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Role of Oxygen and Effect of Solvents on Nematogens—A Computational Analysis

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A comparative computational analysis on two nematogens, p-n-heptylbenzoic acid (7BAC), and p-n-heptyloxybenzoic acid (7OBAC) 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). The most stable configuration of pairing, during the stacking interactions, has been obtained for 7BAC in CCl_4. Furthermore, an attempt has been made to analyze the role of oxygen and effect of solvents on nematogens at molecular level.

Keywords Configurational probability; nematogen; oxygen and solvents effect

Introduction

Liquid crystal displays (LCDs) have become, in recent years, the most significant and faster growing type of display technology. The operation efficiency of LCDs is essentially determined by the liquid crystalline material properties [1].

The problem of predicting physical properties of liquid crystalline compounds based upon the molecular shape and intermolecular interactions requires the adoption of model potential [2]. The stability of the nematic phase arises from the existence of the strong interactions between pairs of molecules, which promote the positional and orientational order of the mesomorphic compounds. The characterization of phase behavior of the different LCs based on the theoretical grounds needs specific inclusion of information concerning molecular structure, charge distribution, and the other parameters required for accurate determination of intermolecular interactions between LC molecules [3].

The molecular interactions in mesomorphic compounds have engrossed the attention of several researchers [4–8] based on the Rayleigh–Schrodinger perturbation method. These studies have indeed tried to establish the anisotropic nature of the pair potential, and

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subsequently find out the minimum energy configuration of a pair of mesogens. Further, it has been observed that the dissolving of a thermotropic LC compound in a nonpolar organic solvent produces ferroelectric LCs with the remarkable properties [9]. The electro-optic properties of the solutions are, to some extent, better than those of "pure" LCs. Hence, the solvent effect studies on LC are more informative and useful model for electro-optic devices.

The present article deals with the interaction energy/configurational probability of two nematogens p-n-heptylbenzoic acid (7BAC) and p-n-heptyloxybenzoic acid (7OBAC) 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 role of oxygen and effect of solvents on nematogens have been analyzed at molecular level.

Also, instead of finding the exact minimum energy configuration, an attempt has been made to elucidate the general behavior of the molecules surrounded a fixed molecule in a particular frame of reference.

Computational Details

The molecular geometries of 7BAC [10] and 7OBAC [11] have been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles. The following computations have been carried out:

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-valance-electron method. In the present computation, the complete neglect differential overlap (CNDO/2) method [12] 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, which is an extension of the original program QCPE No. 141 for the third row elements of periodic table, has been used. 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.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [13] 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.

According to the second-order perturbation theory for intermediate range interactions [14], 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, 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.

In the present computation, 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 [15] a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [16] for hydrocarbon molecules and the several other molecules and finally gave the expression:

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

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

where $Z = R_{\lambda\nu}/R^0{}_{\lambda\nu}$; $R^0{}_{\lambda\nu} = [(2R^{\text{w}}_\lambda)\,(2R^{\text{w}}_\nu)]^{1/2}$, 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 $K_\lambda K_\nu$ allows the energy minimum to have different values according to the atomic species involved.

Computation of Configurational Probabilities

The total interaction energy values obtained through these computations have been used as an 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:

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

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.

An orthogonal coordinate system has been considered to facilitate the above calculation. The origin has been chosen at almost midpoint of the molecule. The x-axis has 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.

Though the aim of the present investigation is to calculate the interaction energies/configurational probabilities of the different configuration allowing free rotation and translation of one molecule in the presence of another molecule at a fixed position, the terms like stacking, in-plane, and terminal interactions will be used to maintain the continuity with my previous work [18].

(a) 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.

(b) In-Plane Interactions: The interacting molecule has been kept at a separation of 8 Å along the 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.

(c) 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 7BAC and 7OBAC are shown in Fig. 1. The results of interaction energy calculations during the different modes of interactions in "pure" and nonpolar solvents, i.e., CCl_4, and $CHCl_3$ are discussed below:

Solvents Effect on Stacking Interactions

The variation of total interaction energy component with respect to rotation about the *z*-axis corresponding to the configuration $x(0^0)$ $y(0^0)$ has been carried out. It has been observed that the dispersion energy is mainly responsible for the attraction between molecular pair of 7BAC and 7OBAC, 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 the *x*-axis corresponding to configuration $y(0^0)$ $z(0^0)$ is shown in Figs 2 and 3 for 7BAc and 7OBAC molecules. The variation of energy is almost constant in the region of -2 ± 2 Å for 7BAC while 8 ± 2 Å in the case of 7OBAC shows a sliding of 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. Further, the considerable rise in the probabilities of interactions has been observed due to redistribution of energy in case of both the molecules.

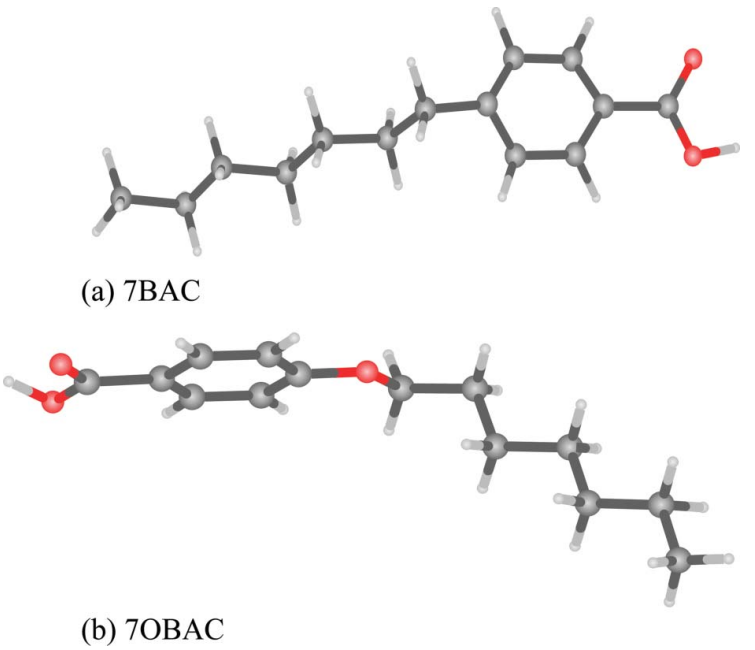

Figure 1. Molecular geometries of (a) 7BAb, (b) 7OBAC molecules.

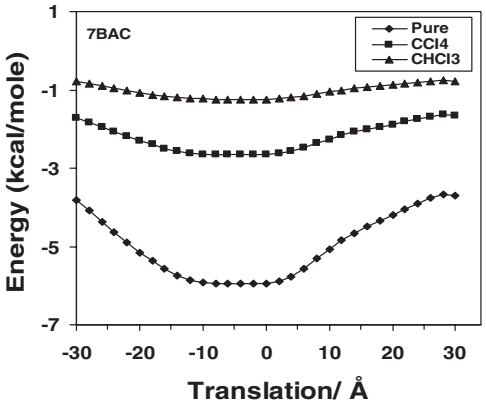

Figure 2. The variation of total interaction energy component with respect to translation along the *x*-axis corresponding to configuration $y(0^0)$ $z(0^0)$ during the stacking interactions for 7BAC molecule.

The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for the small intervals. The global search for the minimum energy configuration or the study of variation of interaction energy under preselected conditions will have completely 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. Accuracy of 0.1 Å in translation and 1^0 in rotation of one molecule with respect to the other has been achieved. It is important to note here that the path of minimization strictly depends on the objective of the computations.

Solvents Effect on In-Plane Interactions

The variation of total interaction energy component with respect to rotation about the *x*-axis corresponding to configuration $y(0^0)$ has been carried out, and it has been observed

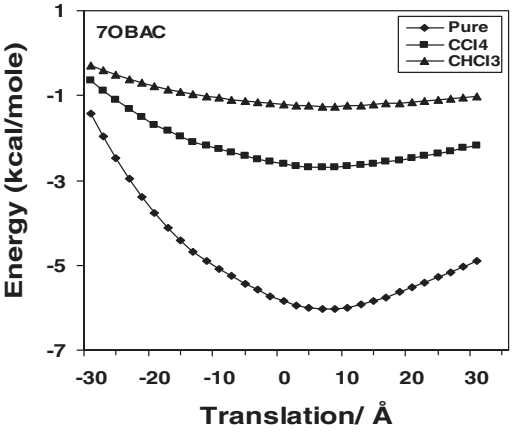

Figure 3. The variation of total interaction energy component with respect to translation along the *x*-axis corresponding to configuration $y(0^0)$ $z(0^0)$ during the stacking interactions for 7OBAC molecule.

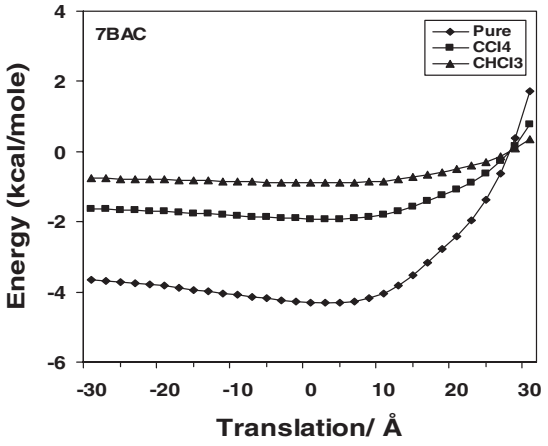

Figure 4. The variation of total interaction energy component with respect to translation along the *x*-axis corresponding to configuration $y(0^0)$ during the in-plane interactions for 7BAC molecule.

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 the *x*-axis at the equilibrium condition, and the energy is brought down, and interaction energy is further investigated with respect to the translation along the *x*-axis. The nematic character of LCs is generally manifested by its translational freedom along the long molecular axis.

The variation of total interaction energy component with respect to translation along the *x*-axis corresponds to configuration $y(0^0)$ has been shown in Figs 4 and 5 for 7BAC and 7OBAC molecule. It has been observed that the 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 antiparallel molecular ring orientation. Further, the total interaction energy is nearly constant

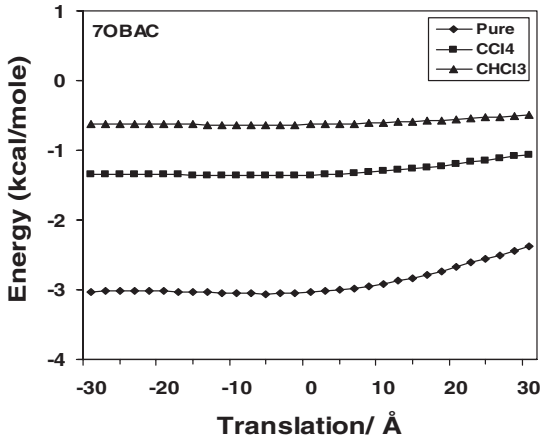

Figure 5. The variation of total interaction energy component with respect to translation along the *x*-axis corresponding to configuration $y(0^0)$ during the in-plane interactions for 7OBAC molecule.

in the range of 0 ± 2 Å for both the molecules without any significant change in the energy, and hence is capable of retaining the molecular order up to 30 Å against increased thermal agitation. The same trend of energy redistribution has been observed like the stacking interactions but interactions are comparatively weak.

Solvents Effect on Terminal Interactions

In the absence of strong polar groups at the ends of the molecules, the terminal interactions are much weaker (after due consideration of short contact) and shows almost no preference for angle of rotation about the *x*-axis corresponding to configuration $y(0^0)$ for 7BAC, and 7OBAC molecules. However, for rotation about the *y*-axis, it has been observed that there is slight preference for the molecular axis being on the same line.

Role of Oxygen and Solvents Effect

In order to examine the substituent effects on the nematogens, a comparative picture of the total energy, binding energy, and total dipole moment of the compounds is presented in Table 1. Evidently, the substation of oxygen causes a minimization in the total energy, binding energy, and increases the total dipole moment of 7OBAC molecule.

Table 2 shows the relative probabilities of the different minimum energy configurations calculated for the nonpolar organic solvents (i.e., CCl_4 and $CHCl_3$) during the different modes of molecular interactions that provide information about the molecular arrangements inside a bulk of materials. Evidently, the considerable rise in the probabilities of interactions has been observed due to redistribution of energy in nonpolar organic solvents, although the order of preference remains the same. The most favorable configuration $x(0^0)$ $y(0^0)$ has been obtained for 7BAC in CCl_4, during the stacking interactions, with 58.47% probability at room temperature 300 K.

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, 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.

Table 1. A comparative picture of the total energy[a], binding energy[aa], and total dipole moment of 7BAC and 7OBAC molecules

Molecule	Total energy (a.u.)	Binding energy (a.u.)	Total dipole moment (Debye)
7BAC	−151.44	−16.19	−1.10
7OBAC	−169.77	−16.44	−2.29

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

[aa]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.

Table 2. Relative probabilities of the different minimum energy configurations obtained for 7BAC and 7OBAC during the stacking, in-plane, and terminal interactions in nonpolar organic solvents, i.e., CCl_4 and $CHCl_3$ at room temperature 300 K

Configuration	Energy in vacuum (Kcal/mole)	Probability (%) at 300 K	
		CCl_4	$CHCl_3$
7BAC			
$x\ (0^0)\ y\ (0^0)$[a]	−11.83	58.47	46.15
$y\ (0^0)\ z\ (0^0)$[a]	−11.31	39.60	38.49
$y\ (0^0)$[b]	−6.21	0.86	6.49
$x\ (180^0)$[b]	−6.47	1.05	7.11
$y\ (0^0)$[c]	−2.43	0.00	1.73
7OBAC			
$x\ (0^0)\ y\ (0^0)$[a]	−10.87	54.96	45.84
$y\ (0^0)\ z\ (0^0)$[a]	−10.57	43.90	38.76
$y\ (0^0)$[b]	−4.26	0.38	6.54
$x\ (180^0)$[b]	−4.93	0.63	7.11
$y\ (0^0)$[c]	−2.60	0.10	1.73

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

Conclusions

The salient features of the present work are:

(1) These calculations provide an insight of the molecular arrangements inside a bulk of materials. The substitution of oxygen causes a minimization in the total energy, binding energy, and increases the total dipole moment of 7OBAC molecule.
(2) The 7BAC and 7OBAC molecules produce the remarkable property in nonpolar organic solvents, i.e., the considerable rise in the probabilities of interactions due to the redistribution of energies although the order of preference remains the same. The most stable configuration of pairing, during the stacking interactions, has been obtained for 7BAC in CCl_4 at room temperature 300 K.
(3) The molecular pair interaction energy during stacking interactions is dominant because the face-to-face orientation of molecular rings produces large attractive dispersion energy. But, the electrostatic energy during 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.

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