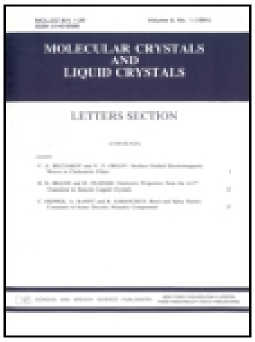

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The Influence of Alkyl Chain Length and Solvents on Configurational Probability of Liquid Crystalline Materials: A Computational Approach

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The influence of alkyl chain length and solvents on two liquid crystalline materials, p-n-butylbenzoic acid (4BAC), and p-n-pentylbenzoic acid (5BAC) has been carried out with respect to the translational and orientational motions. The atomic net charge and dipole moment components at each atomic center have been evaluated using the complete neglect differential overlap (CNDO/2) method. The modified Rayleigh–Schrodinger Perturbation theory with the multicentered-multipole expansion method has been employed to evaluate the long-range interactions, and a "6-exp." potential function has been assumed for the short-range interactions. The minimum energy configurations obtained during the different modes of interactions have been taken as input to calculate the configurational probability using the Maxwell–Boltzmann formula in nonpolar organic solvents, i.e., carbon tetrachloride (CCl_4), and chloroform ($CHCl_3$) at room temperature 300 K. It has been observed that the increase of alkyl chain length causes a minimization in the binding energy, and increases the total energy of 5BAC molecule. Further, the molecules produce remarkable property in the solvents.

Keywords Chain and solvent effects; configurational probability; liquid crystals; quantum chemistry

Introduction

The liquid crystal technology has had a major effect in many areas of science and engineering, as well as device technology. Applications for this kind of materials are still being discovered and continue to provide effective solutions to many different problems. The thermotropic liquid crystals have paid considerable attention due to their extensive applications, such as liquid crystal displays, adaptive optic devices, and optical switchable windows [1]. It has been observed that the dissolving of a thermotropic liquid crystal compound in a nonpolar organic solvent produces ferroelectric liquid crystals with the remarkable properties [2]. The electro-optic properties of the solutions are, to some extent, better than those of "pure" liquid crystals. Study of the effect of solvents on the molecules forms an

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important subject for research, and it can play a significant role in the photo physics. The solvent environment determines important changes in the electro-optical properties of the spectrally active molecules [3].

The majority of mesogenic molecules are composed of an aromatic core to which attached one or two alkyl chains. The primary role of the alkyl chains to enhance the liquid crystal range by lowering the melting point. The liquid crystal properties, such as the nematic-isotropic transition temperature and the entropy of transitions, are influenced by the presence of alkyl chain [4, 5]. The molecular interactions [6–10] in mesomorphic compounds have been reported by the several authors based on the Rayleigh–Schrodinger perturbation method [11]. These studies have indeed to establish the anisotropic nature of the pair potential, and subsequently find out the minimum energy configuration of a pair of mesogens.

The molecular structure is a basic starting point for understanding and predicting its physico-chemical properties. Further, the calculated properties of predicted structures could be used as a screen for molecules/ materials with novel properties, such as balance between electro-optic response, order, and high nonlinear optical response. The calculations can be performed in advance of synthesizing the molecule, so they have the potential to streamline research by narrowing down experimental investigations to the most promising candidates. Computational methods of predicting molecular geometries could play a large part in this research, both in identifying all possible polymorphic forms, and judging their relative stabilities [12, 13]. This acts as an examination, and evaluation of all possible crystal structures of a given compound is a step toward the understanding and, perhaps, control of polymorphism.

The nematic liquid crystal phase is technologically the most important. The stability of the nematic phase arises from the existence of the strong interactions between pairs of molecules, which promote the positional and orientational of the mesomorphic compounds. The present article deals with the interaction energy/configurational probability of two nematogens 4BAC, and 5BAC in pure and nonpolar solvents, i.e., CCl_4 and $CHCl_3$ at room temperature 300 K. Interaction energies/configurational probabilities of a molecular pair have been computed at an intermediate distance 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for the terminal interactions. Further, the influence of alkyl chain length and solvent on liquid crystalline materials has been analyzed at molecular level. At molecular level, the phases of matter are basically determined by the interplay between molecular structure, intermolecular interactions, and the molecular motion.

Computational Methods

In view of the practical difficulties and the increasing enforce to predict the properties of unsynthesized molecular materials; it is evidently of considerable importance to develop computational methods for the calculation of physical properties. It is well known that subtle alternations in molecular structure can have profound effects on the stability and properties of mesophases. The molecular geometries of 4BAC and 5BAC have been constructed on the basis of published crystallographic data [14] with the standard values of bond lengths and bond angles. The advancing the structure and energetic effects are helpful in employing the molecular models. The computations have been carried out in three steps:

First Step Computation

The complete neglect differential overlap (CNDO/2) method [15] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule because the simplified formula for interaction energy calculations requires the evaluation of atomic net charges and dipole moment components at each atomic centre through an all-valance electron method. The program language is FORTRAN IV. The program is capable of computing CNDO wave functions for open- and closed-shell molecules containing the elements hydrogen to chlorine.

Second Step Computation

The computational scheme based on simplified formula provided by Claverie [16] 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 has been used for this purpose with the further modification.

The total pair interaction energy of molecules (U_{pair}), according to the second order perturbation theory for intermediate range interactions [17], 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, electrostatic term is expressed as:

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

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 significantly the electrostatic interaction energy and the calculation only up to dipole-dipole term gives satisfactory result. The computation of electrostatic term has, therefore, been restricted only up to dipole-dipole energy term.

The dispersion and short-range repulsion terms are considered together because the several semiempirical approach, viz. the Lennard–Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky introduced [18] a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [19] for hydrocarbon molecules and the several other molecules and finally gave the expression:

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

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

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 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_{λ} K_{ν} allows the energy minimum to have different values according to the atomic species involved.

Third Step Computation

In order to obtain a better insight, the total interaction energy values obtained through the different modes of interactions have been used as input to calculate the probability of occurrence of a particular configuration i using the Maxwell–Boltzmann formula [20]:

$$P_i = \exp(-\beta\varepsilon_i)/\Sigma_i \exp(-\beta\varepsilon_i)$$

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 the configuration i to the minimum energy value in a particular set for which the probability distribution is computed.

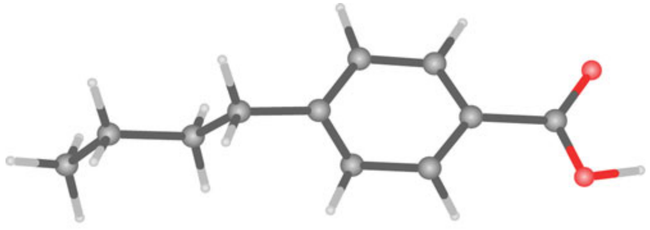
In this case, the origin has been chosen at almost midpoint of the molecule. The x-axis been chosen along a bond parallel to the long molecular axis while the y-axis lies in the plane of the molecule, and z-axis is perpendicular to the x-y plane. The terms like stacking, in-plane and terminal interactions will be used to maintain the continuity with the previous work [20].

Computation of Stacking Interactions

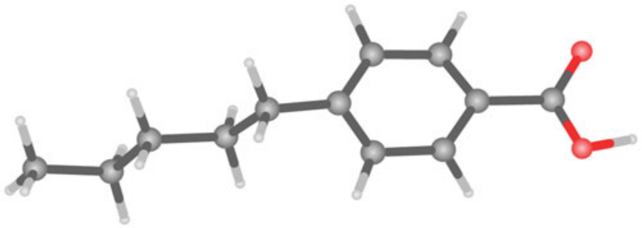
The interacting molecule has been placed at a separation of 6 Å along the z-axis with respect to the fixed molecule. The choice of the distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the range of short- and medium-range interactions.

Computation of In-Plane Interactions

The interacting molecule has been kept at a separation of 8 Å along y-axis with respect to the fixed one. The distance chosen for these calculations are such that the possible van der Waals contacts are avoided.



(a) 4BAC



(b) 5BAC

Figure 1. Molecular geometries of (a) 4BAC and (b) 5BAC molecules.

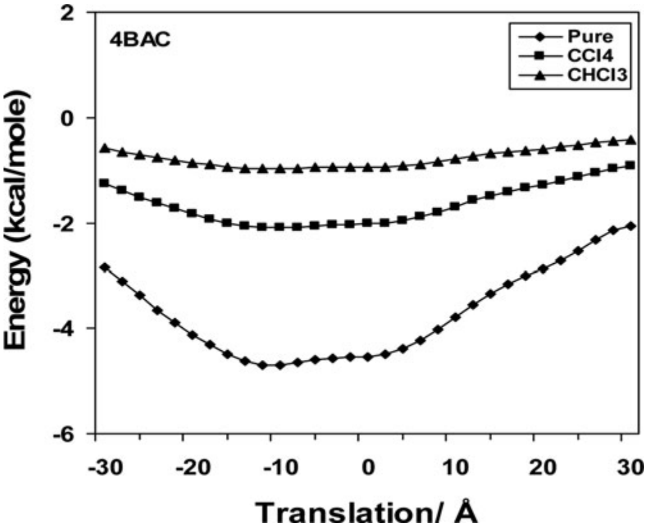


Figure 2. The variation of total interaction energy component with respect to translation along x-axis corresponding to configuration $y(0°)z(0°)$ during the stacking interactions for 4BAC molecule.

Computation of Terminal Interactions

To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the x-axis by 22 Å with respect to the fixed one.

Results and Discussion

The molecular geometries of 4BAC and 5BAC are shown in Fig. 1. The results of interaction energy calculations during the different modes of interactions in 'pure' and non-polar solvents, i.e., CCl_4, and $CHCl_3$ are discussed below.

Role of Stacking Interactions

A graphical representation of total interaction energy component with respect to rotation about z-axis corresponding to the configuration $x(0°)y(0°)$ has been carried out. It has been observed that the dispersion energy is mainly responsible for the attraction between molecular pair of 4BAC, and 5BAC, although the exact minimum is always estimated from the Kitaygorodsky energy curve, which has gross similarity with the total energy curve. The variation of total interaction energy component with respect to translation along x-axis corresponding to configuration $y(0°)z(0°)$ is shown in Fig. 2 for 4BAC molecule. The variation of energy is almost constant in the region of -6 ± 2 Å for 4BAC molecule that shows a sliding of one molecule over the other is energetically allowed for a small range. This may be correlated with the fluidity of the compound maintaining its alignment in mesophase. The same trend of energy distribution has been observed in the case of 5BAC molecule. However, the considerable rise in the probabilities of interactions has been observed due to redistribution of energy in the 4BAC, and 5BAC molecules.

The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for the small intervals. It is important to note here that the path of minimization strictly depends on the objective of the computations. The global search

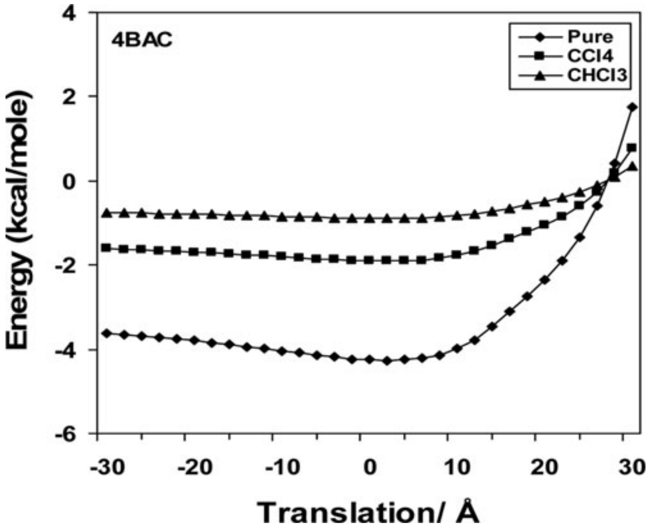


Figure 3. The variation of total interaction energy component with respect to translation along *x*-axis corresponding to configuration *y*(0°) during the in-plane interactions for 4BAC molecule.

for the minimum energy configuration or the study of variation of interaction energy under preselected conditions will have completely the different paths and, therefore, one has to be careful in choosing the specific route. The energy has been minimized with respect to the translations and rotations about the *x*, *y*, and *z*-axis. The accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other has been achieved.

Role of In-Plane Interactions

A plot of total interaction energy component with respect to rotation about *x*-axis corresponding to configuration *y*(0°) has been carried out, and it has been observed that the rotation about the *x*-axis does not alter the configurational energy drastically. The interacting configurations have been refined with respect to rotation about x-axis at the equilibrium condition, and the energy is brought down, and interaction energy is further investigated with respect to the translation along *x*-axis. The nematic character of liquid crystals is generally manifested by its translational freedom along the long molecular axis.

The variation of total interaction energy component with respect to translation along x- axis corresponds to configuration *y*(0°) has been shown in Fig. 3 for 4BAC molecule. However, the small variation of energy with the same graphical nature has been observed in case of 5BAC molecule. Further, the observed electrostatic energy during the in-plane interactions is more effective than the stacking, since the antiparallel orientation of molecular rings provides a more effective dipole-dipole attraction. In addition, repulsive quadrupole-quadrupole interactions become very much less effective due to the slipped anti-parallel molecular ring orientation. The total interaction energy is nearly constant in the range of 4 ± 2 Å for both the molecules without any significant change in the energy, and hence is capable to retaining the molecular order up to 30 Å against increased thermal agitation. The same nature of energy curve has been observed like the stacking interactions with comparatively weak interactions.

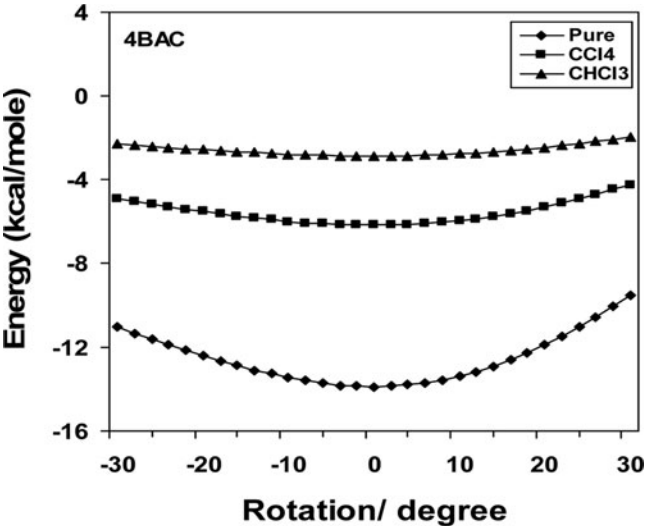


Figure 4. The variation of total interaction energy component with respect to rotation about x-axis corresponding to configuration $y(0°)$ during the terminal interactions for 4BAC molecule.

Role of Terminal Interactions

The terminal interactions are much weaker in the absence of strong polar groups at the end of the molecules and show almost no preference for angle of rotation about x-axis corresponding to configuration $y(0°)$ for 4BAC molecule (Fig. 4). The same trend of energy distribution has been observed in the case of 5BAC molecule with small variation in the total energy. However, for rotation about y-axis, it has been observed that there is slight preference for the molecular axis being on the same line.

Role of Planarity of the Molecules

The most prominent energy minima of the above interactions are further refined, and it has been observed that due to planarity of the molecules, the refinement corresponding to stacking energy is maximum with the larger magnitude than in-plane, and terminal interactions energies.

Influence of Alkyl Chain Length and Solvents

It is well known that physical and chemical properties of liquid crystal molecules change with the length of alkyl chains. In order to examine the results more closely, a comparative picture of the total energy, binding energy, and total dipole moment compounds is presented in Table 1. Evidently, the increase of alkyl chain length causes a minimization in the binding energy, total dipole moment, and increases the total energy of 5BAC molecule.

The most common approach to the challenge of structure prediction has been to search for all possible configurations. The lowest energy structure (the global minimum) is assumed to be the most likely structure of the molecule. In this approach, the two major challenges are: (i) the search for all possible ways to pack the molecule and (ii) accurately calculating the energies of these putative structures. Such calculations are becoming somewhat reliable for small molecules, at least in proposing the observed forms amongst a handful of possibilities.

Table 1. A comparative picture of the total energy*, binding energy**, and total dipole moment of 4BAC, and 5BAC molecules

Molecule	Total energy (a.u.)	Binding energy (a.u.)	Total dipole moment (Debye)
4BAC	−125.52	−12.59	1.12
5BAC	−134.16	−13.79	1.11

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

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

The different minimum energy configurations obtained for 4BAC and 5BAC during the stacking, in-plane, and terminal interactions have been reported in Table 2 to understand the influence of solvents on the basis of the relative probabilities in CCl_4 ($\varepsilon = 2.24$), and $CHCl_3$ ($\varepsilon = 4.81$). Evidently, the considerable rise in the probabilities of interactions has been observed due to redistribution of energy in non-polar organic solvents, although the order of preference remains the same. Furthermore, this provides information about the molecular arrangements inside a bulk of materials.

It is clear from the above discussion that, in a molecular assembly, a number of local minimum energy configurations exist. Each of these has its 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, however,

Table 2. Relative probabilities of the different minimum energy configurations obtained for 4BAC and 5BAC during the stacking, in-plane, and terminal interactions in nonpolar organic solvents, i.e., CCl_4, and $CHCl_3$ at room temperature 300 K

		Probability (%) at 300 K	
Configuration	Energy in vacuum (Kcal/mole)	CCl_4	$CHCl_3$
4BAC molecule			
$x(0°)y(0°)$[a]	−13.87	56.27	50.32
$y(0°)z(0°)$[a]	−13.54	43.71	44.73
$y(0°)$[b]	−4.69	0.00	2.04
$x(180°)$[b]	−4.27	0.00	1.76
$y(0°)$[c]	−2.99	0.00	1.12
5BAC molecule			
$x(0°)y(0°)$[a]	−13.70	59.07	51.30
$y(0°)z(0°)$[a]	−13.21	40.82	43.18
$y(0°)$[b]	−5.22	0.10	2.65
$x(180°)$[b]	−4.30	0.00	1.92
$y(0°)$[c]	−2.21	0.00	0.90

[a]Stacking interactions; [b]in-plane interactions; [c]terminal interactions.

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 other minima have the sequential preference depending on their individual relative probabilities. Further, the additional alkyl group of 5BAC reduces the packing density due to the elongated molecular size. This may enhance relative probability of the molecule. The most favorable stacked configuration $x(0^\circ)y(0^\circ)$ has been obtained for 4BAC, and 5BAC in CCl_4 with 56.27%, 59.07% probabilities at room temperature 300 K. Further, it has been observed that the increment in alkyl chain length enhance the probability, whereas the solvent dielectric constant lowers the probability.

Conclusions

The salient features of the present work are:

1. The present computations are helpful in analyzing the phase organization/stability of liquid crystalline materials at molecular level. Further, advancing the structure and energetic effects are helpful in employing the molecular models.
2. The electrostatic energy during the in-plane interactions is more effective than stacking since the antiparallel orientation of molecular rings provide a more effective dipole-dipole attraction, which aids in the energetic stabilization of the mesophase.
3. The increase of alkyl chain length causes a minimization in the binding energy, total dipole moment, and increases the total energy of 5BAC molecule. Further, the consideration of relative probabilities among the minimum energy configurations obtained during the stacking, in-plane, and terminal interactions provide information about the molecular arrangements inside a bulk of materials.
4. The considerable rise in the molecular interactions has been observed due to the redistribution of energy in CCl_4 and $CHCl_3$, i.e., the molecules produce the remarkable property in solvents.
5. The most stable configuration $x(0^\circ)y(0^\circ)$ of molecular pairing among the minimum energy configurations has been obtained for 5BAC molecule in CCl_4 at room temperature 300 K during the stacking interactions.

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