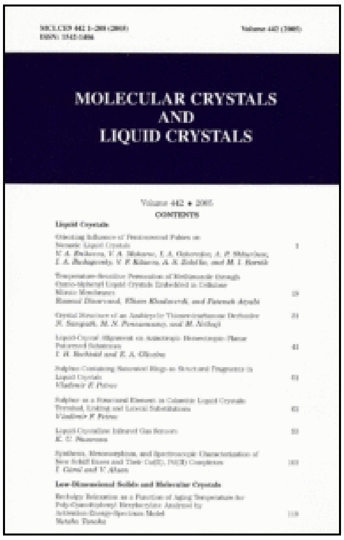

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Ordering of a Strong Polar Nematogen (6CBB) in a Dielectric Medium: A Computational Analysis

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A computational analysis of molecular ordering of a strongly polar nematogen 4-cyanobiphenyl-4′-hexylbiphenyl carboxylate (6CBB), has been carried out with respect to translational and orientational motions. 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 the multicentered-multipole expansion method, has been employed to evaluate the long-range intermolecular interactions, while the 6-exp *potential function has been assumed for short-range interactions. The total interaction energy values obtained through these computations were used as input for calculating the probability of each configuration in a dielectric medium (i.e., noninteracting and nonmesogenic solvent, benzene) at the nematic-isotropic transition temperature (633 K) using the Maxwell-Boltzmann formula. On the basis of stacking, in-plane, and terminal interaction energy calculations, all possible geometrical arrangements of molecular pairs have been considered. It has been observed that the energies are redistributed in a dielectric medium, and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same. The present article provides a new and interesting way of looking at the nematogen in a dielectric medium.*

Keywords 6CBB; dielectric medium; nematogen; quantum chemistry

Introduction

Liquid crystals (LCs), as crystals that flow, have intrigued crystallographers and device engineers, and are intermediary in structure and molecular organization between amorphous liquid state and the solid crystalline state. Theoretical ideas that underlie the strategies for modeling of these molecules is an active area of research using the information about the structure, properties of molecules, their most probable orientations, and the nature and energies of intermolecular interactions [1]. The stability and material properties of liquid crystals have their origins in the structure and bonding of individual molecules. In a recent study of the phase sequence of LCs (mesomorphism), much attention has been paid to molecules possessnig three or four aromatic groups [2,3]. The structural characteristics of such systems depend on

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Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada 520 008, A.P., India. E-mail: durga_ojha@hotmail.com fine structural features of their molecules, including the addition/alteration of aromatic and/or cyclo aliphatic fragments in the model LC system. Such investigations explore many interesting dimensions not only for understanding the chemical and physicochemical properties but also for designing new materials with tailored applications [4].

The underpinning prerequisite for liquid crystallinity is that the mesophase owes its stability to the anisotropic shape of the molecules. The scenario of phase transitions in LCs requires the breakdown of the molecular packing order under the influence of rapid rotation about the long axis of the molecule to give a smectic phase, in which the long-range positional order is lost. When the local packing order is destroyed but the orientational order still remains with the molecules reorganizing so that their long axes lie in the same direction, this produces the nematic phase. From a technological and basic research point of view, it is worth stressing the importance of understanding the link between molecular structure and the resulting collective organization as a significant aid in molecular design. However, it is a complex task, because the molecules forming the mesophase are normally quite complex, with rigid aromatic cores (the source of anisotropy), flexible chains, and shape asymmetry, as well as dipoles or quadrupoles. An appropriate modeling of these features can yield a unique insight into molecular ordering, fluidity, and phase anisotropy of the liquid-crystalline compounds [5,6].

The problem of predicting physical properties of liquid-crystalline compounds based upon molecular shape and intermolecular interactions requires the adoption of a model potential [7]. A significant contribution to the total pair energy can be achieved by the electrostatic interactions in a molecular pair; but, more importantly, their anisotropy plays a significant role in molecular recognition. The nonbonded interactions involve coulombic and, dispersion forces. Many LC molecules have a permanent dipole moment and, therefore a dipole-dipole term is also necessary. Higher order multipole terms are thought to influence the bulk structure but are often excluded due to the lack of the experimental measurements of quadrupole moments. Molecular interactions can promote or oppose polar organization in mesophases. Thus, the adopted model potential has a crucial role in a better understanding of mesomorphism.

The role of molecular interactions in mesomorphic compounds has received the attention of several workers [8–10] 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. Thus, the main emphasis was on finding out the minimum energy with observed crystal structure, the basic motive for ordering of 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 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. Because 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 a strongly polar nematogen 4-cyanobiphenyl-4′-hexylbiphenyl carboxylate (6CBB) in terms of the configurational probabilities between a molecular pair of 6CBB in a dielectric medium (i.e., the noninteracting and nonmesogenic 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? for stacking and 8? for in-plane interactions. Similarly, a distance of 22? has been kept for terminal interactions. The choice of distance has been 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 behavior of the molecules surrounding a fixed molecule in a particular frame of reference. An examination of thermodynamic data has revealed that 6CBB exhibits nematic-isotropic transition at 633 K [11].

Method of Calculation and Formalism

The molecular geometry of 6CBB has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [11]. Depending on the property interest, a number of following methodologies have been employed in this work.

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 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 incorrect 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 that 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. These are equivalent to Lowdin orthogonalized charges [13,14]. A revised version QCPE No. 142, 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.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on a simplified formula provided by Claverie [15] 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 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 [16] for intermediate-range interactions, the total pair interaction energy of molecules (U_{pair}) is represented as the sum of various terms contributing to the total energy:

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

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

$$U_{el} = U_{QQ} + U_{QMI} + U_{MIMI} +, \cdots,$$

where U_{QQ}, U_{QMI}, U_{MIMI}, etc., are monopole–monopole, monopole–dipole, and dipole–dipole terms, respectively. In fact, the inclusion of higher order multipoles does not significantly, affect the electrostatic interaction energy and the calculation only up to dipole–dipole term gives satisfactory results [17]. The computation of an 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 several semiemperical approaches, viz. the Lennard-Jones or Buckingham-type approaches, actually proceed in this way. Kitaygorodsky [17] introduced a Buckingham formula whose parameters were later modified by Praveen and Ojha for hydrocarbon molecules [17] and several other molecules and finally gave the expression:

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

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

where $Z = R_{\lambda\nu}/R^{0}_{\lambda\nu}$; $R^{0}_{\lambda\nu} = \left[\left(2R^{w}_{\lambda}\right)\left(2R^{w}_{\nu}\right)\right]^{1/2}$, 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. The necessary formulae may be found elsewhere [18].

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 along a bond parallel to the long molecular axis while the y-axis lies in the plane of the molecule and z-axis perpendicular to the x-y plane.

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 [19] in order to obtain a better insight:

$$P_i = \exp(-\beta\varepsilon_i) \Big/ \sum\nolimits_i \exp(-\beta\varepsilon_i)$$

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.

Results and Discussion

The molecular geometry of 6CBB is shown in Fig. 1. Calculated atomic charges and dipole moment components are listed in Table 1. The results of the probability distribution corresponding to the different modes of interactions are discussed below.

Stacking Interactions

One of the interacting molecules is fixed in the x-y plane, and the second has been kept at a separation of 6 Å along the z-axis with respect to the fixed one. The study of the variation of probability with respect to translation along the x-axis corresponding to configuration y (0°) z (0°) is shown in Fig. 2. Evidently, the variation of probability is constant in the region of 1.8 Å ± 1.2 Å, which shows that a sliding of one molecule over an other is energetically allowed for a small range, which may be correlated with the fluidity of the compound maintaining its alignment in the mesophase. Having refined the interacting configuration with respect to translation along the x-axis at the equilibrium condition, the energy is brought down and the configurational probability is further investigated with respect to rotation about the x-axis.

Figure 3 shows the variation of probability with respect to rotation about the x-axis corresponding to configuration y (180°) z (0°) has been carried out, and it has been observed that the maximum probability corresponds to 6CBB at −2 degrees rotation, indicating a slight preference for the aligned structure of this configuration. The minimum energy thus obtained is taken as the starting point and the entire process is repeated for small intervals. The energy is minimized with respect to translations and rotations about x, y, and z-axes. An accuracy of 0.1 Å in translation and 1 degree in rotation of one molecule with respect to the other was achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. The global search for 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.

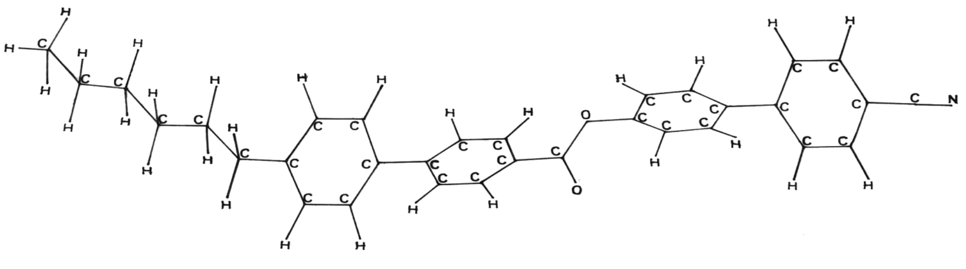

Figure 1. Molecular geometry of 6CBB along with various atoms.

Table 1. Calculated atomic net charges and dipole moments for 6CBB molecule. These are Complete Neglect Differential Overlap (CNDO) charges and are equivalent to Lowdin orthogonalized charges

			Atomic dipole components		
S. no.	Atom	Charge	μ_X	μ_Y	μ_Z
1	C	0.075	−0.109	0.012	0.006
2	C	0.034	−0.056	−0.042	−0.019
3	C	0.017	0.037	−0.055	0.115
4	C	−0.004	−0.065	−0.040	0.109
5	C	0.035	−0.075	0.019	0.005
6	C	−0.004	−0.067	0.035	−0.118
7	C	0.013	0.037	0.074	−0.140
8	C	0.021	0.044	0.021	−0.001
9	C	0.002	0.048	0.009	0.114
10	C	−0.001	−0.059	0.017	0.102
11	C	0.031	−0.075	−0.007	−0.023
12	C	−0.002	−0.050	−0.021	−0.109
13	C	−0.001	0.048	−0.004	−0.127
14	C	0.008	−0.015	0.007	0.051
15	C	0.016	0.052	−0.007	−0.091
16	C	0.017	−0.042	0.012	0.079
17	C	0.016	0.050	−0.012	−0.075
18	C	0.016	−0.034	0.014	0.075
19	C	0.015	0.050	−0.012	−0.073
20	O	−0.019	−0.027	0.022	0.083
21	O	−0.022	0.062	−0.021	−0.093
22	C	−0.008	−0.156	−0.016	0.022
23	C	0.167	−0.080	0.243	0.001
24	C	−0.032	−0.163	−0.070	−0.001
25	C	0.004	−0.089	−0.120	−0.016
26	C	−0.035	0.069	−0.120	−0.016
27	C	0.190	−0.192	0.034	−0.012
28	C	−0.037	0.042	0.185	0.029
29	C	0.010	−0.086	0.090	0.010
30	C	0.409	0.234	0.095	−0.050
31	C	−0.053	−0.013	−0.053	0.019
32	C	0.033	0.031	0.162	−0.037
33	C	0.021	0.016	−0.118	0.012
34	C	−0.006	0.125	0.123	−0.013
35	N	−0.071	−0.859	1.630	0.009
36	H	−0.001	0.000	0.000	0.000
37	H	−0.008	0.000	0.000	0.000
38	H	−0.007	0.000	0.000	0.000
39	H	−0.001	0.000	0.000	0.000
40	H	−0.012	0.000	0.000	0.000

(*Continued*)

Table 1. Continued

S. no.	Atom	Charge	Atomic dipole components μ_X	μ_Y	μ_Z
41	H	−0.013	0.000	0.000	0.000
42	H	−0.013	0.000	0.000	0.000
43	H	−0.009	0.000	0.000	0.000
44	H	−0.004	0.000	0.000	0.000
45	H	0.000	0.000	0.000	0.000
46	H	−0.006	0.000	0.000	0.000
47	H	−0.007	0.000	0.000	0.000
48	H	−0.008	0.000	0.000	0.000
49	H	−0.008	0.000	0.000	0.000
50	H	−0.007	0.000	0.000	0.000
51	H	−0.007	0.000	0.000	0.000
52	H	−0.008	0.000	0.000	0.000
53	H	−0.008	0.000	0.000	0.000
54	H	−0.007	0.000	0.000	0.000
55	H	−0.008	0.000	0.000	0.000
56	H	−0.008	0.000	0.000	0.000
57	H	−0.007	0.000	0.000	0.000
58	H	−0.007	0.000	0.000	0.000
59	H	−0.007	0.000	0.000	0.000
60	H	0.000	0.000	0.000	0.000
61	H	−0.004	0.000	0.000	0.000
62	H	0.000	0.000	0.000	0.000
63	H	0.003	0.000	0.000	0.000
64	H	−0.007	0.000	0.000	0.000

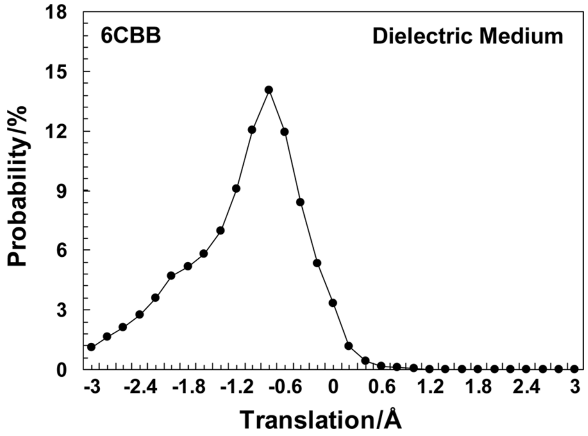

Figure 2. Variation of probability with respect to translation along the x-axis during stacking interactions at nematic-isotropic transition temperature 633 K corresponding to configuration y (0°) z (0°).

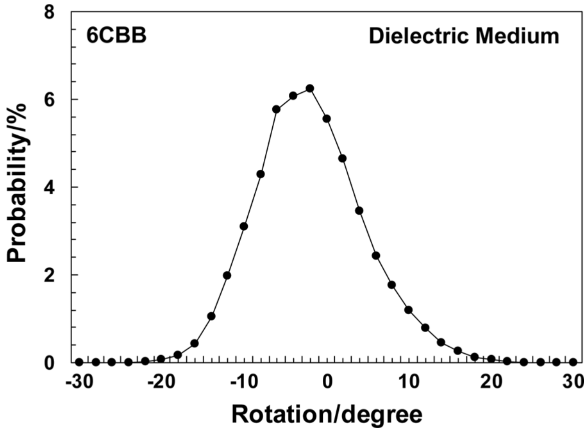

Figure 3. Variation of probability with respect to rotation about the x-axis during stacking interactions at nematic-isotropic transition temperature 633 K corresponding to configuration y (180°) z (0°).

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 effect of translation along the x-axis corresponding to the configuration y (0°) is shown in Fig. 4 at nematic-isotropic transition temperature (633 K). Because in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. It is evident from the figure that the maximum probability occurs at the equilibrium position. The interacting configurations have been refined with respect to translation along the x-axis at the equilibrium condition, the energy is brought down, and the probability is further investigated with respect to rotation about x-axis.

Figure 5 shows the variation of probability with respect to rotation about the x-axis corresponding to configuration y (180°). Evidently, a pronounced peak exists

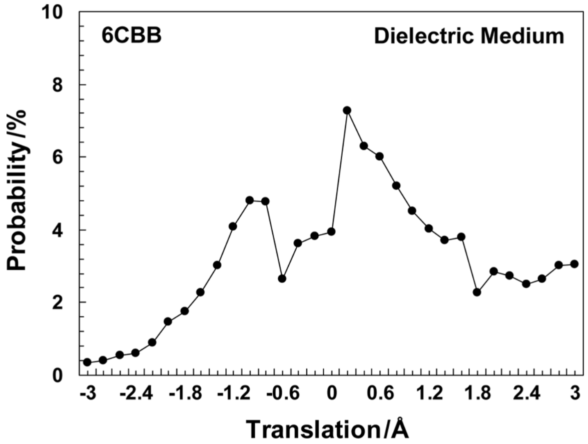

Figure 4. Effect of translation along the x-axis during in-plane interactions at nematic-isotropic transition temperature 633 K corresponding to configuration y (0°).

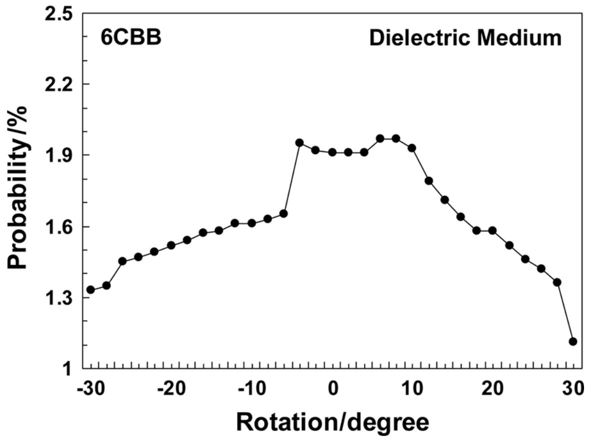

Figure 5. Variation of probability with respect to rotation about the x-axis during in-plane interactions at nematic-isotropic transition temperature 633 K corresponding to configuration y (180°).

at the equilibrium point, and all the remaining regions have negligible probability compared to this configuration. Furthermore, it may be observed that the rotational freedom is much more pronounced compared to the stacking interactions. The variation of the probability with respect to rotation about the y-axis corresponding to the configuration x (0°) has also been carried out, and it is observed that the rotation about the y-axis does not alter the configurational probability drastically.

Terminal Interactions

To investigate the terminal interactions apart from van der Waals forces, the interacting molecules have been shifted along the x-axis by 22 Å with respect to each other, and rotations were allowed about the x-axis. The rotations about the x-axis corresponding to configuration y (0°) show (Fig. 6) no preference for any angle; that is, the molecules are completely free to rotate about their long molecular axes.

Translational Effect

The present calculation may be reasonably correlated with the nematic character of a the system. The nematic character of a liquid crystal is generally manifested by its translational freedom along the long molecular axes. Figure 7 shows that the translational rigidity parameter[1] as a function of temperature along the long molecular axis is 0.59 at the nematic-isotropic transition temperature (633 K) in dielectric medium. However, at room temperature (300 K) the value is 0.67, indicating a strong binding at low temperature, but with an increase of temperature, the molecules obtain sufficient freedom to slide along the long molecular axis. Such translational freedom is much more pronounced in planar interactions. Evidently, even at room temperature this value is 0.56, which reduced to 0.43 at nematic-isotropic transition temperature (633 K). It may be noted that though the freedom is considerable for smaller

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[1] This has been defined as the ratio of probability being at maximum probable point having +0.2 Å displacement along the long molecular axes.

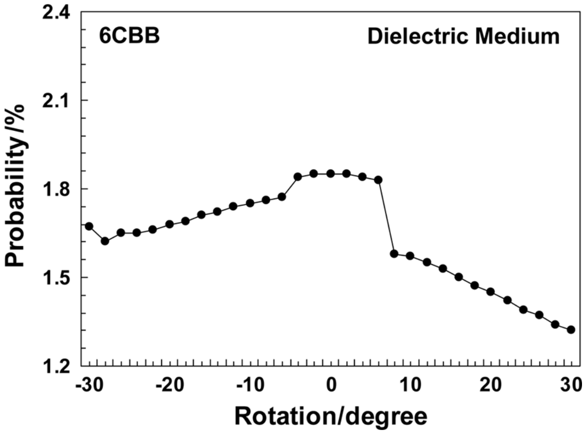

Figure 6. Variation of probability with respect to rotation about the x-axis during terminal interactions at nematic-isotropic transition temperature 633 K corresponding to configuration y (0°).

translation, longer translations are not generally permitted. Thus, in the mesomorphic range, only small movements of a molecule are possible. However, the comparable values in both the cases (i.e., stacking and in-plane interactions) show that the molecule 6CBB does not show extraordinary preference in forming the stacked layers and hence justifies the nematic character.

The Effect of Dielectric Medium

In order to examine the effect of a dielectric medium on a nematogen, the various possible geometrical arrangements between a molecular pair have been considered. Table 2 shows the relative probabilities of different minimum energy configurations,

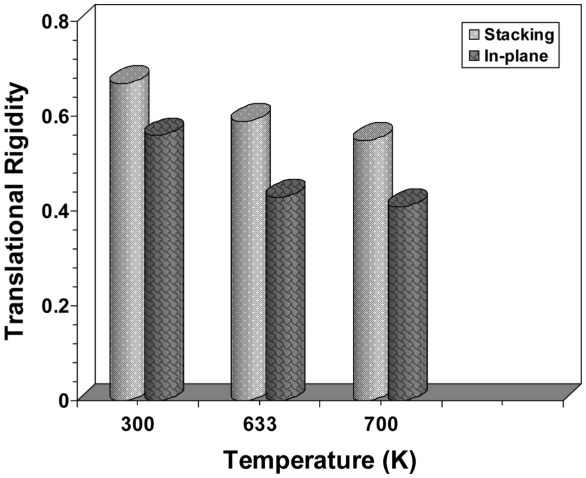

Fig. 7. Translational rigidity parameters as a function of temperature during stacking and in-plane interactions at room temperature (300 K), nematic-isotropic transition temperature (633 K), and above transition temperature (700 K).

Table 2. Relative probabilities of different minimum energy configurations obtained for stacking, in-plane, and terminal interactions in vacuum and in dielectric medium (benzene) at nematic-isotropic temperature (633 K). Average dielectric constant of benzene is taken as 2.25

Configuration	Energy in vacuum (kcal/mol)	Energy in dielectric medium (kcal/mol)	Probability (%)	
			A	B
y (0°) z (0°)[a]	−3.89	−1.72	13.43	20.52
y (180°) z (0°)[a]	−5.97	−2.65	74.62	43.66
y (0°)[b]	−2.56	−1.13	4.47	12.66
y (180°)[b]	−2.91	−1.29	5.97	14.41
y (0°)[c]	−1.46	−0.64	1.49	8.73

[a] Stacking interactions.
[b] In-plane interactions.
[c] Terminal interactions.
A = Probability in vacuum; B = probability in dielectric medium.

calculated for vacuum and dielectric medium during the different modes of interactions. Evidently, the energy/probabilities are redistributed in dielectric medium, and there is a considerable rise in the probabilities of interactions, although the order of preference remains same. This provides theoretical support to the experimental observations [20]. Furthermore, the most favorable stacked configuration y (180°) z (0°) of pairing (i.e., 43.66% probability) has been obtained with the energy of −2.65 kcal/mol in dielectric medium at nematic-isotropic transition temperature (633 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 (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 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 is, however, of paramount importance because while cooling down 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 sequential preference depending on their individual relative probabilities.

Conclusion

It may be concluded that the energies are redistributed in dielectric medium, and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same. This provides a new and interesting way of looking at the nematogen in dielectric medium.

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