Theoretical Study of Molecular Ordering in Nematogens:4-(4propoxy benzilidine amino) benzoic acid

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Abstract- The peculiar changes-characteristics of mesomorphic behaviour, which occur at phase transitions, are primarily governed by intermolecular interactions acting between sides, planes and terminals of a pair of liquid crystalline molecules. In view of this fact, intermolecular interactions between a pair of 4-(4-propoxybenzilidineamino) (3BABA) molecules have been evaluated using modified second order perturbation treatment along with multicentred- multipole expansion method. Using the results of stacking, in-plane and terminal interaction energy studies, probability calculations at varied angular and positional configurations in a molecular pair of 3 BABA have been carried out employing Maxwell-Boltzmann formula. An attempt has been made to elucidate the nematogenic behaviour of 3 BABA molecules in terms of translational freedom, orientational flexibility etc.

Keywords- Intermolecular interactions, Liquid crystals, ab initio , Molecular ordering, Nematogens, Phase Transition, Interaction energy

1.Introduction

Liquid crystalline phases are stable condensed phases in which molecules pack together with order that is intermediate between the three-dimensional order of a crystalline solid and the disorder of an isotropic liquid. Liquid crystals always have partial orientational order of the molecules. Some liquid crystalline phases also have partial positional order of the molecules. The partial molecular ordering, which is the characteristic of liquid crystallinity occurs frequently in both natural and synthetic materials. Thus, liquid crystals are of considerable basic and applied interest [1-3].In view of the key role of molecular interactions in mesogenic compounds, semi-emperical studies have been carried out by several workers.

Considerable progress has been made in understanding the liquid crystalline phases using computer simulation techniques [4-10]. Since mesogenic properties are related to molecular aggregation in a specific manner, probability distribution calculations based on interaction energy results are expected to provide information about most probable molecular aggregation, as well as tendency to retain translational and orientational order at different transition temperatures [11-15]. The present paper embodies the results of probability studies carried out in case of a nematic liquid crystal namely 4-(4-propoxy benzilidine aminobenzoic acid (3BABA) ;which passes from crystal to nematic at 463 K and nematic to isotropic phase at 545K [16].

2. Method

Net charge and corresponding dipole moment components at each of the atomic centres of the molecule have been computed by an ab-initio method,(GAMESS) with 6-31*G basis set method . Modified Rayleigh-Schrodinger second order perturbation theory along with multicentred-multipole expansion technique has been used to evaluate intermolecular interactions between a pair of 3BABA molecules. Energy minimization has been carried out, separately, for both stacking and in-plane (side-to-side and end-to-end) interactions. Accuracies up to 0.1 Å in sliding (translation) and 1□ in rotation have been achieved.

The calculation of probabilities of various molecular pairs has been carried out using the Maxwell-Boltzmann formula :

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

where P_i is the probability corresponding to the configuration *i* and $\beta = 1/kT$, where k and T are Boltzmann constant and absolute temperature respectively; and $\square_i$ represents the energy of configuration *i* relative to the minimum energy value in a particular set for which the probability distribution is being computed. The details of mathematical formalism and optimization process can be found in literature [11-15].

3. Results and Discussion

3.1 Stacking Interactions

Table 1: Comparative probability of minimum energy stacked complexes of 3BABA with respect to translation along Z-axis corresponding to various rotational sets

Configuration	Separation	Energy	Probability(%)		
	(Å)	kcal/mol	300 K	463K	545K
X(0□)Y(0□)	3.5	-11.56	0.15	1.18	2.01
X(0□)Y(180□)	3.5	-15.33	84.15	71.11	65.25
X(180□)Y(0□)	3.5	-12.04	0.34	1.99	3.12
X(180□)Y(180□)	3.5	-14.31	15.10	23.36	25.34

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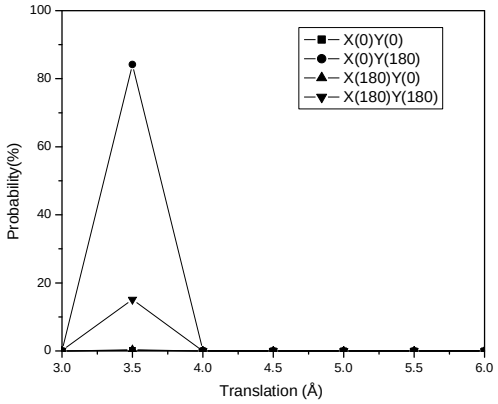

Fig 1 : Variation of probability of various molecular pairs of 3BABA with respect to translation of one of the stacked molecules along an axis perpendicular to the molecular plane and passes through the centre of mass(Z-axis) at 300K

The variation of probability with respect to translation of one of the stacked molecules along the Z-axis corresponding to four sets of axial rotations viz. X(0□)Y(0□), X(0□)Y(180□), X(180□)Y(0□) and X(180□)Y(180□) has been shown in Fig 1. It is clear from Fig 1 that the configuration X(0□)Y(180□) shows a maximum probability of 84% with energy -15.33 kcal/mole at an inter-planar separation of 3.5 Å. It is seen that for further translation, probability decreases and reduces to zero at 4.0 Å.

The configuration X(180□)Y(180□) has probability of 15.10% with energy -14.31 kcal/mole at the same inter-planar separation 3.5 Å. The probability distribution of the rotational sets X(180□)Y(0□) and X(0□)Y(0□) shows their maxima at 3.5 Å with 0.34% and 0.15% respectively. An analysis of the relative probability of being at maxima points is shown in Table 1. It is obvious that the configuration X(0□)Y(180□) has 71.11% probability of occurrence at crystal to nematic transition temperature while configurations X(180□)Y(180□), X(180□)Y(0□) and X(0□)Y(0□) have probabilities 23.36, 1.99 and 1.18% respectively. In subsequent calculations, therefore, configuration X(0□)Y(180□) has been chosen. The effect of translation along X-axis has been studied for the configuration X(0□)Y(180□).

Table 2: Comparative probability of the minimum energy stacked complexes during translation along X-axis of 3 BABA

molecules corresponding to four selective rotations about Z-axis.

Rotation about	Energy	Probability(%)		
Z-axis	kcal/mole	300K	463K	545K
0□	-15.33	16.82	16.56	15.70
90□	-10.45	0.005	0.08	0.17
180□	-15.86	27.59	29.21	25.43
270□	-10.44	0.005	0.08	0.17

The variation of probability with respect to sliding of one of the stacked molecules along the X-axis corresponding to four sets of selective rotation about Z-axis by 0, 90, 180 and 270□ has been shown in Fig 2. It may be observed that the configuration with Z(180□) shows a relatively sharp peak with energy value of -15.86 kcal/mole and about 40.4% probability at the maxima. Further as shown in Table 2, the configuration Z(0□) has probability of occurrence 16.82% with energy-15.33 kcal/mole. The configuration Z(90□) and Z(270□) have nearly same probability of 0.005% respectively. Thus, the minimum energy configuration for a stacked pair of 3BABA corresponds to X(0□)Y(180□)Z(180□). This clearly indicates that perpendicularly stacked patterns of liquid crystal molecules are energetically unfavoured. Variation of probability with respect to translation of one of the stacked molecules along Y-axis is shown in

fig 3, which shows a peak at 40.5% probability value with energy-18.36k cal/mole at the intermolecular separation of-1.2 Å. Further for translations in a narrow range ,the decrement in the probability is also small (nearly 5-10%). This indicates that translation along Y-axis, in a small range, is probable at increased temperatures.

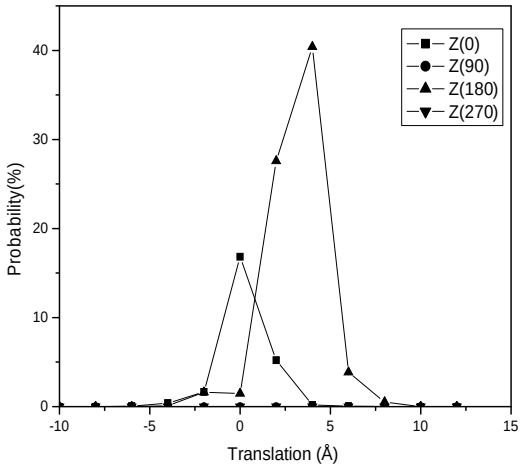

Fig 2: Variation of probability of various molecular pairs of 3BABA with respect to translation with respect to translation of one of the stacked molecules along its long molecular axis (X-axis).

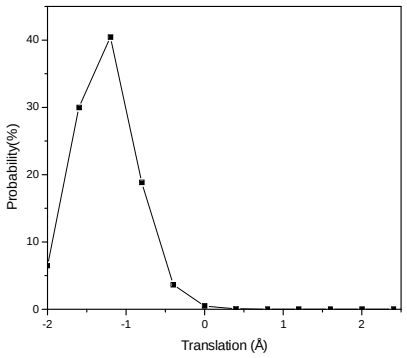

Fig 3: Variation of probability of various molecular pairs of 3 BABA with respect to translation of one of the stacked molecules along an axis perpendicular to the long molecular axis and lying in the molecular plane (Y-axis)

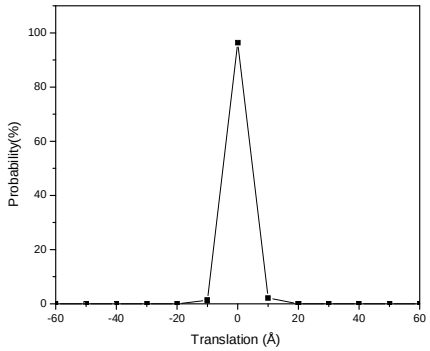

Fig 4: Variation of probability of various molecular pairs of 3BABA with respect to rotation of one of the stacked molecules along an axis perpendicular the molecular plane and passing approximately through the centre of mass of the 3BABA molecule (Z-axis).

The optimum inter- planar distance is 3.5 A and one of the stacked possesses X(0)Y(180)Z(180) configuration.
As observed from fig 4, maximum probability 96.5% lies at perfectly aligned structure with energy value -21.19 kcal/mole at relative orientation 0□. The peak becomes sharper at decreased temperatures and, hence, makes configuration more rigid.

3.2In-plane Interactions

The variation of probability at 300K with respect to in-plane (side-to-side) translation of one of the molecules along X-axis relative to other during in-plane interactions has been shown in Fig 5.

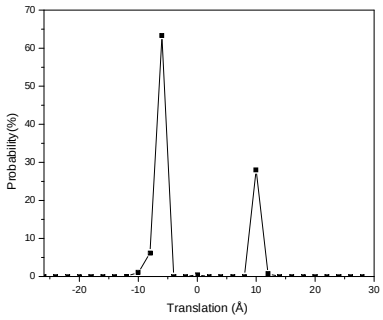

Fig5: Variation of probability of various molecular pairs of 3BABA with respect to translation of one of the molecules along the long molecular axis (X-axis) during in plane (side to side) interactions.

The intermolecular separation along Y-axis is 5.5 Å and one of the molecules possesses X(0□)Y(0□)Z(0□) configuration. As evident from Fig 5, maximum probability (nearly 63%) occurs when one of the interacting molecules is displaced by 2.0 Å along X-axis.Similarily the transition of one of the molecules along y-axis gives rise to a probability maximum at nearly 40% value.This indicates that molecules of 3BABA a translation freedom in a small range during side-by-side interaction also.

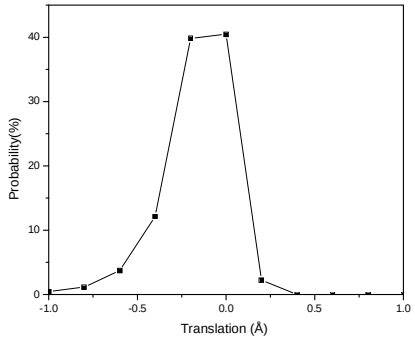

Fig:6 Variation of probability of various molecular pairs of 3BABA with respect to translation of one of the molecules along Y-axis during in plane (side to side) interactions.

3.3 Terminal Interactions

4-(4-Propoxy benzilidene amino) benzoic acid (3 BABA) is associated with –OCH_3 at one end and -COOH at the other Terminal interactions have been evaluated. All possible interacting combinations between terminal groups have been considered. It has been observed that most stable

configuration corresponds to (-OCH_3---HOOC-) interacting groups with energy -5.05 k cal/ mole and the minimum inter-group separation is 2.1 Å . Other possible interacting groups such as (-COOH---HOOC-) and (-OCH_3--CH_3O-), show energy values less than 1 kcal/mole.

Variation of probability with respect to translation along the long molecular axis in case of terminal interactions is shown in Fig 7.Maximum probability comes out to be 22% which implies a lesser possibility of the existence of end to end paired configurations of 3 BABA molecules.

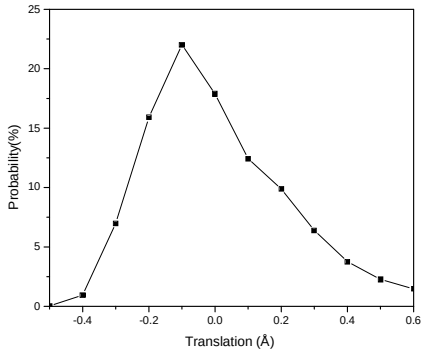

Fig 7: Variation of probability of various molecular pairs of 3BABA with respect to translation of one of the molecules along the long molecular axis (X-axis) during terminal interactions corresponding to (-OCH_3---HOOC-) interacting groups.

4. Conclusion

The present investigations reveals that 3BABA molecule has a strong preference for aligned structure at transition temperature. In a stacked molecular pair, both orientational flexibility and transitional freedom are minimal corresponding to minimum energy configuration. Other configurations show greater translational flexibility alongwith their intrinsic preference for aligned structure. Induced dipole interactions are dominant in stabilising the molecular pairs. These results favour the nematic behaviour of the 3BABAmolecule.

Acknowledgements

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