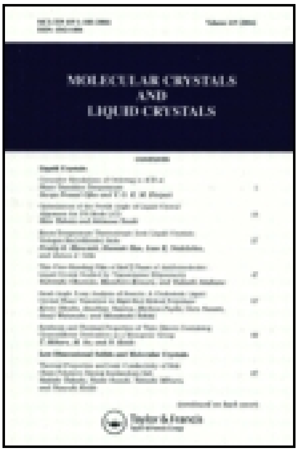

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Solvent Effects on Phase Stability of a Nematogen—A Molecular Level Approach

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The phase stability of a nematogen 4′-n-pentyloxy-4-biphenylcarbonitrile (POCB) 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 along 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 in nonpolar organic solvents, i.e., carbon tetrachloride (CCl_4), benzene (C_6H_6), and chloroform ($CHCl_3$) at room temperature (300 K). A comparison among the different solvents has been made to analyze the solvent effects. The most stable configuration has been obtained in CCl_4 during the stacking interactions. This provides a new and attention-grabbing molecular model for nematogen in nonpolar organic solvents.

Keywords Configurational probability; molecular interactions; nematogen; solvent effects

Introduction

The design of a mesogen is a distinctive object in the physics of liquid crystals as it combines both the order and mobility on a molecular level. It is of great attention for materials science and is found in the different classes of compounds [1]. At molecular level, the phases of matter are basically determined by the interplay between molecular structure, intermolecular interactions, and molecular motions [2].

The demands with respect to the chemical properties and phase behavior being largely satisfied with numerous studies [3,4], attention has been shifted to the methods of influencing the physical properties. However, there is a two-fold purpose in this regard; the properties of the molecules themselves and the interactions through which a molecular property influences the macroscopic behavior [5]. Quantum Chemical computations can yield more detailed information, but they are still restricted by the contemporary computer power due to rather large size of the mesogens molecules [6,7]. Therefore, the semiempirical approaches are often used for the calculation of molecular properties [8]. Furthermore,

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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, Andhra Pradesh, India. E-mail: durga_ojha@hotmail.com the role of the anisotropic shape as inimitable feature necessary to observe liquid crystalline phases has been confirmed by many reports [9,10].

The role of the molecular interactions in mesomorphic compounds has engrossed the attention of several researchers based on the Rayleigh–Schrodinger perturbation method [9–11]. These studies have intended to establish the anisotropic nature of the pair potential and, subsequently, find out the minimum energy configuration of a pair of mesogens. It has been observed thus the interaction energies for pair of mesogens indicates the preference of a particular configuration over the other. These values do not replicate the actual relative preference, which can only be obtained through their probabilities corresponding to each configuration. Usoltseva et al. [12] has observed that the dissolving of a thermotropic liquid crystal compound is a nonpolar organic solvent that produces ferroelectric liquid crystals with remarkable properties. The electro-optic switching properties of the solutions are, to some extent, better than those of "pure" liquid crystals [13]. These results encouraged the authors to carry out the present analysis. The solvent effect studies on present analysis. The solvent effect studies on liquid crystal are helpful in characterizing the model compound for electro-optic devices.

Hence, in the present paper, the authors report the interaction energy/configurational probability of a nematogen 4′-*n*-pentyloxy-4-biphenylcarbonitrile (POCB) in nonpolar solvents, i.e., CCl_4, C_6H_6, and $CHCl_3$ at room temperature (300 K). Interaction energies/configurational probabilities of a molecular pair have been computed 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 choice of distance has been made to eliminate the possibility of van der Waals contacts completely, and to keep the molecules within the short- and medium-range interactions. A comparison has been made to analyze the solvent effect at molecular level.

Computational Method

The molecular geometry of POCB has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [14]. The length of the most extended conformation was found to be 17.5 Å, which is the calculated length of the molecule in the crystalline state. The apparent length of the molecule in the nematic phase was found to be 24.5 Å, which is nearly 1.4 times the calculated length in the crystalline state [14]. The following computations have been carried out.

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 [15] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [16] for the evaluation of interaction energy between a molecular pair has been used to calculate the energy for fixed configuration. According to the second order perturbation theory for intermediate range interactions [17], the total pair interaction energy of molecules (U_{pair})

is represented as 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, electrostatic term is expressed as

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

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 [9–11,18]. The computation of electrostatic term has, therefore, been restricted only up to dipole–dipole energy term.

The polarization energy of a molecule(s) is obtained as the sum of polarization energies of the various bonds:

$$U_{pol}^{(s)} = C(-1/2)\sum_{u}^{(s)} \xi_u^{(s)} A_u^{=(s)} \xi_u^{(s)},$$

where $A_u^{=}$ is the polarizability tensor of the bond u and $\xi_u^{(s)}$ the electric field created at this bond by the surrounding molecules. If the molecular charge distributions are represented by the atomic charges, it is found that

$$\xi_u^{(s)} = \sum_{t\neq s}\sum_{\lambda}^{(t)} q_\lambda^{(t)} R_{\lambda\mu}/R_{\lambda\mu}^3,$$

where $R_{\lambda\mu}$ is the vector joining the atom λ in molecule t to the "center of polarizable" charge on the bond u of the molecule(s).

In the present computation, the dispersion and short-range repulsion terms are considered together because the several semiempirical approach, viz. the Lennard–Jones or Buckingham type approach, actually proceed in this way. Kitaygorodsky [19] introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [20] for hydrocarbon molecules and the several other molecules and finally gave the expression:

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

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

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

Computation of Configurational Probabilities

The total interaction energy values obtained through these computations have been used as an 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:

$$P_i = \exp(-\beta\varepsilon_i) / \sum\nolimits_{i\,\exp} (-\beta\varepsilon_i),$$

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.

An orthogonal coordinate system has been considered to facilitate the above calculation. The origin has been chosen at almost midpoint of the molecule. The x-axis has 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.

Results and Discussion

The molecular geometry of POCB is shown in Fig. 1. The results of interaction energy calculations during the different modes of interactions in "pure" and nonpolar solvents, i.e., CCl_4, C_6H_6 and $CHCl_3$ are discussed below.

Stacking Interactions in "Pure" and Solvents

In a molecular pair, one of the interacting molecules has been fixed in x–y plane such that x-axis lies along a bond parallel to the long molecular axis, while the other has been kept at a separation of 6 Å along the z-axis with respect to the fixed one. The variation of total interaction energy component with respect to rotation about x-axis corresponding to the configuration y (0°) z (0°) has been shown in Fig. 2. It has been observed that the dispersion energy is mainly responsible for the attraction between molecular pair of POCB, although the exact minimum is always estimated from the Kitaygorodsky energy curve, which has gross similarity with the total energy curve. The variation of total interaction energy component with respect to translation along x-axis corresponding to configuration y (180°) z (0°) is shown in Fig. 3. The variation of energy is almost constant in the region of 0.8 ± 0.2Å, 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 mesophase. Evidently, the energies are redistributed in nonpolar solvents and there is a considerable rise in the molecular interactions.

The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for the small intervals. The energy has been minimized with respect to the translations and rotations about the x, y, and z axes. Accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other has been achieved.

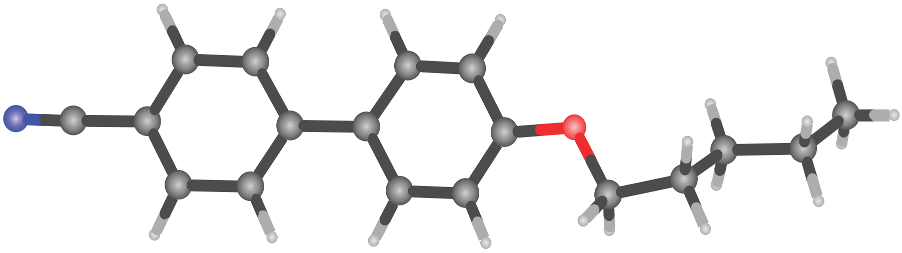

Figure 1. Molecular geometry of POCB.

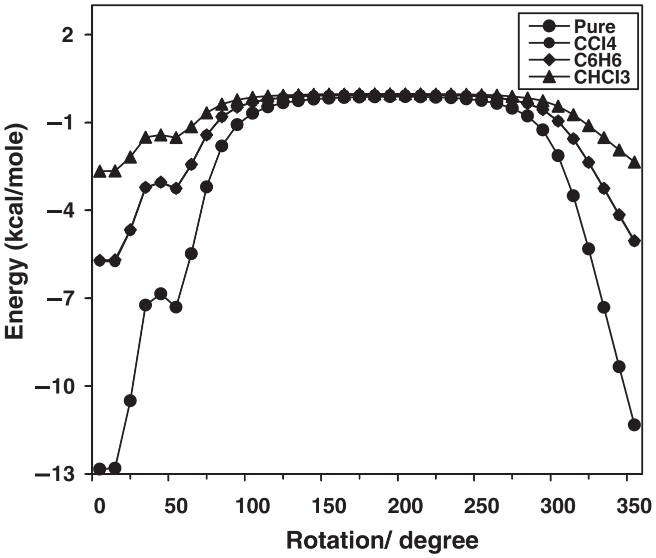

Figure 2. Variation of total interaction energy with respect to rotation about x-axis during the stacking interactions corresponding to the configuration y (0°) z (0°).

It is important to note here that the path of minimization strictly depends on the objective of the computations. The global search for the minimum energy configuration or the study of variation of interaction energy under preselected conditions will have completely the different paths and, therefore, one has to be careful in choosing the specific route.

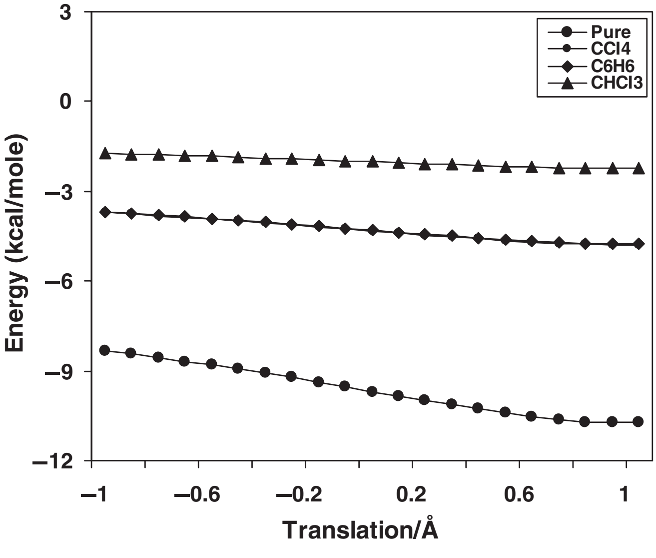

Figure 3. Variation of total interaction energy with respect to translation along x-axis during the stacking interactions corresponding to the configuration y (180°) z (0°).

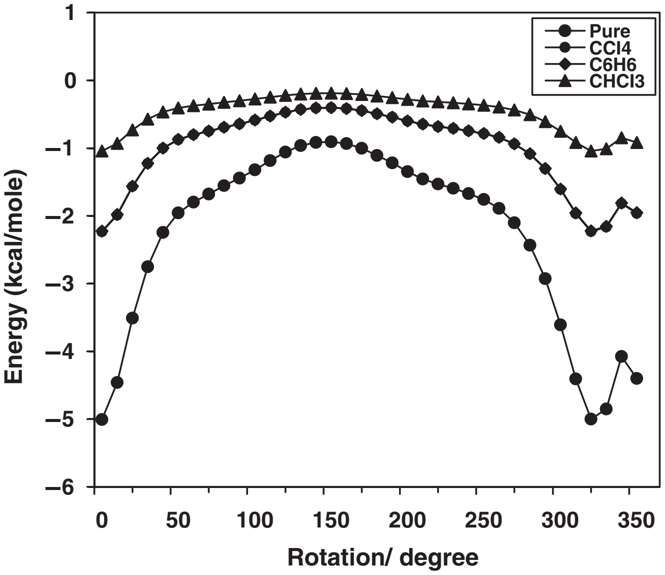

Figure 4. Variation of total interaction energy with respect to rotation about x-axis during the in-plane interactions corresponding to the configuration y (0°).

In-Plane Interactions in "Pure" and Solvents

The interacting molecule has been kept at a separation of 8 Å along y-axis with respect to the fixed one. The variation of total interaction energy component with respect to rotation about x-axis corresponding to configuration y (0°) has been plotted in Fig. 4. The variation of interaction energy with respect to rotation about y-axis corresponding to configuration x (0°) has been carried out, and it has been observed that the rotation about the y-axis does not alter the configurational energy drastically. The interacting configurations have been refined with respect to rotation about x-axis at the equilibrium condition, and the energy is brought down, and interaction energy is further investigated with respect to the translation along x-axis. The variation of total interaction energy component with respect to translation along x- axis corresponding to configuration y (180°) has been shown in Fig. 5. It has been observed that the electrostatic energy during the in-plane interactions is more effective than the stacking, since the antiparallel orientation of molecular rings provides a more effective dipole–dipole attraction. In addition, repulsive quadrupole–quadrupole interactions become very much less effective due to the slipped antiparallel molecular ring orientation.

Terminal Interactions in "Pure" and Solvents

The interacting molecule has been shifted along the x-axis by 22 Å in order to investigate the terminal interactions away from the van der Waals contacts. The terminal interactions are much weaker as compared to the stacking or in-plane interactions, and show almost no preference for angle of rotation about x-axis corresponding to configuration y (0°).

The most prominent energy minima of the above mentioned interactions are further refined, and the values thus attained with all the contributing terms to enable comparison have been listed in Table 1. The results indicate that due to the planarity of the molecule, the

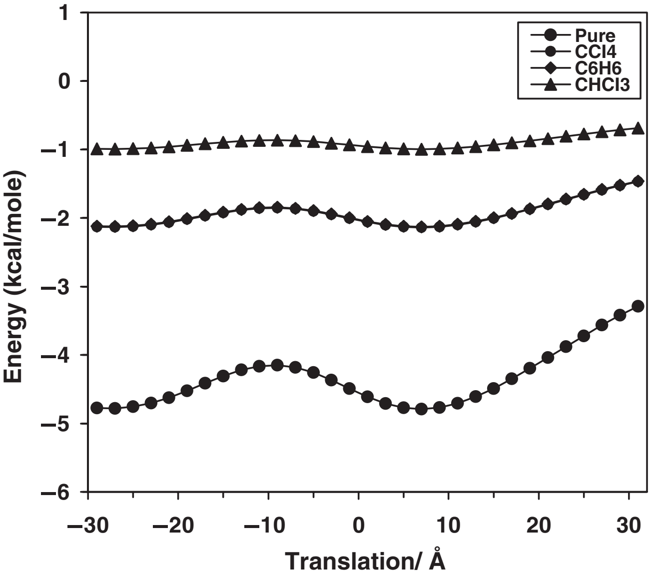

Figure 5. Variation of total interaction energy with respect to translation along x-axis during the in-plane interactions corresponding to the configuration y (180°).

refinement corresponding to the stacking energy is maximum and the ultimate magnitude of the stacking energy is much higher than the in-plane and terminal interaction energies.

Solvent Effects at Molecular Level

To understand the nonpolar organic solvents (i.e., CCl_4, C_6H_6, and $CHCl_3$) effect on a nematogen at molecular level, the various possible geometrical arrangements between molecular pairs have been considered that provide information about the molecular arrangements inside the bulk materials. In a molecular assembly, a number of local minimum energy configurations exist. Each of these has its 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, however, of paramount importance because while descending from a very high temperature, where the molecules have

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

Energy terms	Stacking energy	In-plane energy	Terminal energy
U_{el}	−0.92	0.53	0.02
U_{pol}	−0.69	−0.09	−0.01
U_{disp}	−18.03	−7.50	−2.74
U_{rep}	6.81	2.06	0.75
U_{total}	−12.83	−5.01	−1.96

U_{el} = electrostatic; U_{pol} = polarization; U_{disp} = dispersion; U_{rep} = repulsion; and U_{total} = total.

Table 2. Relative probabilities of the different minimum energy configurations obtained for POCB during the stacking, in-plane, and terminal interactions in nonpolar organic solvents, i.e., CCl_4, C_6H_6, and $CHCl_3$ at room temperature 300 K

Configuration	Energy in vacuum (kcal/mole)	Probability (%)		
		CCl_4	C_6H_6	$CHCl_3$
y (0°) z (0°)[a]	−10.73	17.05	17.14	39.00
y (180°) z (0°)[a]	−12.83	82.50	82.39	53.13
y (0°)[b]	−4.78	0.19	0.19	3.20
y (180°)[b]	−5.00	0.23	0.23	3.45
y (0°)[c]	−1.96	0.01	0.02	1.19

[a]Stacking interactions; [b]In-plane interactions; [c]Terminal interactions.

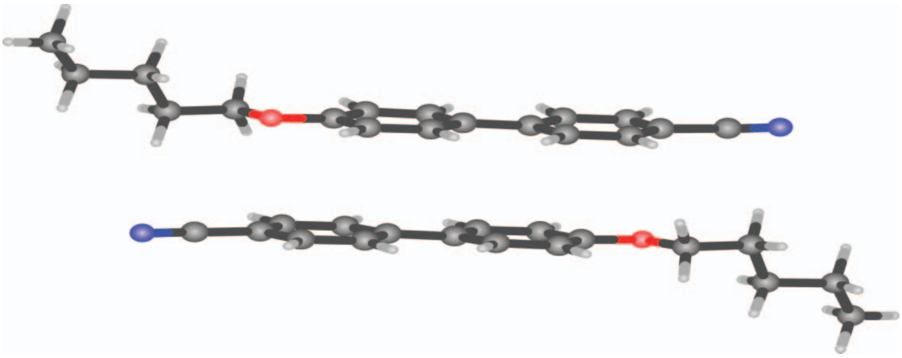

Figure 6. The most stable configuration obtained for stacked pair interactions (82.5% probability) in CCl_4 with energy −5.73 kcal/mole.

a completely disordered distribution, the global minimum has the maximum probability of occupancy and other minima have the sequential preference depending on their individual relative probabilities.

Table 2 shows the relative probabilities of the different minimum energy configurations calculated for the nonpolar organic solvents during the different modes of molecular interactions. Evidently, the energy is redistributed in nonpolar organic solvents and there is considerable rise in the probabilities of interactions, although the order of preference remains the same. The most favorable configuration y (180°) z (0°) has been obtained in CCl_4 during the stacking interactions (82.50% probability) with energy −5.73 kcal/mole (Fig. 6). This provides a new and interesting molecular model for nematogen.

Conclusions

1. The present computational studies provide a new and attention-grabbing model for nematogen in nonpolar organic solvents, i.e., CCl_4, C_6H_6, and $CHCl_3$. The energies are redistributed in the solvents, and there is considerable rise in the probabilities of interactions although the order of preference remains the same. Furthermore, the most stable configuration has been obtained in CCl_4 during the stacking interactions.

2. The study on conformational behavior of the molecules provides the valuable information on configurational freedom of the molecule that may be useful in understanding the phase stability and transitions.
3. This provides information on relative order of configurations and preference of a particular configuration over the other. A comparative study on other systems may lead to more general conclusions.

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