Smectogenic Behaviour of 7O.6 at it's Phase Transition Temperature: A Computational Analysis

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A computational analysis has been carried out to determine the configurational preference of a pair of *N*-(4-*n*-heptyloxybenzylidine)-4-hexylaniline (**7O.6**) molecules with respect to translatory and orientational motions. The **CNDO/2** method has been employed to evaluate the net atomic charge and atomic dipole components at each atomic centre of the molecule. The configurational energy has been computed using the modified Rayleigh-Schrödinger perturbation method. The obtained energies were used to calculate the probability of each configuration at phase transition temperature, using Maxwell-Boltzmann's formula. The flexibility of various configurations has been studied in terms of variations of the probability due to small departures from the most probable configuration. The results are discussed in the light of experimental as well as other theoretical observations. The smectogenic character of the molecule has been correlated with the parameters introduced in this paper.

Key words: 7O.6, CNDO/2 Method; Quantum Chemistry; Computer Simulation.

Introduction

In recent years there has been increasing in stable phases mediating different liquid crystalline phases [1]. In particular, interest has focused on smectic liquid crystals in which the degree of order within the layers changes, quite often very subtly, form one phase to another. In smectic *A*, for example, the director is parallel to the normal of the layer. The homolgous series of *N*-(p-*n*-alkoxybenzylidene)p-*n*-alkylanilines (popularly known as *n*O.*m* compounds in which *n* and *m* represent the number of carbon atoms in the alkoxy and alkyl chains, respectively), which exhibit not only rich and subtle liquid crystal polymesomorphism [2, 3] at ambient temperatures, but are also useful as model systems in phase transition phenomena, have been extensively studied by different experimental techniques [4–6].

The role of intermolecular forces in the mesomorphic behaviour has attracted attention of many workers [7–12]. The characteristics of the mesomorphic behaviour, which occur at phase transitions, are primarily governed by the intermolecular interactions acting between sides, planes and ends of a pair of molecules [13]. The melting point, the temperature at which an ordered geometrical arrangement collapses and gives rise to an disordered isotropic melt, depend to a very large extent on the intermolecular interaction existing within the system.

Liquid crystalline materials are known for their anomalous physical properties near phase transitions. There have been many attempts to measure the long-range orientational order of liquid crystals and to explain it [14]. It is generally agreed that the prime requirement for the formation of a thermotropic liquid crystal is anisotropy in the molecular interaction [15]. In recent time, substantial increase of computer speed has lead to the use of computer simulation as a tool for understanding liquid crystal phases [16–18]. However, it is essential to study simple models in some 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 successful application of statistical models in elucidating the nematogenic behaviour of the compounds [11, 12] has lead us to extend similar investigations to smectogenic compound. In the present paper, an attempt has been made to explain the smectogenic behaviour of the **7O.6** molecule at an intermediate distance of 6 Å for stacking and 7 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 possiblity of van der Waals contacts and to keep the molecule within the range of short and medium-range interactions.

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The heptoxy chain of **7O.6** forms an all *trans*-conformation which lies almost in one plane with the two coplanar phenyl rings. The hexyl group also exists in an extended form in a plane which is rotated against the plane of the mesogenic unit. The overlap of the mesogenic cores and the alkoxy groups of adjacent molecules results in a protrusion of the hexyl groups on both sides of the layers and an interdigitation of neighbouring layers [19]. The compound exhibits a tetra phase variant, viz. smectic A, smectic C, smectic F, and smectic G phases, as given below [19]

$$\text{Solid} \xleftrightarrow{310.5\text{ K}} S_G \xleftrightarrow{328\text{ K}} S_F \xleftrightarrow{339\text{ K}} S_C \xleftrightarrow{341.5\text{ K}} S_A \xleftrightarrow{353\text{ K}} 1,$$

Computational Details

The molecular geometry of **7O.6** has been obtained on the basis of the published crystallographic data with standard values of bond lengths and bond angles [20]. The origin has been chosen on an atom close to the centre of the mass of molecule. The X-axis has been chosen along the long molecular axis, while the Y-axis lies in the plane of the molecule and the Z-axis perpendicular to the molecular plane. The **CNDO/2** method [21] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule.

The computations have been carried out in two parts:

(A) The second order perturbation theory as modified for intermediate range interactions [22], the total interaction energy (E_{total}) between a pair of molecules is given by

$$E_{\text{total}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}},$$

where E_{el}, E_{pol}, E_{disp}, and E_{rep} represent the electrostatic, polarization, dispersion and repulsion components, respectively.

The electrostatic term is expressed as

$$E_{\text{el}} = E_{\text{QQ}} + E_{\text{QMI}} + E_{\text{MIMI}} + \ldots,$$

where E_{QQ}, E_{QMI}, and E_{MIMI} are the monopole-monopole, monopole-dipole and dipole-dipole terms, respectively. The inclusion of higher order multipoles does not affect significantly the electrostatic interaction energy.

In the present work the dispersion and short-range repulsion terms are considered together because several semiemperical approaches, viz. the Lennard-Jones or Buckingham type approach, actually proceed in this way [23]. Kitaigorodskii introduced a Buckingham formula whose parameter were later modified by Kitaigorodskii and Mirskay for hydrocarbon molecules and several other molecules [11].

(B) The total interaction energies obtained by these computations were used as input to calculate the intrinsic probability of each configuration with the help of the Maxwell-Boltzmann formula [24]

$$P_i = \exp(-\beta\varepsilon_i)/\Sigma_i \exp(-\beta\varepsilon_i);\ \beta = 1/kT,$$

where P_i is the probability of a particular configuration, and ε_i the energy of configuration i relative to the minimum energy configuration.

Results and Discussion

The molecular geometry of **7O.6** is shown in Figure 1. The results of the probability distributions based on the interaction energy corresponding to the three modes of interactins are discussed below:

Stacking Interactions

In the molecular pair, one of the molecules is fixed in X-Y plane such that the X-axis lies along the long molecular axis while the second molecule has been kept at a distance of 6 Å along the Z-axis with respect to the fixed one. The variation of the probability with respect to translation along the long molecular axis, as shown in Fig. 2, shows a maximum corresponding to the minimum energy point. The curve shows the tendency of the **7O.6** molecules to form a layered structure. The angular dependence of the probability with respect rotation about the Z-axis is shown in Figure 3. The flexibility of rotation is sufficiently small, which accounts for the smectic character of the molecule. Further, it indicates that a finite probability for alignment at low temperature exists when the thermal agitation does not drastically disturb the molecular alignments. Having refined the interacting configuration with respect to translation along the Y-axis at equilibrium, the energy is brought down and the probability is further investigated with re-

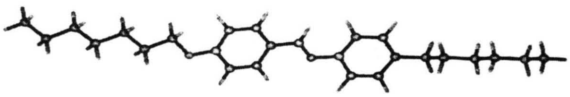

Fig. 1. Molecular geometry of N-(4-n-heptyloxybenzylidene)-4′-hexylaniline (**7O.6**).

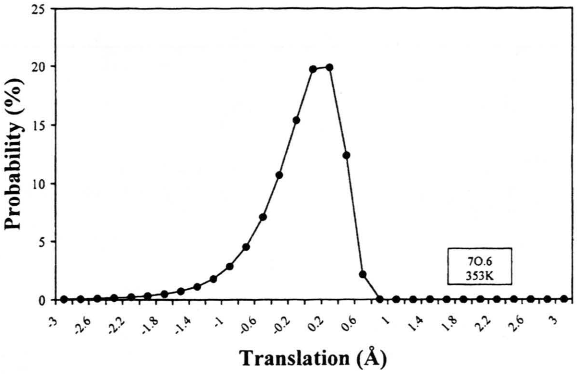

Fig. 2. Variation of the probability with respect to translation along the X-axis during stacking interactions at the phase transition temperature.

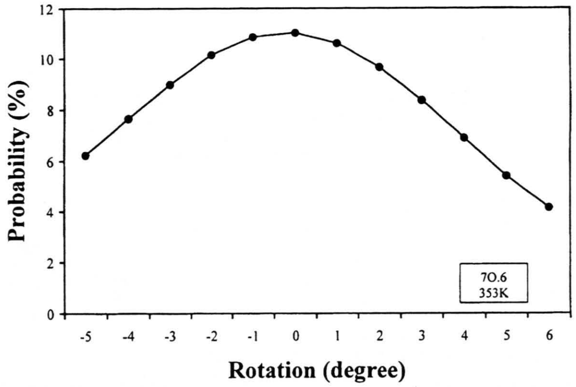

Fig. 3. Variation of the probability with respect to rotation about the Z-axis during stacking interactions at phase transition temperature.

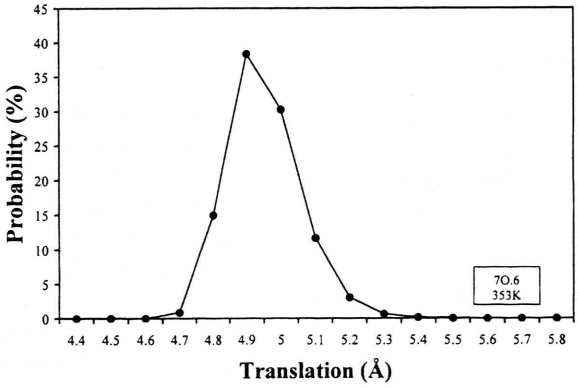

Fig. 4. Variation of the probability with respect to translation along the Z-axis during stacking interactions at phase transition temperature.

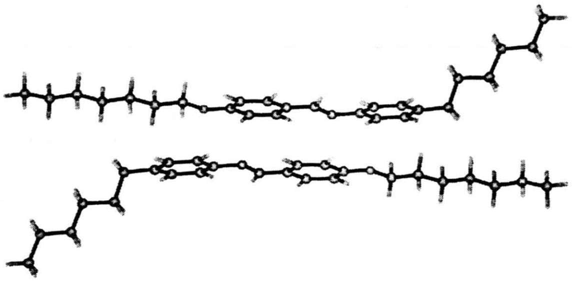

Fig. 5. The lowest stacked energy configuration with an energy -17.09 kcal/mole at an intermolecular separation of 3.50 Å.

spect to translation along the Z-axis (Fig. 4). The probability of perpendicular stacking is almost negligible, which agrees with the fact that mesogenic compounds are least expected to have a perpendicular stacked configuration.

The minimum energy so obtained is then taken as starting point and the entire process is repeated with smaller intervals. 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. The final lowest stacked geometry was thus obtained for an interplaner separation of 3.50 Å with an energy of -17.09 kcal/mole (Fig. 5). This configuration agrees with those obtained from crystallographic studies [20].

In-plane Interactions

To avoid van der Waals contacts, the interacting molecule has been kept at a separation of 7 Å along the *Y-axis* with respect to the fixed one. Similar calculations have been performed for in-plane interactions. Figure 6 shows the results corresponding to rotations about the X-axis. Evidently, the probability is almost constant for a region of $-8^\circ \pm 2^\circ$ near the equilibrium position, which shows that rotation of one molecule about the other is only energetically allowed for a very small range. This may be correlated with the mobility of the compound maintaining its alignment in the mesophase. Figure 7 represents the variation of the probability with respect to translation along the X-axis. It is evident from the figure that the probability is maximum at the equilibrium position. Figure 8 shows the variation of the probability with respect to translation along the Y-axis. Evidently the probability changes drastically in the range of

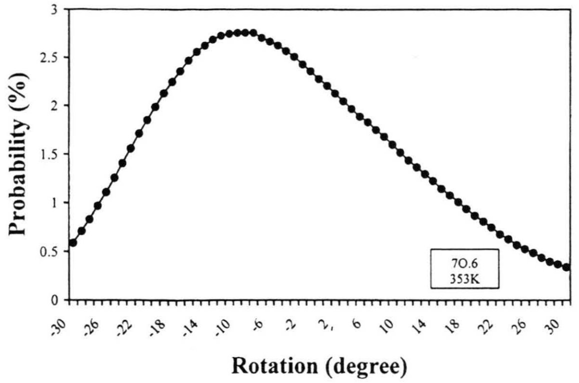

Fig. 6. Variation of the probability with respect to rotation about the X-axis during in-plane interactions at phase transition temperature.

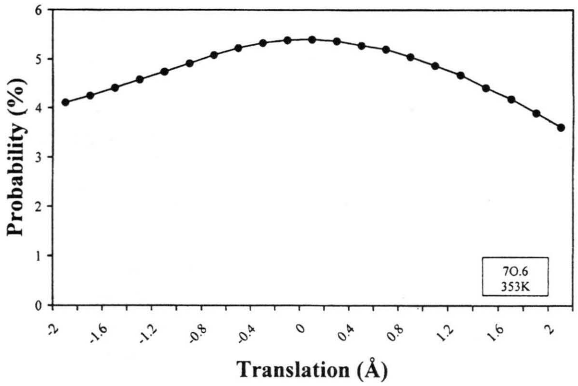

Fig. 7. Variation of the probability with respect to translation along the X-axis during in-plane interactions at the phase transition temperature.

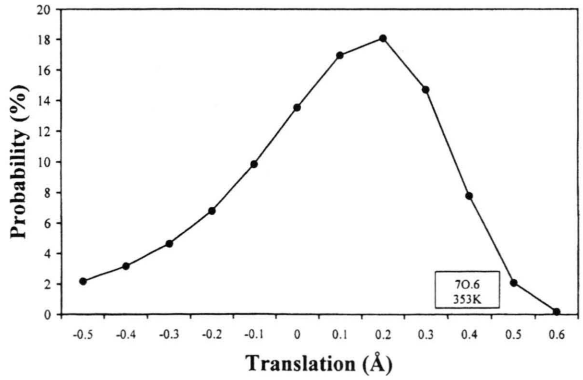

Fig. 8. Variation of the probability with respect to translation along the Y-axis during in-plane interactions at the phase transition temperature.

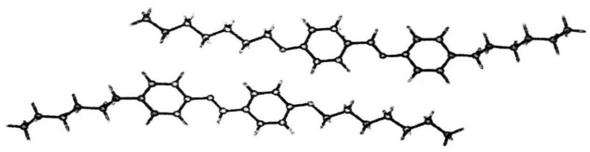

Fig. 9. The lowest in-plane energy configuration obtained with an energy of −7.09 kcal/mole at an intermolecular separation of 3.55 Å.

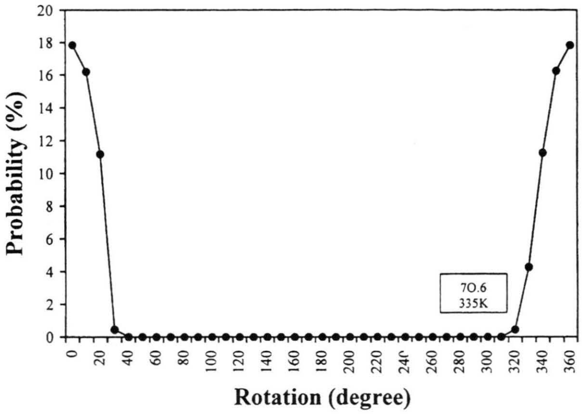

Fig. 10. Variation of the probability with respect to rotation about X-axis during terminal interactions at phase transition temperature.

±0.2 Å, which restricts the translational freedom of stacked molecules along the Y-axis and favours an overlapped layered structure in the mesophase.

Again, the energy has been minimized with respect to translation and rotation about all axes. The lowest in-plane geometry is obtained at a separation of 3.55 Å with an energy of –7.79 kcal/mole (Fig. 9).

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. The terminal interactions are much weaker than the stacking and in-plane interactions. Rotation about the X-axis (Fig. 10) shows no preference for any angle. The salient features have been reported in Table 1.

The refined interaction energies corresponding to the minimum energy configuration of each type of interaction, i.e. stacking in-plane and terminal, are reported in Table 1 with all the contributing terms to enable comparison. It seems important to note that the largest at-

Table 1. Minimum energies obtained during stacking, in-plane and terminal interactions between a pair of **7O.6** molecules after refinement. Energy is expressed in kcal/mole.

Energy terms	Stacking energy	In-plane energy	Terminal energy
E_{QQ}	–0.052	–0.080	0.018
E_{QMI}	0.009	0.002	0.000
E_{MIMI}	–0.090	–0.475	–0.026
E_{el}	–0.133	–0.553	–0.008
E_{pol}	–0.324	–0.206	–0.014
E_{disp}	–27.949	–10.073	–6.149
E_{rep}	11.818	3.038	2.718
E_{total}	–17.088	–7.794	–3.453

Table 2. Translational rigidities along the *X*, *Y*, and *Z*-axis during stacking and in plane interactions between a pair of **7O.6** molecules.

Temperature (K)	Rigidity during stacking interactions		Rigidity during in-plane interactions	
	along *X*-axis ±0.2 Å	along *Z*-axis ±0.1 Å	along *X*-axis ±0.2 Å	along *Y*-axis ±0.1 Å
300	0.64	0.92	0.51	0.56
310.5	0.63	0.90	0.51	0.58
353 S_A-I	0.62	0.85	0.50	0.57

tractive contribution in stabilizing the stacked, in-plane and terminal interacting pair of **7O.6** molecules comes from dispersion forces. Further, all possible geometrical arrangement of a molecular pair during stacking, in-plane and terminal interactions have been considered and provide information about the molecular arrangements inside bulk materials.

Correlation of the Results

In order to examine the results more closely, some parameters have been calculated and an attempt has been made to understand the molecular behaviour in terms of their relative order:

The Translational Rigidity has been defined as the ratio of the probabilities of being at the most probable point to that of being displaced by ±0.2 Å along the *X*-axis, while the displacement amounts to ±0.1 Å along the *Z*-axis during stacking interactions. Table 2 compares the translational rigidities for stacking and in-plane interactions. It may be noted that the rigidities decrease slowly with increasing temperature. Further, the nature of the curve in Fig. 2 shows the tendency of 7O.6 molecules to form a layered structure.

Table 3. Rotational rigidities during stacking, in plane, and terminal interactions between a pair of **7O.6** molecules.

Temperature (K)	Rigidity during stacking interactions	Rigidity during in-plane interactions
	about *Z*-axis ±1°	about *X*-axis ±1°
300	0.52	0.50
310.5	0.52	0.50
353 S_A-I	0.51	0.50

The Rotational Rigidity has been defined as the ratio of the probabilities of being at the most probable point to that of being notated by ±1° about the *Z*-axis during stacking interactions, while the rotation is extended about the *X*-axis for in-plane interactions (Table 3). It may, therefore, be concluded that the flexibility of rotation about the *Z*-axis is sufficiently small (Fig. 3), which accounts for the smectic character of the molecule.

These calculations show that **7O.6** molecules have a strong capacity of forming a layered structure. Translational motion of a stacked dimer along either of the axes is least probable, while orientational freedom is completely restricted. All these parameters favour the smectogenic behaviour of the compund.

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