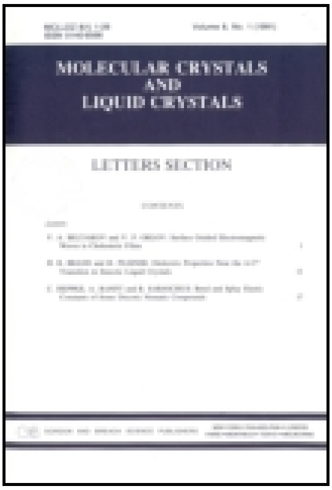
This article was downloaded by: [Xian Jiaotong University]
On: 11 December 2014, At: 13:23
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Conformational Behavior and Influence of Organic Solvents on a Strong Polar Group Nematogen at Room Temperature—A Computational Model

Durga P. Ojha[a]
[a] Liquid Crystal Research Laboratory, School of Physics, Sambalpur University, Sambalpur, Odisha, India

Published online: 27 May 2014.

To cite this article: Durga P. Ojha (2014) Conformational Behavior and Influence of Organic Solvents on a Strong Polar Group Nematogen at Room Temperature—A Computational Model, Molecular Crystals and Liquid Crystals, 593:1, 104-113, DOI: 10.1080/15421406.2013.867227

To link to this article: http://dx.doi.org/10.1080/15421406.2013.867227

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 593: pp. 104–113, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.867227

Conformational Behavior and Influence of Organic Solvents on a Strong Polar Group Nematogen at Room Temperature—A Computational Model

DURGA P. OJHA*

Liquid Crystal Research Laboratory, School of Physics, Sambalpur University, Sambalpur, Odisha, India

The conformational behavior and influence of organic solvents on a nematogen, 4'-n-alkyl-4-cyanobiphenyl, with strong polar group propyl (3CB) that is of commercial and application interest has been studied with respect to the translational and orientational motions. The atomic net charge and dipole moment components at each atomic center have been evaluated using the complete neglect differential overlap (CNDO/2) method. The modified Rayleigh-Schrodinger Perturbation theory with the multicentered-multipole expansion method has been employed to evaluate the long-range interactions, and a "6-exp." potential function has been assumed for the short-range interactions. The minimum energy configurations obtained during the different modes of interactions have been taken as input to calculate the configurational probability using the Maxwell–Boltzmann formula in nonpolar organic solvents, i.e., carbon tetrachloride ((CCl_4)), and chloroform ($(CHCl_3)$) at room temperature 300 K. It has been observed that the molecules show the interesting property in the organic solvents. The interaction energies of dimer complexes have been taken into consideration in order to investigate the most energetically stable configuration. An attempt has been made to develop an interesting computational model for nematogen at molecular level.

Keywords Conformational behavior; nematogen; organic solvents

Introduction

Liquid crystals (LCs) have the ability to self-organize into highly anisotropic and ordered structures. The mutual competition between this ability with suitable optical and electronic properties results in model building blocks for smart materials in optoelectronic devices [1,2]. However, the influential role played by the intermolecular interactions is accountable for self-organization, which can also have a dramatic control on the electrical and photophysical properties of molecules [3].

The recent research on these molecular devices explores new innovations with much attention to the molecular interactions, suitable aromatic groups and functional groups that causes/vanishes liquid crystallinity [4]. It has been observed that the dissolving of a thermotropic LC compound in a non-polar organic solvent produces ferroelectric LCs with the remarkable properties [5]. The electro-optic properties of the solutions are, to some

---

*Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, School of Physics, Sambalpur University, Jyoti Vihar 768 019, Sambalpur, Odisha, India, e-mail: durga_ojha@hotmail.com extent, better than those of “pure” LCs. Study of the effect of solvents on the molecules forms an important subject for research, and it can play a significant role in the photo physics. The solvent environment determines important changes in the electro-optical properties of the spectrally active molecules [5]. The molecular interactions in mesomorphic compounds have been reported by the several authors [6–10] based on the Rayleigh–Schrodinger perturbation method. These studies have indeed to establish the anisotropic nature of the pair potential, and subsequently find out the minimum energy configuration of a pair of mesogens.

The nematic LC phase is one in which the molecules have long-range orientational ordering, which retaining the randomness of translational motion and centre of mass position of the isotropic liquid phase. The long-range orientation consists of an imperfect configuration of the long axes of the molecules in the liquid, with the nematic director, a space fixed symmetry axes for the phase. The behavior of nematogens is believed to derive form anisotropy in their intermolecular interactions. This anisotropy is based in physical properties common to all nematogen molecules. 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 present article is an attempt to establish an interesting computational model for a nematogen in organic solvents, i.e., CCl_4 and $CHCl_3$ at room temperature 300 K. Computation of configurational probabilities between a pair of 3CB molecule has been carried out at an intermediate distance 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for the terminal interactions. The configurationally probability distribution picture based on the interaction energy results will provide valuable information in this respect.

Computational Approach

The quantum chemical computations can yield more detailed information, but they are still restricted by the contemporary computer power due to the rather large size of mesogenic molecules. Therefore, the semi-empirical approaches are often used for calculations of molecular properties. The molecular geometry of 3CB has been constructed on the basis of published crystallographic data [11] with the standard values of bond lengths and bond angles. The advancing the structure and energetic effects are helpful in employing the molecular models. The computations have been carried out in three steps:

First Step

The complete neglect differential overlap (CNDO/2) method [12] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule because the simplified formula for interaction energy calculations requires the evaluation of atomic net charges and dipole moment components at each atomic centre through an all-valance electron method. It is expected that the specific charge distribution and electrostatic interactions in LC molecules play an influential role in the formation of various mesophases. The program language is FORTRAN IV. The program is capable of computing CNDO wave functions for open- and closed-shell molecules containing the elements hydrogen to chlorine.

Second Step

The computational scheme based on simplified formula provided by Claverie [13] 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 has been used for this purpose with the further modification.

The total pair interaction energy of molecules (U_{pair}), according to the second-order perturbation theory for intermediate range interactions [14], 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}, $U_{\text{pol,}}$ U_{disp}, and U_{rep} are the electrostatic, polarization, dispersion, and repulsion energy terms respectively. Again, electrostatic term is expressed as:

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

where U_{QQ}, U_{QMI}, and U_{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 dipole-dipole term gives satisfactory result. The computation of electrostatic term has, therefore, been restricted only up to dipole-dipole energy term.

The dispersion and short-range repulsion terms are considered together because the several semi-empirical approach, viz. the Lennard–Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky introduced [15] a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [16] for hydrocarbon molecules and the several other molecules and finally gave the expression:

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

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

where $Z = R_{\lambda\nu}/R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^w_{\lambda})(2R^w_{\nu})]^{1/2}$, 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_{λ} K_{ν} allows the energy minimum to have different values according to the atomic species involved.

Third Step

In order to obtain a better insight, the total interaction energy values obtained through the different modes of interactions have been used as input to calculate the probability of occurrence of a particular configuration *i* using the Maxwell–Boltzmann formula [17]:

$$P_i = \exp(-\beta\varepsilon_i)/\Sigma_i \exp(-\beta\varepsilon_i)$$

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.

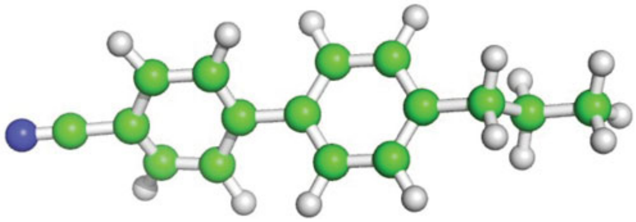


Figure 1. Molecular geometry of 3CB molecule.

In this case, the origin has been chosen at almost midpoint of the molecule. The *x*-axis been chosen along a bond parallel to the long molecular axis while the *y*-axis lies in the plane of the molecule, and *z*-axis is perpendicular to the *x*-*y* plane. The terms like stacking, in-plane, and terminal interactions will be used to maintain the continuity with the previous work [17].

Computation of Stacking Interactions. The interacting molecule has been placed at a separation of 6 Å along the *z*-axis with respect to the fixed molecule. The choice of the distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the range of short- and medium-range interactions.

Computation of In-Plane Interactions. The interacting molecule has been kept at a separation of 8 Å along *y*-axis with respect to the fixed one. The distance chosen for these calculations are such that the possible van der Waals contacts are avoided.

Computation of 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 with respect to the fixed one.

Results and Discussion

The molecular geometry of 3CB has been shown in Fig. 1. The results of configurational probability distribution during the different modes of intermolecular interactions in nonpolar solvents, i.e., CCl_4, and $CHCl_3$ are discussed below:

Influence of Organic Solvents on Stacking Interactions

The variation of the probability with respect to translation along the long molecular axis (*x*-axis) corresponding to configuration *y* (0°) *z* (0°) in CCl_4 and $CHCl_3$ at room temperature 300 K has been shown in Fig. 2. Evidently, the configuration shows a sharp preference toward the minimum energy point. The variation of probability is almost constant in the region of 24 ± 2 Å. It shows that the sliding of one molecule over another is allowed energetically in a small range that may be correlated with the fluidity of the compound maintaining its alignment in 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.

The variation of probability with respect to rotation about *x*-axis corresponding to configuration *y* (0°) *z* (180°) in CCl_4 and $CHCl_3$ at room temperature 300 K has been carried

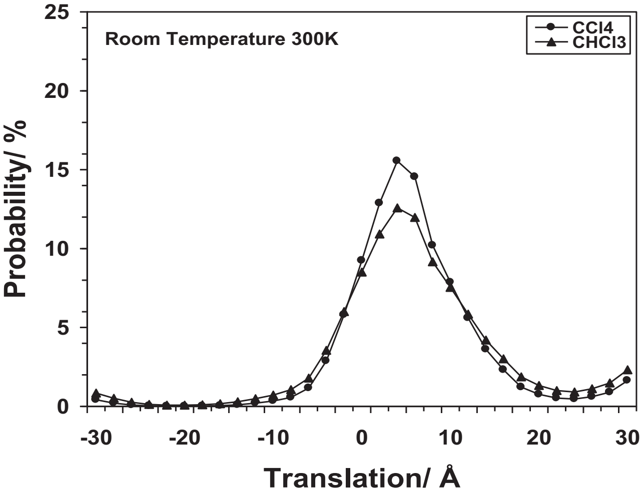


Figure 2. Variation of probability with respect to translation along *x*-axis during stacking interactions corresponding to configuration *y* (0°) *z* (0°) for 3CB molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

out that indicating a slight preference for the aligned structure of this configuration. The variation of probability with respect to rotation about *z*-axis corresponding to configuration *x* (0°) *y* (0°) has also been carried out at room temperature 300 K. It has been observed that the configuration shows a sharp preference toward the minimum-energy point. The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for small intervals. The energy has been minimized with respect to translations and rotations about the *x*-, *y*-, and *z*-axes. An accuracy of 0.1 Å in translation and 1° rotation of one molecule with respect to the other have been achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. The global search for the minimum energy configuration or the study of variation of interaction energy under pre-selected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route. The most stable configuration after refinement has been obtained in CCl_4 with energy −11.32 kcal/mole as shown in Fig. 3.

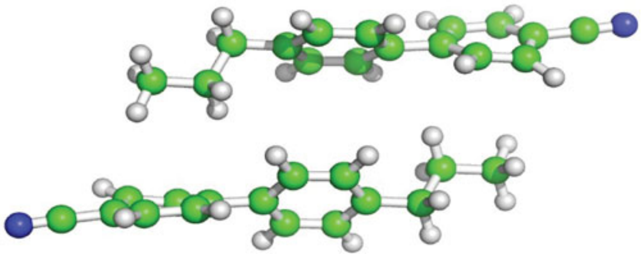


Figure 3. The most stable configuration obtained during the stacking interactions after refinement with energy −11.32 kcal/mole in CCl_4.

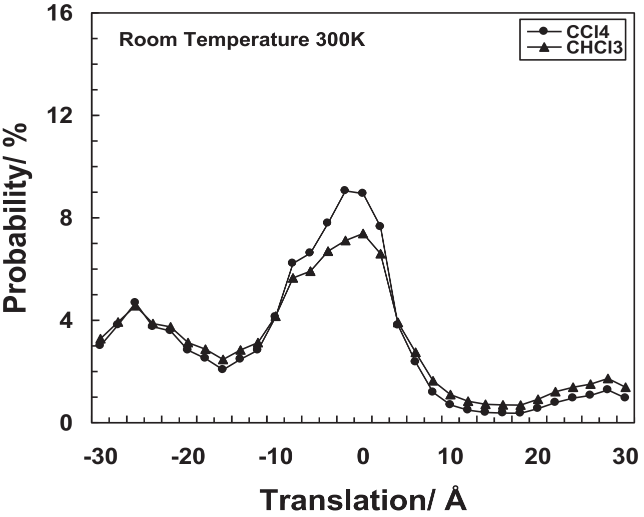


Figure 4. Variation of probability with respect to translation along *x*-axis during in-plane interactions corresponding to configuration *y* (0°) for 3CB molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

Influence of Organic Solvents on In-Plane Interactions

The variation of probability with respect to translation along *x*-axis corresponding to the configuration y (0°) in CCl_4 and $CHCl_3$ at room temperature 300 K is shown in Fig. 4. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed with the maximum probability at −4 Å in CCl_4. 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.

The variation of probability with respect to rotation about the *x*-axis corresponding to configuration *y* (180°) in CCl_4 and $CHCl_3$ at room temperature 300 K has been carried out. It has been observed that a pronounced peak exists at the one particular rotation point, and all the remaining regions have negligible probability as compared to this configuration. Furthermore, it is observed that the rotational freedom is much more pronounced as compared to the stacking interactions. The variation of the probability with respect to rotation about the *y*-axis corresponding to the configuration *x* (0°) in solvents at room temperature 300 K has also been carried out, and it is observed that the rotation about the *y*-axis does not alter the configurational probability drastically.

The energy has been minimized and most stable configuration obtained has been shown in Fig. 5 with energy −8.75 kcal/mole in CCl_4.

Influence of Organic Solvents on Terminal Interactions

The end-to-end interactions are weakest but become more important when the molecules possesses polar group at either or both ends, or if there is a possibility of hydrogen bonding. Fig. 6 shows the variation of probability with respect to rotation about *x*-axis corresponding to configuration *y* (0°) in CCl_4 and $CHCl_3$ at room temperature 300 K. The terminal interactions are much weaker as compared to stacking or in-plane interactions. However,

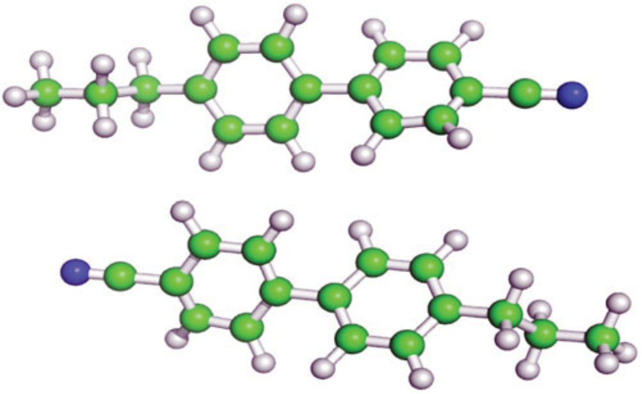


Figure 5. The most stable configuration obtained during the in-plane interactions after refinement with energy −8.75 kcal/mole in CCl_4.

the significant peaks have been observed due to the strong polar group (cyano) associated with the molecule. After refinement, the most stable configuration has been obtained in CCl_4 with energy –3.44 kcal/mole (Fig. 7).

Influence of Organic Solvents on Nematogen

In order to understand the influential role of organic solvents on strong polar group nematogen (3CB), the various possible geometrical arrangements between a molecular pair during the different modes of interactions have been considered that provide information about the molecular arrangements inside the bulk materials. Further, it is clear from the above

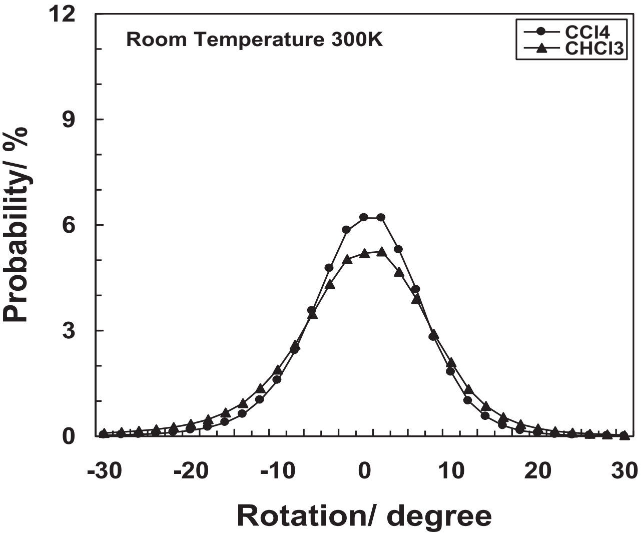


Figure 6. Variation of probability with respect to rotation about *x*-axis during terminal interactions corresponding to configuration *y* (0°) *z* (0°) for 3CB molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

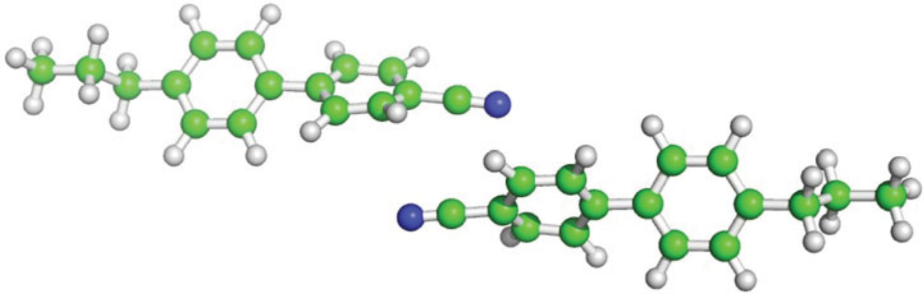


Figure 7. The most stable configuration obtained during the terminal interactions after refinement with energy −3.44 kcal/mole in CCl_4.

discussion that 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 local minimum-energy configurations. The global minimum is, however, of paramount importance because while descending 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.

Influence of Planarity and Conformational Behavior of 3CB Molecule

The most prominent energy minima of the above-mentioned interactions are further refined and the values thus obtained have been listed in Table 1 with all contributing terms to enable comparison. The results indicate that due to the planarity of the molecule, the refinement corresponding to stacking energy is maximum and the ultimate magnitude of stacking energy is much higher than in-plane and terminal interaction energies.

In order to understand the self organizing ability of nematogen, the different types of molecular interactions have been taken into consideration between a pair of 3CB molecule.

Table 1. The minimum energy obtained after refinement during stacking, in-plane, and terminal interactions between a molecular pair of 3CB. Energy is expressed in kcal/mole

Energy terms	Stacking energy	In-plane energy	Terminal energy
U_{QQ}	0.18	−0.02	0.01
U_{QMI}	−0.02	−0.21	−0.08
U_{MIMI}	−1.09	−0.09	−0.01
U_{el}	−0.92	−0.32	−0.07
U_{pol}	−0.31	−0.13	−0.01
U_{disp}	−17.39	−4.99	−1.34
U_{rep}	4.23	1.07	0.47
U_{total}	−14.39	−4.37	−0.96

U_{QQ} = monopole-monopole; U_{QMI} = monopole-dipole; U_{MIMI} = dipole-dipole; U_{el} = electrostatic; U_{pol} = polarization; U_{disp} = dispersion; U_{rep} = repulsion; and U_{total} = total.

The basic idea underlying the study of molecular conformation is to study the physical and chemical properties of compounds that are closely related to the preferred conformation.

The conformational behavior of LC displays a large variation in intermolecular effects that depends on the nature and magnitude of interactions. Each conformation may exist the distinct energy, and lower energy conformations will be populated in preference to those of higher energy. The most stable configuration of 3CB during stacking, in-plane, and terminal interactions has been obtained in CCl_4 as shown in Figs. 3, 5, and 7 respectively. A comparison of dimers suggests that the extension of the chain length, a recognizable segregation of the dimers into a highly tilted layer structure has been obtained. The mutual interaction between the dimers in the structure is, however, quite weak, in particular to chain atoms. Hence, the end chains provide enough disorder to the crystal to pass on to nematic phase. Further, the phase stability is expected to be high with extension of chain length. As the length of end chain becomes shorter, the introduction of solvent medium will inevitably increase the conjugation in the main chain with permanent coupling between electroactive properties and order.

Conclusions

The present analysis leads to the following conclusions:

1. The consideration of relative probabilities among the minimum energy configurations obtained during the stacking, in-plane, and terminal interactions provide information about the molecular arrangements inside bulk materials. Further, the phase stability is expected to be high with extension of chain length.
2. The considerable rise in the molecular interactions has been observed due to the redistribution of energy in CCl_4 and $CHCl_3$, i.e., the molecules produce the remarkable property in solvents. The most stable configuration of paring during the stacking, in-plane, and terminal interactions has been obtained in CCl_4.
3. The mutual interaction between the dimers in the structure is quite weak, in particular to chain atoms. Hence, the end chains provide enough disorder to the crystal to pass on to nematic phase.

Acknowledgments

The financial support rendered by the DAE-BRNS, Mumbai, SERB-DST, and CSIR, New Delhi, India is gratefully acknowledged.

References

[1] Fradkin, F., Kivelson, S. A., Lawler, M. J., Eisenstein, J. P., & Mackenzie, A. P. (2010). *Annu. Rev. Condens. Matter Phys.*, *1*, 153–158.

[2] Bailey, C., & Jakli, A. (2007). *Phys. Rev. Lett.*, *99*, 207801–207808.

[3] Cammidge, A. N. (2006). *Phil. Trans. R. Soc., A*, *364*, 2697–2702.

[4] Bisi, F., Longa, L., Pajak, G., & Rosso, R. (2010). *Mol. Cryst. Liq. Cryst.*, *525*, 1–8.

[5] Usol'tseva, N., Praefcke, K., Singer, D., & Gundogan, B. (1994). *Liq. Cryst.*, *16*, 601–616.

[6] Ryzhov, V. N., Guriev, K. I., & Nelnichenko, N. N. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 803–811.

[7] Sarkar, P., Paul, S., & Mandal, P. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 535–542.

[8] Yayloyan, S. M., Bezhanova, L. S. & Yayloyan, A. P. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 747–754.

[9] Tiwari, S. N., Mishra, M., & Shukla, R. (2007). *Indian J. Pure & Appl. Phys.*, *45*, 83–88.

[10] Ojha, D. P. & Praveen, P. L. (2013). *J. Phys. Chem. Solids*, *24*, 1653–1659.

[11] Haase, W., Paulus, H., & Pendzialck, R. (1983). *Mol. Cryst. Liq. Cryst.*, *100*, 211–218.

[12] Pople, J. A., & Beveridge, D. L. (1970). *Approximate Molecular Orbital Theory*, New York: Mc-Graw Hill.

[13] Claverie, P. (1978). In: *Intermolecular Interactions: From Diatomics to Biopolymers*, Pullman, B. (Ed.), New York: John Wiley.

[14] Praveen, P. L., & Ojha, D. P. (2011). *Mat. Chem. Phys.*, *126*, 248–252.

[15] Kitaygorodsky, A. I. (1961). *Tetrahedron.*, *14*, 230–236.

[16] D. P. Ojha, (2001). *Z. Naturforsch.*, *56a*, 316–323.

[17] Praveen, P. L., & Ojha, D. P. (2012). *J. Phys. Chem. Solids*, *73*, 57–62.