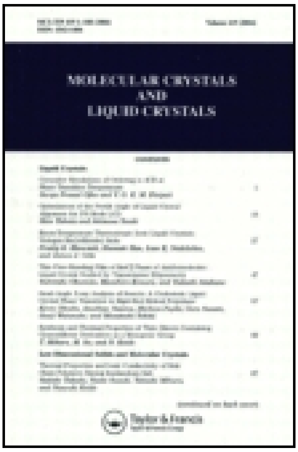

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The Remarkable Effect of Solvents on Smectogen Having a V-Shaped Conformation – A Computational Model

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The effect of solvents on a smectogen, N-n-undecyl-D-gluconamide, having a V-shaped conformation has been carried out with respect to translational and orientational motions. The complete neglect differential overlap method has been employed to compute the net atomic charge and atomic dipole moment components at each atomic center. The modified Rayleigh–Schrodinger perturbation theory along with the multicentered–multipole expansion method has been employed to evaluate the long-range intermolecular interactions, while a "6-exp" potential function has been assumed for short-range interactions. The total interaction energy values obtained through these computations have been used as input to calculate configurational probability in non-polar organic solvents, i.e., carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) using the Maxwell–Boltzmann formula at room temperature (300 K). It has been observed that the molecule produce remarkable property in the solvents. Further, an attempt has been made to develop a new and interesting model for smectogen at molecular level.

Keywords Effect of solvent; *N-n*-undecyl-D-gluconamide; smectogen

Introduction

The smectic (Sm) liquid crystals (LCs) have higher molecular order that leads to potential applications in functional devices and the fabrication of new types of anisotropic materials. Carbohydrate liquid crystals have a sizeable attention, and numerous studies [1–3] have reported for amphiphillic compounds that are relevant for biological functions or monophillic mesogens. The liquid crystal research only explicitly recognizes the structure–property relationships [3] of many compounds, have never been tested for their mesomorphic properties and the relation between the "physical state" of matter for their biological functions. The thermotropic liquid crystals have paid considerable attention due to their extensive applications, such as liquid crystal displays, adaptive optic devices, and optical switchable windows [4]. It has been observed that the dissolving of a thermotropic liquid crystal compound in a non-polar organic solvent produces ferroelectric liquid crystals with remarkable properties [5]. The electro-optic properties of the solutions are, to some extent, better than those of "pure" liquid crystals. Study of the effect of solvents on the molecules forms an important subject for research, and it can play a significant role in photophysics.

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The interesting feature associated with phase behavior and thermotropic transitions of the homologous series, including N-*n*-undecyl-D-gluconamide (Sm), is the melting point, which is relatively consistent irrespective of alkyl chain length. This suggests that at the transition from crystal to liquid crystal, a core of stacked alkyl chains is retained rather than hydrogen-bonded carbohydrate moieties [6]. Moreover, gluconamides with alkyl chains longer than eight carbon atoms form monolayers, and those with shorter chains form micelles.

Based on the Rayleigh–Schrodinger perturbation method, the role of molecular interactions in mesomorphic compounds has engrossed the attention of several workers [7–10]. 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. 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, the author has evaluated the relative probability of occurrence of each configuration.

The present paper deals with the configurational probabilities of a smectic in non-polar solvents, i.e., carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) at room temperature (300 K). The configurationally probability distribution picture based on the interaction energy results will provide the valuable information in this respect.

Computational Method

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, semi-empirical approaches are often used for calculations of molecular properties. The molecular geometries of the smectic phase have been constructed on the basis of published crystallographic data [6] with the standard values of bond lengths and bond angles. The advancing structure and energetic effects are helpful in employing the molecular models. The computations have been carried out in three steps.

Computational Step-1

The complete neglect differential overlap (CNDO/2) method [11] 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. 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.

Computational Step-2

The computational scheme based on the simplified formula provided by Claverie [12] for the evaluation of interaction energy in a molecular pair has been used to calculate energy for fixed configuration. The computer program, INTER, originally developed by Claverie, has been used for this purpose with further modification.

The total pair interaction energy of molecules (U_{pair}), according to the second-order perturbation theory for intermediate range interactions [13], is represented as a 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

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

where U_{QQ}, U_{QMI}, and U_{MIMI} 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 the dipole–dipole energy term.

The dispersion and short-range repulsion terms are considered together because several semi-empirical approaches, viz., the Lennard–Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky [14] introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [15] for hydrocarbon and several other molecules, and finally gave the following 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 $Z = R_{\lambda\nu}/R^{\circ}_{\lambda\nu}$; $R^{\circ}_{\lambda\nu} = [(2R^{w}_{\lambda})\ (2R^{w}_{\nu})]^{1/2}$, where R^{w}_{λ} and R^{w}_{ν} are the van der Waals radii of atoms λ and ν respectively. The parameters A, B, and γ do not depend on atomic species. But $R^{\circ}_{\lambda\nu}$ and factor $K_\lambda K_\nu$ allow the energy minimum to have different values according to the atomic species involved.

Computational Step-3

In order to obtain a better insight, the total interaction energy values obtained through different modes of interactions have been used as inputs to calculate the probability of occurrence of a particular configuration i using the Maxwell–Boltzmann formula [16]:

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

where P_i stands for the probability. $\beta = 1/kT$, where 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 has been chosen along a bond parallel to the long molecular axis, the y-axis lies in the plane of the molecule, and z-axis is perpendicular to the x–y plane.

(a) 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 completely eliminate the possibility of the van der Waals contacts, and to keep the molecule within the range of short- and medium-range interactions.

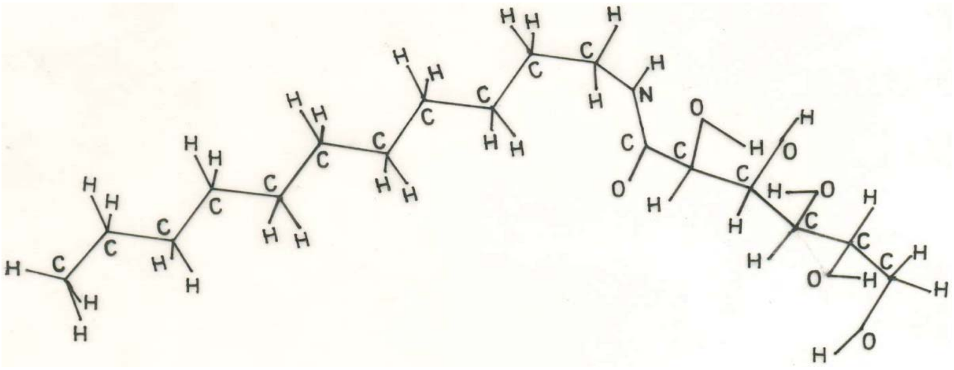

Figure 1. Molecular geometry of N-*n*-undecyl-D-gluconamide with various atoms.

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

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

Results and Discussion

The molecular geometry of N-*n*-undecyl-D-gluconamide is a V-shaped conformation as shown in Fig. 1. The total energy, binding energy, total dipole moment, and its components are listed in Table 1. The results of configurationally probability distribution in CCl_4 and $CHCl_3$ corresponding to different modes of interactions are discussed below.

(a) Stacking Interactions in CCl_4 and $CHCl_3$

The variation of probability with respect to rotation about the *z*-axis corresponding to configuration x(0°)y(0°) at room temperature (300 K) is shown in Fig. 2. It has been

Table 1. The total energy[a], binding energy[b], and total dipole moment of smectic (Sm) molecule. Total energy = −272.47 a.u.; binding energy = −25.55 a.u., and total dipole moment = 7.91 Debye

Components	X	Y	Z
Densities	1.728	6.882	−4.528
Sp hybridization moment	−0.216	−0.713	−0.202
Pd hybridization moment	0.000	0.000	0.000
Total	1.511	6.169	−4.730

[a] Total energy corresponds to the sum of atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

[b] Binding energy of a molecule is the difference between the total energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms.

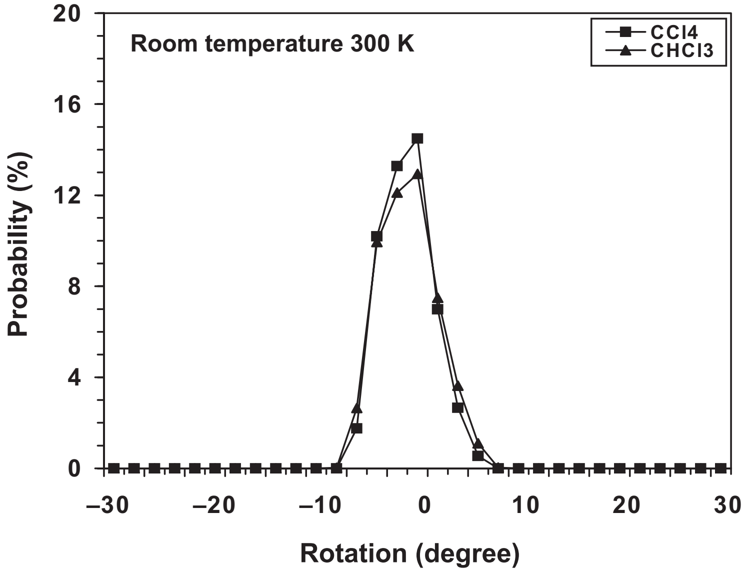

Figure 2. Variation of probability with respect to rotation about the *z*-axis during stacking interactions in non-polar organic solvents CCl_4 and $CHCl_3$ corresponding to configuration x(0°)y(0°) at room temperature.

observed that the configuration shows a sharp preference toward the minimum-energy point with maximum probability at the equilibrium position. The flexibility of rotation is sufficiently small, which accounts for the smectic character of the molecule. Further, it indicates that a finite probability for alignment at low temperature exists when the thermal vibration does not drastically disturb molecular alignments.

The variation of the probability with respect to translation along the long molecular axis (*x*-axis) corresponding to configuration y(0°)z(0°) at room temperature (300 K) is shown in Fig. 3. Evidently, the configuration shows a sharp preference toward the minimum energy point. The variation of probability is almost constant in the region of (20 ± 4) Å without any significant change in energy, and hence is capable of retaining the molecular order against increased thermal agitation. The maximum probability has been achieved at 2 Å. 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 the *x*-axis corresponding to configuration y(0°)z(180°) at room temperature has been carried out. It has been observed that the maximum probability achieved at 2° rotation indicates slight preference for the aligned structure of this configuration. The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for small intervals. The energy minimization is an auto process. 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 another has been achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. 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

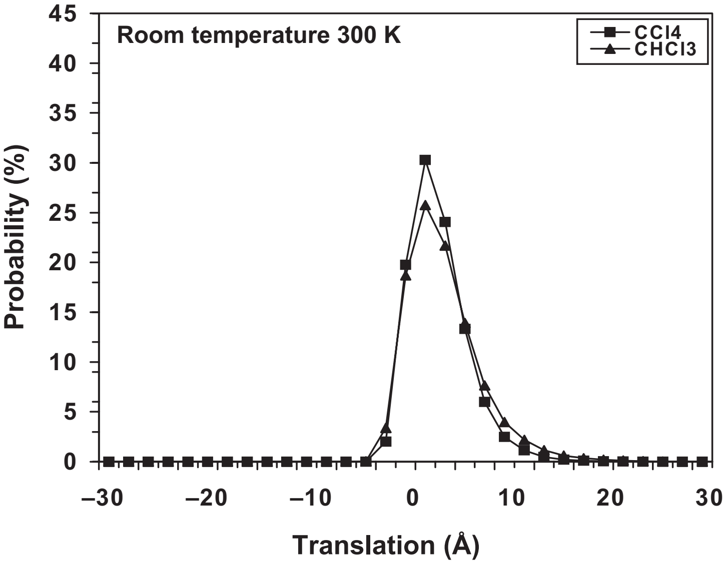

Figure 3. Variation of probability with respect to translation along the *x*-axis during stacking interactions in non-polar organic solvents CCl_4 and $CHCl_3$ corresponding to configuration y(0°)z(0°) at room temperature.

has to be careful in choosing the specific route. Further, the effectiveness/appropriateness of minimization methods also depends on the objective of computation.

(b) In-Plane Interactions in CCl_4 and $CHCl_3$

The electrostatic energy during in-plane interactions is more effective than stacking, since the antiparallel orientation of molecules provides a more effective dipole–dipole attraction. In addition, repulsive quadrupole–quadrupole interactions become very much less effective due to the slipped antiparallel molecular orientation. These factors ultimately cause large variations in total interaction energy and thereby in the probability of the configuration. The variation of probability with respect to translation along the *x*-axis corresponding to the configuration y(0°) 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 maximum probability at 4 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 the *x*-axis.

The variation of probability with respect to rotation about the *x*-axis corresponding to configuration y(180°) has been carried out and it has been observed that a pronounced peak exists at 2° rotation point at room temperature (300 K), 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°) has also been carried out. It has been observed that the rotational freedom of the molecule is restricted along the *y*-axis, and favors an overlapped layered structure in mesophase.

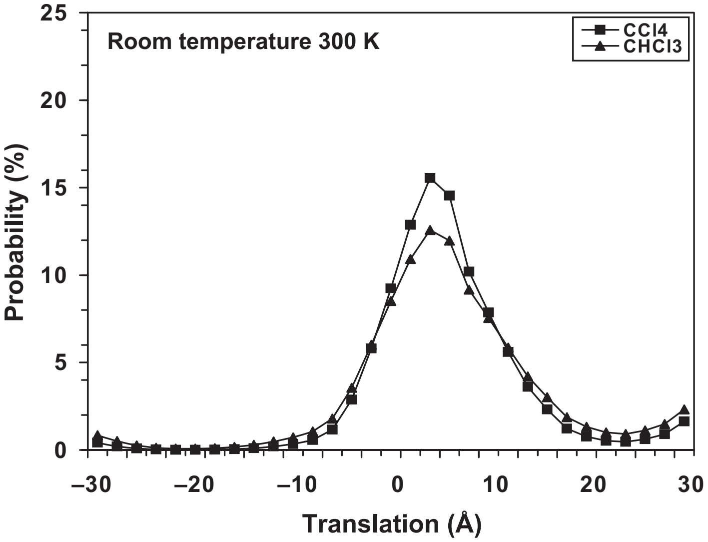

Figure 4. Variation of probability with respect to translation along the *x*-axis during in-plane interactions in non-polar organic solvents CCl_4 and $CHCl_3$ corresponding to configuration y(0°) at room temperature.

(c) Terminal Interactions in CCl_4 and $CHCl_3$

The end-to-end interactions are weakest but become more important when the molecules possess 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 the *x*-axis

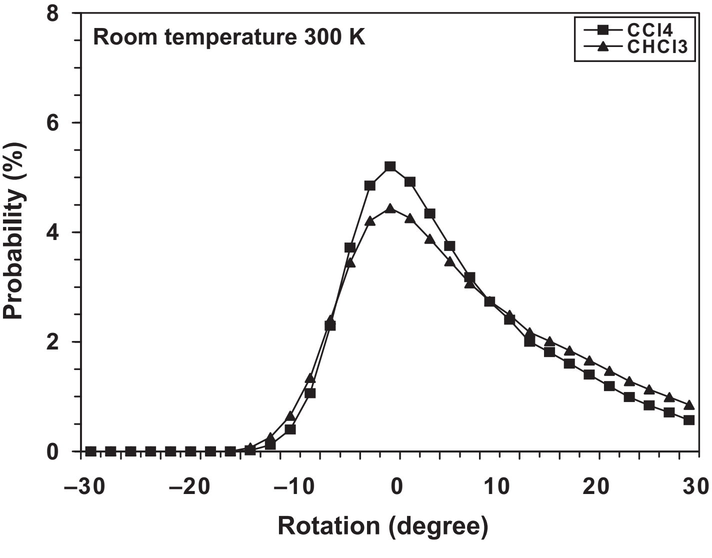

Figure 5. Variation of probability with respect to rotation about the *x*-axis during terminal interactions in non-polar organic solvents CCl_4 and $CHCl_3$ corresponding to configuration y(0°) at room temperature.

Table 2. Stacking, in-plane, and terminal interactions between a pair of Sm molecules after refinement. Energy is expressed in kcal/mole

Interaction energy terms	Stacking energy	In-plane energy	Terminal energy
E_{QQ}	−0.108	0.006	0.009
E_{QM}	−0.421	0.008	0.003
E_{MM}	−0.315	−0.069	0.009
E_{el}	−0.845	−0.055	0.021
E_{pol}	−0.346	−0.086	−0.016
E_{disp}	−8.917	−6.904	−4.441
E_{rep}	3.781	2.359	1.414
E_{total}	−6.326	−4.686	−3.023

corresponding to configuration y(0°) at room temperature (300 K). The terminal interactions are much weaker as compared to stacking or in-plane interactions. However, a significant peak has been observed at equilibrium position due to the possibility of hydrogen bonding.

The refined interaction energy values corresponding to different modes of interactions are presented in Table 2 with the various contributing terms for comparison. Evidently, the largest attractive contribution to stabilize the stacked interacting pair of smectic molecules comes from the dispersion forces.

(d) Remarkable Effect of Solvents on Smectogen

The effect of solvents on smectogen may be understood on the basis of relative probabilities of different minimum energy configurations (Table 3) in CCl_4 and $CHCl_3$ during different modes of interactions. Evidently, considerable rise in the probabilities of interactions has been observed due to redistribution of energy in non-polar organic solvents although the order of preference remains the same. Furthermore, this provides information about molecular arrangements inside a bulk of materials.

Table 3. Relative probabilities of different minimum energy configurations obtained for Sm during the stacking, in-plane, and terminal interactions in non-polar organic solvents, i.e., CCl_4 and $CHCl_3$ at room temperature (300 K)

		Probability (%) at 300 K	
Configuration	Energy in vacuum (Kcal/mole)	CCl_4	$CHCl_3$
x(0°)y(0°)[a]	−13.69	59.05	51.28
y(0°)z(0°)[a]	−13.23	40.84	43.20
y(0°)[b]	−5.32	0.09	2.63
x(180°)[b]	−4.28	0.00	1.95
y(0°)[c]	−2.22	0.00	0.92

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

It is clear from the above discussion that 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, is 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 the sequential preference depending on their individual relative probabilities. The most favorable stacked configuration x(0°)y(0°) has been obtained for a smectic phase in CCl_4 with 59.05% probability at room temperature of 300 K.

Conclusions

The salient features of the present work are as follows:

1. 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. In addition, repulsive quadrupole–quadrupole interactions become very much less effective due to the slipped antiparallel molecular orientation.
2. The molecule has a strong capacity of forming a layered structure. Translational motion of a stacked dimer along either of the axes is least probable, while the orientational freedom is completely restricted. These favor the smectic character of the molecule in terms of their relative order.
3. The relative configurational probabilities among minimum energy configurations obtained during the stacking, in-plane, and terminal interactions provide information about molecular arrangements inside a bulk of materials.
4. The molecule produces a remarkable property, i.e., considerable rise in the probability of interactions due to the redistribution of energy in CCl_4 and $CHCl_3$ at room temperature.
5. The most stable configuration x(0°)y(0°) of molecular pairing has been obtained among the minimum energy configurations in CCl_4 during stacking interactions at room temperature.

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