

Computer Simulations of Ordering in a Nematogen – The Role of Dielectric Medium

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Computer simulations of ordering in a nematic liquid crystal propyl 4-(4'-methoxybenzylidene amino)- α -methyl cinnamate (MBA2C3) was carried out with respect to translatory and orientational motions. The evaluation of atomic charges and dipole moment at each atomic center was carried out through the complete neglect differential overlap (CNDO/2) method. The modified Rayleigh-Schrödinger perturbation method along with 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 in a dielectric medium (i. e., non-interacting and non-mesogenic solvent, e. g. benzene) at room temperature (300 K) using the Maxwell-Boltzmann formula. On the basis of stacking, in-plane, and terminal interaction energy calculations, all possible geometrical arrangements of pairs have been considered. The most favourable configuration of pairing has been obtained. An attempt has been made to develop a new and interesting molecular model of nematogen in dielectric medium.

Key words: Computer Simulations; Nematogen; Quantum Chemistry; Dielectric Medium.

1. Introduction

Advances in modern science and technology can be thoroughly linked with the dream of engineering of molecules and materials with properties and functions tailored to intended applications. This basic idea explores the versatile uses of the concept of ordering in liquid crystalline compounds; especially nematogens. Liquid crystals (LCs), as the crystals that flow, have intrigued crystallographers and device engineers [1, 2]. The simulation of liquid crystal phase behaviour represents a major challenge despite the substantial increase in the availability of computer processing time [3, 4]. However, it is essential to study the simple model in depth in order to understand the forces responsible for mesophase formation. The possibility also exists to extend these simple models by building in realistic features such as molecular flexibility, complicated structural anisotropy, and electrostatic forces.

The nematic liquid crystal phase is technologically the most important mesophase [5]. The underpinning prerequisite for liquid crystallinity is that the mesophase owes its stability to the anisotropic shape of the molecules. Most of the known thermotropic

LCs are calamitic structurally. The conventional structure of calamitic liquid crystals is a rigid core attached with flexible alkyl chains. The core provides the source of anisotropy for the formation of liquid crystal phases, while the disorder associated with the terminal flexible chains reduces the stability of the solid crystal phase, and allows the appearance of liquid crystal mesophases. The terminal chains are either straight alkyl or alkoxy chains, one terminal unit is often a polar substituent. These calamitic molecules form both nematic and smectic mesophases depending upon the type of the substituents and their combinations [6–8].

The problem of predicting physical properties of liquid crystalline compounds based upon molecular shape and intermolecular interactions requires the adoption of a model potential [9]. 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 potential energy is the key quantity, which embodies the chemical specificity of the single molecule and provides a link between the microscopic properties, phase behaviour, and stability [10].

The ability in designing the liquid crystals with specific structures and functions depends on the manipulation of chemical entities forming the whole construct. Such studies are not only of academic value in understanding the structural and mechanistic aspects of phase transitions, but they can also be of technological importance [11].

The role of molecular interactions in mesomorphic compounds has attracted the attention of several workers [12–14] based on the Rayleigh-Schrödinger 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 energy values. These values, however, do not replicate the actual relative preference, which can only be obtained through their probabilities corresponding to each configuration. Hence, in order to obtain a quantitative measure for the relative preference, authors have evaluated the relative probability of occurrence of each configuration. Since mesogenic properties are related to molecular aggregation in a specific manner, probability calculations based on interaction energy results will provide information regarding the most probable molecular aggregation.

In the present article, we report the characteristic features of MBA2C3 in terms of their configurational probabilities between a molecular pair of MBA2C3 in a dielectric medium (i. e., the non-interacting and non-mesogenic solvent benzene, the average dielectric constant of which has been taken to be 2.25 for the entire temperature range) at an intermediate distance of 6 Å for stacking and 10 Å for in-plane interactions. Similarly, a distance of 25 Å has been kept for terminal interactions. The choice of distance was made to eliminate the possibility of van der Waals contacts and to keep the molecule within the short and medium-range interactions. Furthermore, instead of finding the exact minimum energy configuration an attempt was made to elucidate the general behaviour of the molecules surrounding a fixed molecule in a particular frame of reference. Through these computations one can obtain information on dimer complexes; the relative freedom of a molecule in terms of variation in inclination, separation or sliding of one molecule over another etc.

2. Simplified Formula and Computational Technique

The molecular geometry of MBA2C3 has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [15]. Depending on the property interest, a number of following methodologies have been employed in this work:

2.1. 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 [16] 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 of program, 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.

2.2. Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [17] 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 and later on modified at Chemical Physics Group, Tata Institute of Fundamental Research, Bombay, India by Govil and associates has been used for this purpose with further modification. According to the second-order perturbation theory as modified by Caillet and Claverie [18] 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} , and U_{MIMI} etc. are monopole-mono-

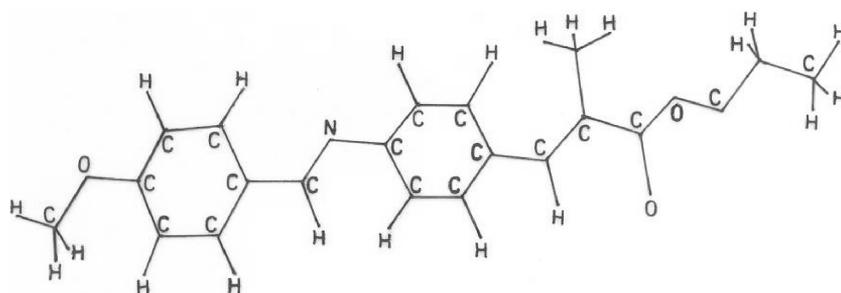


Fig. 1. Molecular geometry of MBA2C3.

pole, 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 satisfactory results [19]. The computation of the electrostatic term has, therefore, been restricted only up to the dipole-dipole energy term.

In the present computation, the dispersion and short-range repulsion terms are considered together because several semiempirical approach, viz. the Lennard-Jones or the Buckingham type approach, actually proceed in this way. Ojha [20] introduced a Buckingham formula whose parameters were later modified by Ojha [21] for hydrocarbon molecules and several other molecules and finally gave the expression

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

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

with $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$ and $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$, where R_{λ}^w and R_{ν}^w are the van der Waals radii of atom λ and ν , respectively. The parameters A , B , and γ do not depend on the atomic species. But $R_{\lambda\nu}^0$ and the 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 in [19].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin on an atom has been chosen at almost midpoint of the molecule. The x -axis is chosen to be along a bond parallel to the long molecular axis while the y -axis lies in the plane of the molecule and the z -axis is perpendicular to the molecular plane.

2.3. 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 [21] in order to obtain a better insight:

$$P_i = \exp(-\beta \epsilon_i) / \sum_i \exp(-\beta \epsilon_i),$$

where P_i stands for the 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.

3. Results and Discussion

The molecular geometry of MBA2C3 is shown in Figure 1. The results of the probability distribution corresponding to the different modes of interactions are discussed below.

3.1. Stacking Interactions in Dielectric Medium

In a molecular pair, one of the interacting molecules is fixed in the x, y -plane, while the second has been kept at a separation of 6 Å along the z -axis with respect to the fixed one. The energy has been 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 has been achieved. It is important to note here that the path of minimization strictly depends on the objective of computation. The global search for minimum energy configuration or the study of variation of interaction energy under pre-selected condition will have completely different path and, therefore, one has to be careful in choosing the specific route.

The nematic character of liquid crystals is manifested in their translational freedom along the long molecular axis. Therefore, translations have been considered corresponding to the configuration y (0°) z (180°) as shown in Figure 2. It may be observed that

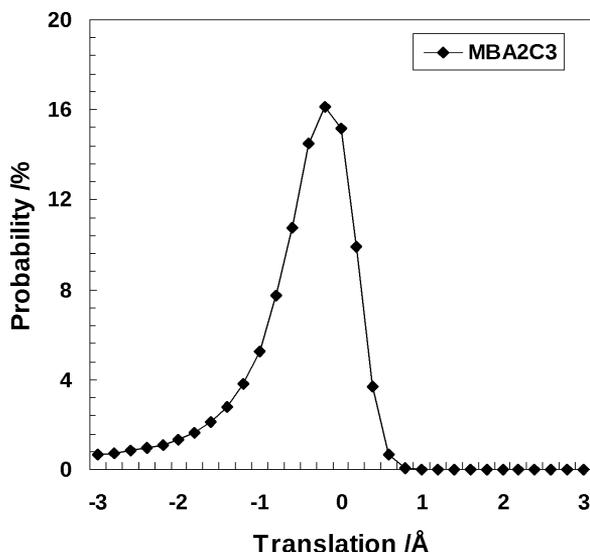


Fig. 2. Variation of probability with respect to translation along the x -axis during stacking interactions at room temperature (300 K).

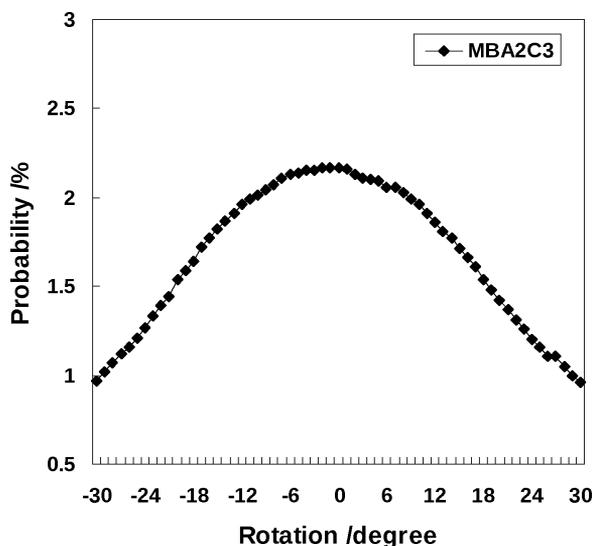


Fig. 3. Variation of probability with respect to rotation about the x -axis during stacking interactions at room temperature (300 K).

the configuration shows a sharp preference towards the minimum energy point. The variation of probability is almost constant in the region of (-2.6 ± 0.2) Å, which shows that 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 the mesophase.

Figure 3 shows the variation of the probability with respect to the rotation about the x -axis corresponding to the configuration y (0°) z (0°) at room temperature (300 K). The maximum probability corresponds to MBA2C3 at an equilibrium position indicating a slight preference for aligned structure of this configuration. However, at room temperature (300 K) the observed value is indicating a strong binding but with the increase of temperature the molecules obtain sufficient freedom to rotate about the long molecular axis.

3.2. In-plane Interactions in Dielectric Medium

The interacting molecule has been kept at a separation of 10 Å along the y -axis with respect to the fixed one. The similar calculations have been performed for in-plane interactions. Again rotations about the y - and z -axes have been given and the corresponding energy has been minimized with respect to translation and rotation about all axes. The variation of probability with respect to translation along x -axis corresponding to the configuration y (0°) at room temperature (300 K) is shown in Figure 4. It may be observed that though there is no drastic preference for an aligned structure, the smooth rise near -0.2 Å and an equilibrium position indicates the existence of an aligned structure at low temperature. Furthermore, the maximum probab-

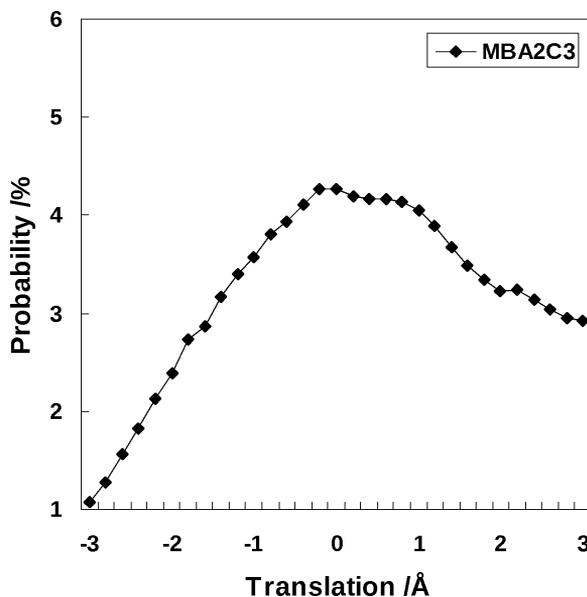


Fig. 4. Variation of probability with respect to translation along the x -axis during in-plane interactions at room temperature (300 K).

ity occurs at an equilibrium position. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. The variation of probability with respect to rotation about the x -axis corresponding to configuration y (180°) has been carried out. It has been observed that no pronounced peak exists at an equilibrium point and all the remaining regions have negligible probability as compared with this configuration. Thus, generally, the molecules may be assumed to be capable of free rotations except at lower temperature, where the molecules prefer being in the same plane.

3.3. Terminal Interactions in Dielectric Medium

The end-to-end interactions are weakest but become important when the molecule possesses a polar group at either or both ends or if there is a possibility of hydrogen bonding. To investigate the terminal interactions away from the van der Waals contacts, the interacting molecule has been shifted along the x -axis by 25 Å with respect to the fixed one. The interactions are further refined with an accuracy of 0.1 Å in translation and 1° in rotation. It has been observed that, due to the planarity of the molecule, the refinement corresponding to the stacking energy is much larger than the in-plane and terminal interactions. Rotation about the x -axis (Fig. 5) shows no more preference for any angle, i. e., the molecules are completely free to rotate about their long molecular axis.

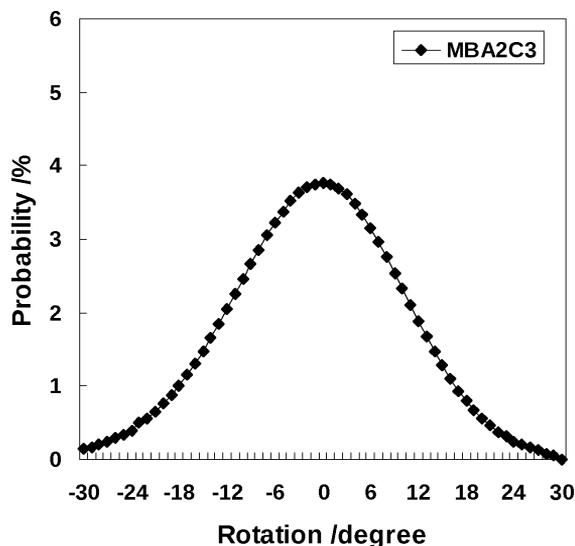


Fig. 5. Variation of probability with respect to rotation about the x -axis during terminal interactions at room temperature (300 K).

Table 1. Relative probabilities of different minimum energy configuration obtained for stacking, in-plane, and terminal interactions in vacuum and in dielectric medium (benzene) at room temperature (300 K). Average dielectric constant of benzene is taken as 2.25.

Configuration	Energy in Vacuum (kcal/mole)	Energy in Medium Dielectric (kcal/mole)	Probability /%	
			A	B
x (0°) y (0°)*	-12.89	-5.72	35.82	36.35
y (0°) z (180°)*	-12.77	-5.68	30.02	33.58
y (0°) z (0°)*	-12.60	-5.60	22.25	29.40
y (0°)**	-6.32	-2.81	11.89	0.25
y (180°)**	-6.93	-3.08	0.00	0.39
y (0°)***	-2.06	-0.92	0.00	0.00

* Stacking interactions; ** In-plane interactions, and *** Terminal interactions. A = Probability in vacuum, B = Probability in dielectric medium.

3.4. Role of Dielectric Medium

In order to examine the role of the dielectric medium more closely, the various possible geometrical arrangements between a molecular pair (during the different modes of interactions) have been considered. Table 1 shows the relative probabilities of different minimum energy configurations calculated for the vacuum and the dielectric medium during the different modes of interactions. Evidently, the most favourable stacked configuration of pairing due to redistribution of energies in the dielectric medium has been obtained for MBA2C3 with 36.35% probability at room temperature (300 K).

It may be concluded 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 their own importance, as in 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 a very high temperature, where the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy, and the local minima have a sequential preference depending on their individual relative probabilities.

4. Conclusions

These computations are able to provide information about the probability of the formation of a dimer com-

plex and the relative freedom of a molecule in terms of variations in inclination, separation or sliding of one molecule over the other. This provides a new and interesting model of nematogen in the non-interacting and non-mesogenic solvent, e. g. benzene.

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