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# Role of configurational entropy on ordering and phase organization of nematic liquid crystals—A molecular model

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ABSTRACT

The temperature dependence of configurational entropy for two mesogens *p*–*n*-heptyloxybenzoic acid (7OBAC) and *p*–*n*-octyloxybenzoic acid (8OBAC) has been estimated. The atomic net charge and dipole moment at each atomic center have been evaluated using the complete neglect differential overlap (CNDO/2) method. The modified Rayleigh–Schrodinger perturbation theory along with multicentered–multipole expansion method has been employed to evaluate the long-range intermolecular interactions, while a '6-exp' potential function has been assumed for short-range interactions. The interaction energy values obtained with respect to translational and orientational motions during the different modes of molecular interactions have been taken as input to estimate the configurational entropy and Helmholtz free energy at room temperature, nematic–isotropic transition temperature, and above transition temperature. An attempt has been made to understand the role of configurational entropy on ordering and phase organization of *n*OBAC ($n = 7, 8$) molecules. The flexibility of a particular configuration at different temperatures has been analyzed in the light of thermodynamic parameters introduced in this paper. These parameters are helpful to develop a new and interesting model for structure-phase stability relationship at the molecular level.

## 1. Introduction

A central problem in modeling of new and advanced materials, particularly complex molecules such as liquid crystals (LCs), is understanding the relation between molecular structure and material properties [1]. The quest for new materials, whether driven by their potential for applications or simply by natural scientific curiosity about structure/phase stability relationship, has always been a vital part of the LC scenario. Indeed, the fundamental research in this direction opened many doors to provide effective solutions to the different problems [2,3]. The applications of LCs have unquestionably added incentive to the quest for designing new materials with superior properties such as transition temperatures, phase behavior and stability [4].

Liquid crystal mesophases are present in materials composed of interacting molecules or aggregates of molecules with shape anisotropy [5]. The chemical constitution of the LC molecules has important consequences for how they pack, and organize in the different molecular interactions/organizations. The description of these molecular motions in liquid crystals is a subject of great importance, both in its own right, and as a tool for the interpretation of experimental results [6]. This problem is particularly severe in the computational methods, which can contribute to our understanding of liquid crystals by relating detailed molecular structure, phase behavior and properties [7,8]. The accomplishments of LC research based on computational methods in advancing the structure and energetic effects of intermolecular interactions are useful in employing molecular models, yielding insight into physicochemical features of phase transition phenomenon [9,10].

The role of molecular interactions in mesomorphic compounds has engrossed the attention of several workers [11–15] 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. 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 energy values. These values, however, do not replicate the actual relative preference, which can only be obtained through their relative energies corresponding to each configuration. Further, significant differences among the energies of various configurations are noticed, in terms of multipole interactions, which must have a marked affect on thermodynamic properties of the system.

The compounds of *p*–*n*-alkyloxybenzoic acid series, with the homologous index *n* ranging from 6 to 9, a texture transition in the nematic range which subdivides the nematic phase in two sub-phases displaying different textures in polarized light analysis have been well documented [16,17]. The present article aims at estimating the configurational entropy of 7OBAC and 8OBAC molecules to analyze the ordering and phase organization phenomenon. The relative

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energies between a molecular pair of 7OBAC and 8OBAC have been computed 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. 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, Helmholtz free energy has been computed to elucidate the thermodynamic stability of the mesophases. An examination of thermodynamic data has revealed that 7OBAC exhibits nematic–isotropic transition temperature at 420 K [18] and 8OBAC exhibits at 419 K [18].

## 2. Computational technique

The molecular geometry of 7OBAC and 8OBAC has been constructed on the basis of published crystallographic data with the standard values of bond lengths, and bond angles [18]. A number of the following computations have been employed in this work.

### 2.1. Computation of atomic net charge and dipole moments

In order to calculate the interaction energy between a molecular pair, it is necessary to compute atomic net charges and dipole moments through an all-valence electron method. Hence, in the present work, the CNDO/2 method [19] has been used to compute the net atomic charges and dipole moments at each atomic center of the molecule because using only the Mulliken atomic net charges (given, for example, by an *ab initio* program) for the calculation of an electrostatic interaction would be in correct for two reasons: (i) the atomic dipoles must be taken into account, and (ii) the homopolar dipoles must be taken into account, or else atomic net charges obtained according to Lowdin's procedure should be used. An *ab initio* program, which gives only Mulliken net charges is, therefore, quite misleading as concerns a reasonable representation of the molecular charge distribution in terms of charges and dipoles [20].

### 2.2. Computation of interaction energy at various configurations

A detailed computational scheme based on simplified formula provided by Claverie [21] for evaluating the interaction energy of a molecular pair has been used to calculate the energy at fixed configurations. According to the second order of the perturbation theory is modified for intermediate range interactions [22], the total pair interaction energy of molecules ($U_{\text{pair}}$) is represented as a sum of several terms contributing to the total energy as follows:

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

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

Further, electrostatic term is expressed as

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

where $U_{\text{QQ}}$, $U_{\text{QMI}}$, $U_{\text{MIMI}}$, 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 the dipole–dipole term gives the satisfactory results [11–15,23]. The computation of electrostatic term has, therefore, been restricted only up to dipole–dipole energy term.

In the present work, 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 introduced a Buckingham formula [23] whose parameters were later modified by Kitaygorodsky and Mirskaya for hydrocarbon molecules and several other molecules and finally given the expression

$$U_{\text{disp}} + U_{\text{rep}} = \sum_{\lambda}^{(1)}\sum_{\nu}^{(2)} U(\lambda, \nu)$$
$$U\,(\lambda, \nu) = K_{\lambda}K_{\nu}\left(-A/Z^{6} + B\,e^{-\gamma Z}\right)$$

where $Z = R_{\lambda\nu}/R^{0}_{\lambda\nu}$; $R^{0}_{\lambda\nu} = [(2R^{\text{w}}_{\lambda})(2R^{\text{w}}_{\nu})]^{1/2}$, where $R^{\text{w}}_{\lambda}$ and $R^{\text{w}}_{\nu}$ are the van der Waals radii of λ and $\nu$ atoms respectively. The parameters $A$, $B$ and $\gamma$ do not depend on the atomic species, but $R^{0}_{\lambda\nu}$ and factors $K_{\lambda}$ and $K_{\nu}$ allow the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [24].

The origin has been chosen on an atom close to the center of mass of molecule. The *x*-axis has been directed along a bond parallel to the long molecular axis, while *y*-axis lies in the plane of the molecule, and the *z*-axis is normal to the molecular plane (*x*–*y*).

### 2.3. Computation of thermodynamic parameters

The total interaction energy values obtained through these computations have been used as input to calculate the following thermodynamic parameters [25] of a particular configuration *i* in order to obtain a better insight into phase organization, and stability of mesogens:

$$A = -kT \ln \Sigma_i \exp\,(-\beta\varepsilon_i)$$
$$S = k \ln \Sigma_i \exp(-\beta\varepsilon_i) + (U/T)$$
$$U = \Sigma_i \varepsilon_i \exp\,(-\beta\varepsilon_i)/\Sigma_i \exp\,(-\beta\varepsilon_i)$$

where $A$ stands for Helmholtz free energy, and $S$ for entropy. $\beta = 1/k\text{T}$, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. $U$ is the internal energy of the system and $\varepsilon_i$ represents the energy of the configuration *i* to the minimum energy value.

## 3. Results and discussion

The molecular geometry of 7OBAC and 8OBAC is shown in Fig. 1. The results of interaction energy calculations during the different modes of interactions are discussed below.

### 3.1. Stacking interactions

In a molecular pair, one of the interacting molecules has been fixed in the *x*–*y* plane such that *x*-axis lies along a bond parallel to the long molecular axis, while the other has been kept at a separation of 6 Å along the *z*-axis with respect to the fixed one. The variation of interaction energy components with respect to rotation about *x*-axis corresponding to the configuration *y* (0°) *z* (0°) is shown in Figs. 2 and 3 for 7OBAC and 8OBAC molecules respectively. It has been observed that the dispersion energy is mainly responsible for the attraction between molecular pairs of *n*OBAC ($n = 7, 8$) molecules, although the exact minimum is estimated always from Kitaygorodsky energy curve, which has gross similarity with the total energy curve. The variation of interaction energy components with respect to translation along *x*-axis corresponding to the configuration *y* (0°) *z* (180°) is shown in Figs. 4 and 5 for 7OBAC and 8OBAC molecules. The variation of energy is almost constant in the region of 8 ± 4 Å, which shows a sliding of one molecule over other is energetically allowed for a small range that may be correlated with the fluidity of the compound maintaining its ordering in mesophase.

The variation of interaction energy components with respect to rotation about the *z*-axis corresponding to configuration *x* (0°) *y* (0°) has been carried out for 7OBAC and 8OBAC molecules. It has been observed that the dominant component of total energy is the