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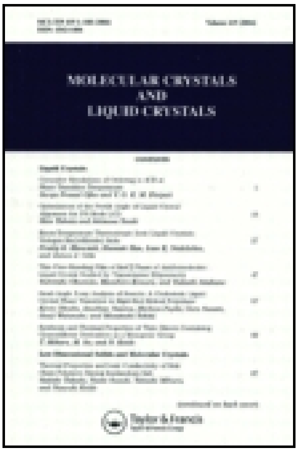

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The Role of Organic Solvents and Conformational Behavior of Nematogens Having *trans* Extended Conformation – A Computational Approach

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The role of organic solvents on nematogenic p-n-alkoxy cinamic acids (nOCAC) with alkyl chain carbon atoms (n = 6, 8) has been reported 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, that is, carbon tetrachloride, and chloroform at room temperature (300 K). It has been observed that the molecules show the remarkable behavior in the solvents. A comparison of stacked dimers between both the molecules suggests that the extension of the chain length to eight carbon atoms, a recognizable segregation of dimers into a highly tilted layer structured has been obtained.

Keywords Configurational probability; nematogen; nonpolar solvents

Introduction

Liquid crystals (LCs) are used extensively for direct-view displays, projection displays, and photonic devices. Material and phase stabilities are primary concern for all devices desiring to have a long operational lifetime [1,2]. The most common nematic LC structure for displays consists of an alkyl chain, one or two cyclohexane rings, a phenyl rings, and a polar group. The aromatic ring system not only imparts structural anisotropy, but also plays a central role in determining the electrical, magnetic, and optical properties of the bulk materials [3].

The thermotropic LCs have paid considerable attention due to their extensive applications, such as LC displays, adaptive optic devices, and optical switchable windows [4]. It has been observed that the dissolving of a thermotropic LC compound in a nonpolar organic solvent produces ferroelectric LCs with the remarkable properties [5]. The electro-optic properties of the solutions are, to some extent, better than those of "pure" LCs. Study of

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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 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 established the anisotropic nature of the pair potential, and subsequently find out the minimum energy configuration of a pair of mesogens.

Even though advances in synthesis and characterization explore many achievements regarding nematic materials, it is often desirable to have a sense of material behavior prior to synthesis. At molecular level, the phases of matter are basically determined by the interplay between molecular structure, intermolecular interactions, and the molecular motion. The present article deals with the interaction energy/configurational probability of nematogens, 6OCAC and 8OCAC, in nonpolar solvents, that is, carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) at room temperature (300 K) but the detailed results have been reported only for 6OCAC molecule. However, the salient features of other have also been reported. 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.

Computational Methods

In view of the practical difficulties and the increasing enforce to predict the properties of unsynthesized molecular materials; it is evident of considerable importance to develop computational methods for the calculation of physical properties. It is well known that subtle alternations in molecular structure can have profound effects on the stability and properties of mesophases. The molecular geometries of nOCAC ($n = 6, 8$) have been constructed on the basis of published crystallographic data [11] with the standard values of bond lengths and bond angles. The structures of the systems have the all-*trans* extended conformation, and the molecules exist in the crystals as planar hydrogen-bonded dimers. The advancing of the structure and energetic effects is helpful in employing the molecular models. The computations have been carried out in three steps.

First Step 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 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. 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 Computation

The computational scheme based on a 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:

$$U_{\mathrm{pair}} = U_{\mathrm{el}} + U_{\mathrm{pol}} + U_{\mathrm{disp}} + U_{\mathrm{rep}},$$

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

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

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. 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 semiempirical approach, viz. the Lennard-Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky [15] introducedthe Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [16] for hydrocarbon molecules and the several other molecules and finally gave the following expression:

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

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

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 $K_{\lambda}\ K_{\nu}$ allows the energy minimum to have different values according to the atomic species involved.

Third Step Computation

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]:

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

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.

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 such as stacking, in-plane, and terminal interactions will be used to maintain the continuity with the previous work [18].

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 is such that the possible van der Waals contacts are avoided.

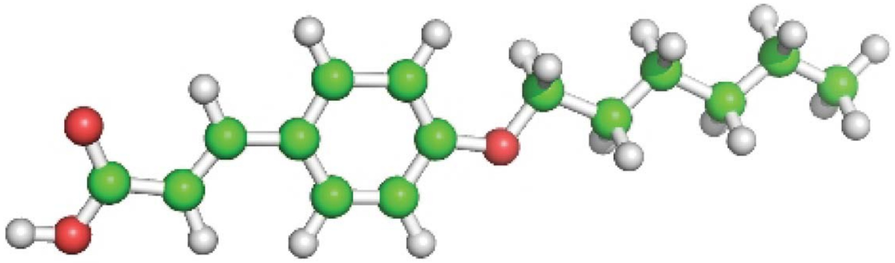
Computation of Terminal Interactions.. To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the *x*-axis by 22 Å with respect to the fixed one.

Results and Discussion

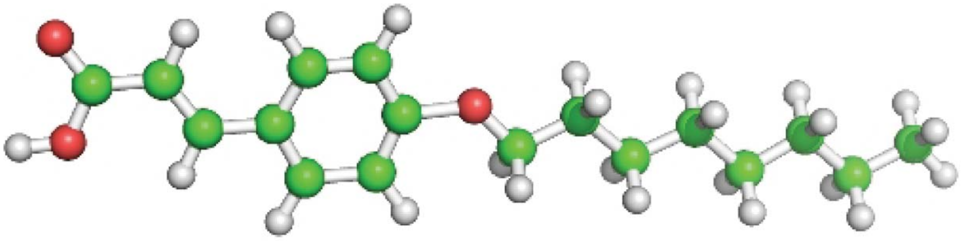
The molecular geometries of *n*OCAC (*n* = 6, 8) have been shown in Fig. 1.

Configurational Probability Distribution

The results of configurational probability distribution during the different modes of intermolecular interactions in nonpolar solvents, that is, CCl_4 and $CHCl_3$ are discussed below.



(a) 6OCAC



(b) 8OCAC

Figure 1. Molecular geometries of (a) 6OCAC and (b) 8OCAC molecules

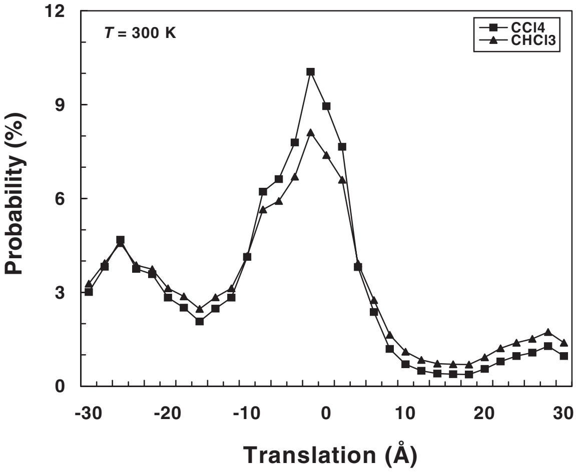


Figure 2. Variation of probability with respect to translation along *x*-axis during stacking interactions corresponding to configuration *y*(0°) *z*(0°) for 6OCAC molecule in CCl_4 and $CHCl_3$ at room temperature (300 K).

Role of Stacking Interactions in Solvents. 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 16 ± 4 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 is shown in Fig. 3. The maximum probability has been achieved at −4° rotation 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 in the solvents 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 has 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 preselected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route.

Role of In-Plane Interactions in Solvents. 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.

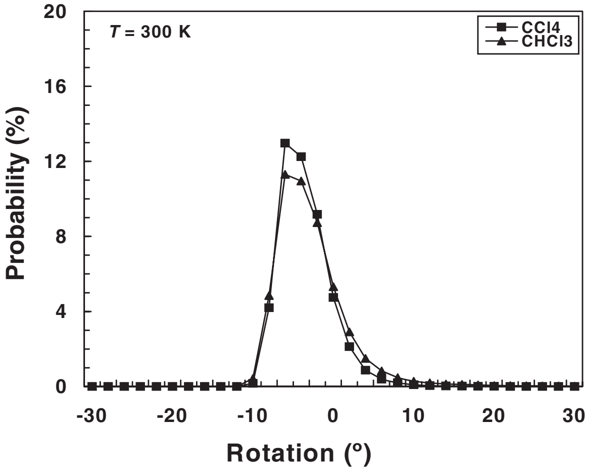


Figure 3. Variation of probability with respect to rotation about *x*-axis during stacking interactions corresponding to configuration *y*(0°) *z*(180°) for 6OCAC molecule in CCl_4 and $CHCl_3$ at room temperature (300 K).

Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed with the maximum probability at −10 Å. 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

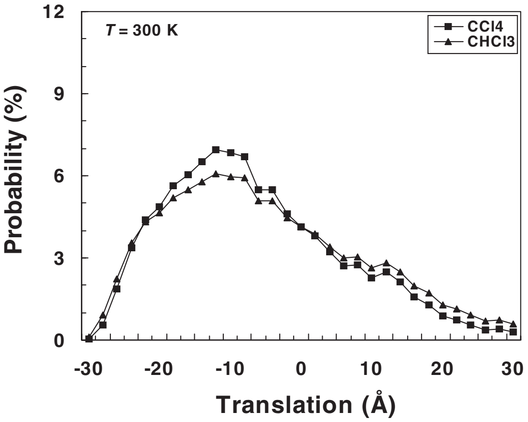


Figure 4. Variation of probability with respect to translation along *x*-axis during in-plane interactions corresponding to configuration *y*(0°) for 6OCAC molecule in CCl_4 and $CHCl_3$ at room temperature (300 K).

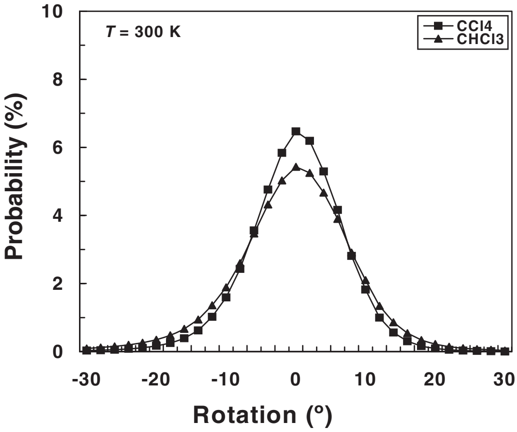


Figure 5. Variation of probability with respect to rotation about *x*-axis during terminal interactions corresponding to configuration *y*(0°) *z*(0°) for 6OCAC molecule in CCl_4 and $CHCl_3$ at room temperature (300 K).

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.

Role of Terminal Interactions in Solvents. 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. Figure 5 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.

Role of Organic Solvents on Nematogens. The role of solvents on nematogens (6OCAC and 8OCAC), the various possible geometrical arrangements between a molecular pair during the different modes of interactions has been considered that provide information about the molecular arrangements inside the bulk materials. Table 1 shows the relative probabilities of different minimum energy configurations, calculated at room temperature (300 K) in CCl_4 and $CHCl_3$ during the different modes of interactions with respect to translational and orientational motions. Further, it is clear from the above discussion (at different modes of interactions) 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.

Conformational Behavior of Molecules

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.

Table 1. Relative probabilities of the different minimum energy configurations obtained for 6OCAC and 8OCAC molecules during the stacking, in-plane, and terminal interactions in nonpolar organic solvents, that is, CCl_4 and $CHCl_3$ at room temperature (300 K)

Configuration	Energy in vacuum (Kcal·mole^{-1})	Probability (%) at 300 K	
		CCl_4	$CHCl_3$
6OCAC molecule			
$x(0°)\ y(0°)^a$	−13.87	56.26	50.33
$y(0°)\ z(0°)^a$	−13.54	43.72	44.72
$y(0°)^b$	−4.69	0.00	2.04
$x(180°)^b$	−4.27	0.00	1.76
$y(0°)^c$	−2.99	0.00	1.12
8OCAC molecule			
$x(0°)\ y(0°)^a$	−13.70	59.07	51.30
$y(0°)\ z(0°)^a$	−13.21	40.82	43.18
$y(0°)^b$	−5.22	0.10	2.65
$x(180°)^b$	−4.30	0.00	1.92
$y(0°)^c$	−2.21	0.00	0.90

[a]Stacking interactions; [b]in-plane interactions; [c]terminal interactions.

The conformational behavior of LC displays a large variation in intermolecular effects that depends on the nature and magnitude of interactions. In each conformation there may exist the distinct energy, and lower energy conformations will be populated in preference to those of higher energy. The most stable configurations of 6OCAC and 8OCAC molecules observed in CCl_4 have been shown in Figs. 6 and 7, respectively. A comparison of stacked dimers between both the molecules suggests that the extension of the chain length to eight carbon atoms, a recognizable segregation of the dimers into a highly tilted layer structure

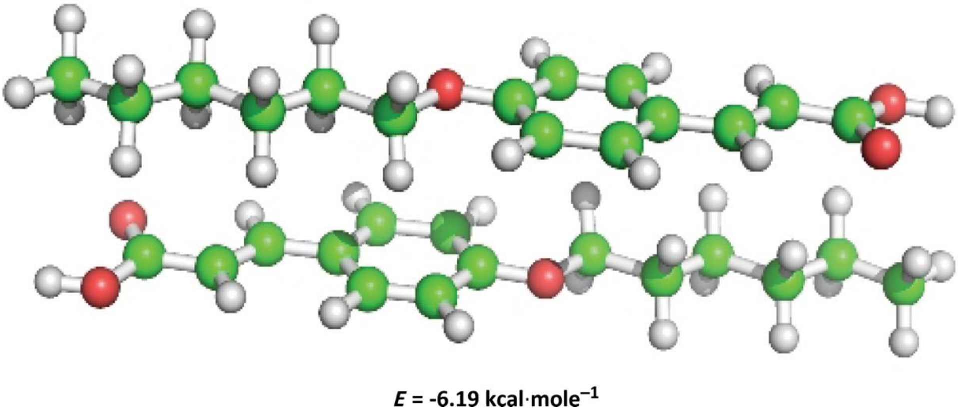


Figure 6. Energetically favorable structure of 6OCAC molecule in CCl_4 during the stacking interactions at room temperature (300 K)

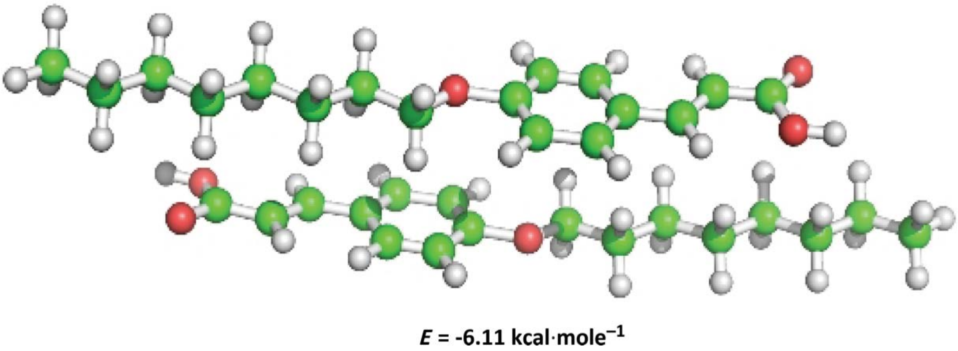


Figure 7. Energetically favorable structure of 8OCAC molecule in CCl_4 during the stacking interactions at room temperature (300 K)

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 rather than smectic phase. The chains have the all-*trans* extended conformation, and molecules exist in the crystal as planar hydrogen-bonded dimers. The dimers are arranged in end-to-end fashion in parallel rows.

Conclusions

The salient features of the present work are as follows:

1. A comparison of stacked dimers between both the molecules suggests that the extension of the chain length to eight carbon atoms, a recognizable segregation of dimers into a highly tilted layer structured has been obtained.
2. The electrostatic energy during the in-plane interactions is more effective than stacking since the antiparallel orientation of molecular rings provides a more effective dipole–dipole attraction, which aids in the energetic stabilization of the mesophase.
3. The consideration of relative probabilities among the minimum energy configurations obtained during the stacking, in-plane, and terminal interactions provides information about the molecular arrangements inside a bulk of materials. Further, the considerable rise in the molecular interactions has been observed due to the redistribution of energy in CCl_4 and $CHCl_3$, that is, the molecules produce the remarkable property in solvents.
4. 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 rather than smectic phase.

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