the translational rigidity parameter¹ as a function of temperature during stacking and in-plane interactions. Evidently, the translational rigidity along the long molecular axis is 0.59 at the nematic–isotropic transition temperature (420 K) for 7OBAC. However, at room temperature (300 K), the value is 0.63, indicating strong binding at lower temperatures. However, with increasing temperature, the molecules obtain sufficient freedom to slide along the long molecular axis. Similar to the case discussed above for 7OBAC, the gross nature of rigidity also remains unchanged for 8OBAC, 9OBAC and 10OBAC molecules. Such translational freedom is much more pronounced in planar interactions. Thus, even at room temperature this value is 0.51 for 7OBAC, which decreases to 0.50 at the nematic–isotropic transition temperature. It may be noted that, although the freedom is considerable for smaller translation, longer translations are not in general 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) show that the molecules 7OBAC, 8OBAC, 9OBAC and 10OBAC do not show a strong preference in forming the stacked layers in accord with the nematic character of the acids.

¹This has been defined as the ratio of probability being at maximum probable point to having ± 0.2 Å displacement along the long molecular axis

Conclusion

The present calculations are helpful in characterizing the nematic character of acids in terms of their relative order. Further, it is clear 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. Thus, in a molecular assembly, a number of local minimum energy configurations exist. Each of them has its own importance, as in the case of closed 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 descending from a very high temperature where 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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