

Role of Dielectric Medium on a Nematogen. A Statistical Approach Based on Quantum Mechanics and Computer Aided Modelling

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A statistical analysis has been carried out to determine the configurational preferences of a pair of 5-(4-ethylcyclohexyl)-2-(4-cyanophenyl) pyrimidine (**ECCP**) molecules. The **CNDO/2** method has been employed to evaluate the net atomic charge and atomic dipole components at each atomic centre of the molecule. The configurational energy has been computed using the Rayleigh-Schrödinger perturbation theory. The total interaction energies obtained by these computations were used to calculate the probability of each configuration in vacuum and in a dielectric medium (benzene) at the phase transition temperature using the Maxwell-Boltzmann formula. On the basis of stacking, in-plane and terminal interaction energy calculations, all possible geometrical arrangements of the molecular pair have been considered. An attempt has been made to explain the nematogenic behavior of liquid crystals and thereby develop a molecular model for liquid crystallinity.

Key words: Liquid Crystal; Quantum Chemistry; Computer Simulation,

Introduction

The mesomorphic behavior of liquid crystalline substances depends on the aggregation of molecular clusters. The molecular property which causes such aggregation needs intense investigation. The theoretical attempts reported in the literature involve largely the evaluation of order parameters, transition temperatures etc. on the basis of a general statistical theory applicable to nematics and partly to smectic liquid crystals, where almost no consideration of the actual molecular structure is taken into account. Recently, Yayloyan et al. [1], Sarkar et al. [2], and Ryzhov et al. [3] have reported the results of theoretical investigations on the role of intermolecular interactions in mesogenic compounds based on the Rayleigh-Schrödinger perturbation theory. These studies were aimed at computing interaction energies between two molecules, but their attempts were directed towards explaining the aligned structure or at best, correlating the minimum energy with the observed crystal structure.

One of the limitations of the work was that the relative preference of different configurations was estimated on the basis of interaction energies which are

not direct related quantities. It seems therefore, seems to be important to investigate the relative freedom of the molecule to depart from the minimum energy configuration in terms of a) variations in orientation, and b) translations along the long molecular axis.

In the present paper we report the characteristic features a of liquid crystal in terms of pair probabilities between two molecules of 5-(4-ethylcyclohexyl)-2-(4-cyanophenyl) pyrimidine (**ECCP**) in vacuum and in a dielectric medium (i. e. the non-interacting and non-mesogenic solvent benzene, the average dielectric constant of which has been taken to be 2.25 for the entire temperature range [4]) at a distance of 10 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions in order to eliminate the possibility of van der Waals contacts and to keep the molecule within short and medium-range interactions. Also, instead of finding the exact minimum energy configuration, an attempt has been made to elucidate the general behavior of the molecules surrounding a fixed molecule in a particular frame of reference.

The thermodynamic data show that **ECCP** exhibits a nematic phase at 397 K and an isotropic melt at 508 K [5].

Simplified Formula and Computational Technique

The molecular geometry of **ECCP** has been constructed on the basis of published crystallographic data with standard values of bond lengths and bond angles [5].

In order to find the interaction energy between two molecules, it is necessary to compute atomic net charges and dipole moments through an all valence electron method. In the present computation, the **CNDO/2** method [6] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule. The calculations have been carried out in two stages A and B:

(A) Computation of Interaction Energy at Various Configurations

A computer program, based on simplified formula for the evaluation of the interaction energy of a molecular pair has been used to calculate the energy for fixed configurations. According to second order perturbation theory as modified for an intermediate range of interactions [7], the total pair interaction energy (U_{pair}) is represented by the sum

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

where U_{el} , U_{pol} , U_{disp} and U_{rep} are the electrostatic, polarization, dispersion and repulsion energy terms respectively.

The electrostatic term is expressed as

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

where U_{QQ} , U_{QMI} , and U_{MIMI} are the monopole-monopole, monopole-dipole and dipole-dipole term, respectively. In fact, the inclusion of higher order multipoles does not affect significantly the electrostatic interaction energy. Therefore our calculations have been performed only upto the dipole-dipole term [8]. Also the dispersion and short-range repulsion terms were considered together, because several semi-empirical approaches, viz. the Lennard-Jones or Buckingham type approach, actually proceed in this way. Kitaigorodskii introduced a Buckingham formula whose parameters were later modified by Kitaigorodskii and Mirskay for hydrocarbon molecules [9]:

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

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

where $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$; $R_{\lambda\nu}^0 = [(2R_{\lambda}^W)(2R_{\nu}^W)]^{1/2}$. $2R_{\lambda}^W$ and $2R_{\nu}^W$ are the van der Waals radii of atom λ and ν , respectively. The parameters A , B , and ν do not depend on the atomic species. But $R_{\lambda\nu}^0$ and the 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 in [10, 11].

In our case, the origin has been chosen on an atom close to the centre of mass of the molecule. The X -axis lies along the long molecular axis, while the Y -axis lies in the plane of the molecule, and the Z -axis perpendicular to the molecular plane.

(B) Computation of the Configurational Probabilities

The total interaction energies obtained through these computations were used as input to calculate the intrinsic probability of each configuration with the help of the Maxwell-Boltzmann formula [9]

$$P_i = \exp(-\beta \varepsilon_i) / \sum_i \exp(-\beta \varepsilon_i); \beta = 1/kT,$$

where P_i is the probability of the occurrence of a particular configuration and ε_i is the energy of the configuration i relative to the energy of the configuration with minimum energy.

Results and Discussion

One geometry of two **ECCP** molecules is shown in Figure 1. One of the molecules is fixed in the

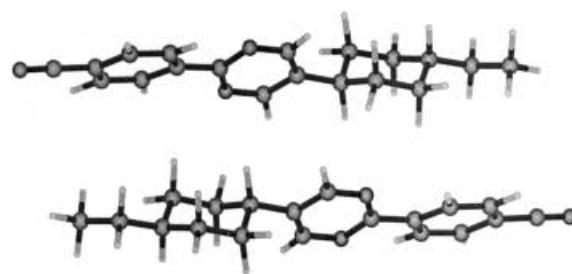


Fig. 1. The lowest stacking energy configuration of two 5-(4-ethylcyclohexyl)-2-(4-cyanophenyl) pyrimidine molecules, obtained with an energy of -12.61 kcal/mole at an intermolecular separation of 3.95 Å.

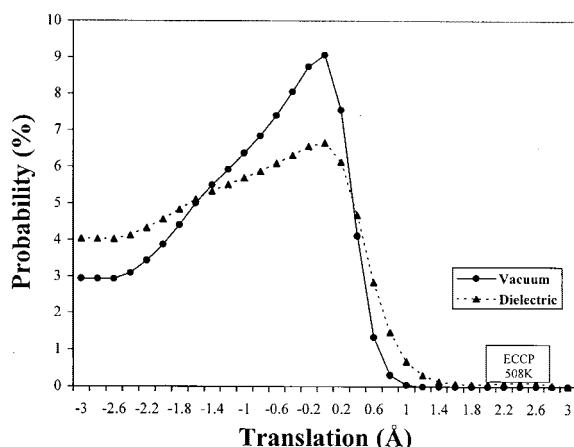


Fig. 2. Variation of the probability on translation along X -axis during stacking interactions at the N-I transition temperature.

X - Y plane with its length along the Z -axis, while the other one is kept in the same direction at a distance of 10 Å from the fixed one. Variation of the stacking interaction energy on rotation about the Z -axis, with respect to $X(0^\circ)Y(0^\circ)$, has been carried out at intervals of 10°, and the interaction energy at each configuration was calculated. The minimum energy so obtained was then taken as starting point, and the entire process was repeated at smaller intervals. The energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to other has been achieved. The lowest stacking geometry, shown in Fig. 1, occurred at an interplanar separation of 3.95 Å with an energy of -12.61 kcal/mole. This configuration agrees with those obtained from crystallographic studies [5].

On rotation about the X -axis during stacking interactions, with respect to the configuration $Y(0^\circ)Z(180^\circ)$, sharp energy minima occurred at equilibrium positions. Further, translational freedom along the long molecular axis has been allowed at intervals of 0.2 Å. The corresponding change in the probability distributions, with respect to the configuration $Y(0^\circ)Z(180^\circ)$, in vacuum and dielectric medium is shown in Figure 2. It is evident that the stacked pair of **ECCP** molecules can slide one above the other in the range of $-2.4\text{ \AA} \pm 0.2$ Å without any significant change in the energy and, hence, is capable of retaining molecular order upto -3 Å against increased thermal agitation.

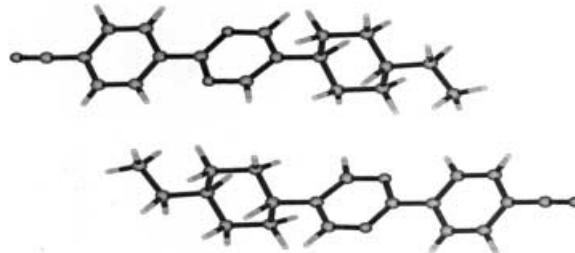


Fig. 3. The lowest in-plane energy configuration obtained with an energy of -6.89 kcal/mole at an intermolecular separation of 3.83 Å.

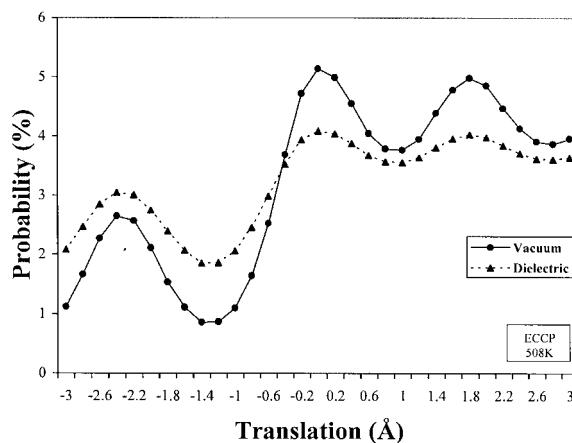


Fig. 4. Variation of the probability on translation along the X -axis during in-plane interactions at the N-I transition temperature.

Similar calculations have been performed for in-plane interactions. The interacting molecule has been kept at the large distance of 8 Å along the Y -axis from the fixed one to avoid van der Waals contacts. Again, rotations about the Y - and X -axis have been obtained, and corresponding energies have been calculated. The energy has been minimized with respect to translation and rotation about all axes. The lowest in-plane geometry was thus obtained at a separation of 3.83 Å with an energy of -6.89 kcal/mole (Fig. 3).

The dependence of the probability on the translation along the X -axis, with respect to the configuration $Y(0^\circ)$, during in-plane interactions is shown in Figure 4. Since the in-plane interactions are weaker than the stacking interactions, a greater freedom of the translation is observed. The maximum probability occurs at an equilibrium position. The probability is almost constant in a region (1 ± 0.2) Å, which may be correlated with the fluidity of the compound main-

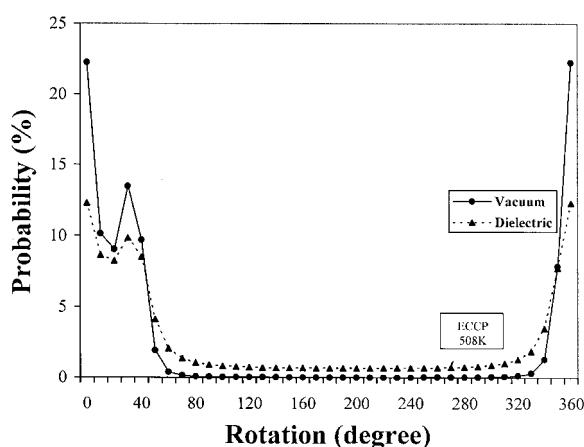


Fig. 5. Variation of the probability on rotation about the X -axis during in-plane interactions at the N-I transition temperature.

taining its alignment in the mesophase. Further, it may be observed that in a dielectric medium the energies are redistributed and there is a considerable rise in the probability of interactions, although the order of preference remains the same.

Figure 5 shows the dependence of the probability on the rotation about the X -axis during in-plane interactions with respect to the configuration $Y(180^\circ)$. It is clear that there is no drastic preference for the aligned structure; the smooth rise near the equilibrium position indicates the existence of an aligned structure at low temperature, where the thermal agitation does not drastically disturb the molecular alignment.

The terminal interactions are much weaker than the stacking or in-plane interactions. To investigate the terminal interactions apart from van der waals forces, the interacting molecule was shifted along the X -axis by 22 \AA and was allowed to rotate about X -axis. The variation of the probability of rotation about the X -axis (Fig. 6) with respect to the configuration $Y(0^\circ)$ shows no preference for any angle, i. e. the molecules are completely free to rotate about their long molecular axis.

The present calculation may be correlated with the mesomorphic behaviour of the system. The nematic character of a liquid crystal is generally manifested by its translational freedom along the long molecular axis. Therefore, for stacking and in-plane interactions translations by 0.2 \AA have been allowed, and the corresponding changes in probabilities (based on interaction energies) have been reported.

Table 1. Translational rigidities* along the long molecular axis (X -axis) during stacking and in-plane interactions between a pair of 5-(4-ethylcyclohexyl)-2-(4-cyanophenyl) pyrimidine molecules in benzene.

Temperature (K)	Probability Ratio	
	Stacking Interactions	In-plane Interactions
300	0.54	0.52
397	0.53	0.52
508 N-I	0.52	0.51

* This has been defined as the ratio of the probabilities of being at the most probable point to having $\pm 0.2 \text{ \AA}$ displacement along the translational axis.

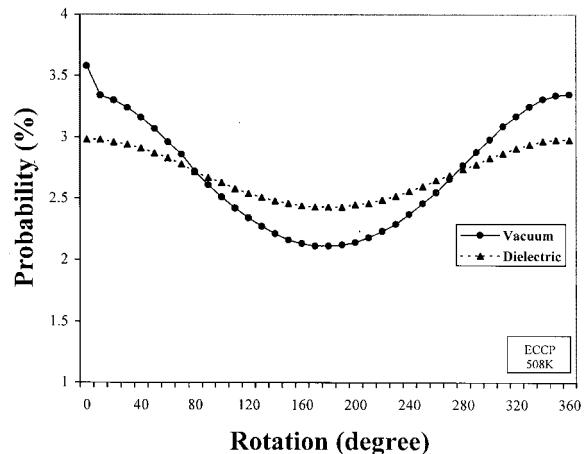


Fig. 6. Variation of the probability on rotation about the X -axis during terminal interactions at the N-I transition temperature.

Table 1 shows that the ratio of the probabilities of being at the most probable point to having $\pm 0.2 \text{ \AA}$ displacement along the long molecular axis is 0.52 at the nematic-isotropic transition temperature (508 K), whereas at room temperature (300 K) the value is 0.54, indicating a strong binding at low temperatures. On increase of the temperature the molecule obtains sufficient freedom to slide along the long molecular axis. Such translational freedom is much more pronounced in in-plane interaction. Thus even at room temperature this value is 0.52, which reduces to 0.51 at the transition temperature. In Fig. 4 it may be noted that, though the freedom is considerable for smaller translation, longer translations are not in general permitted. Thus in the mesomorphic range only small movements of the molecules are possible.

All possible geometrical arrangements between a molecular pair during stacking, in-plane and termi-

nal interactions have been considered and provide an insight of molecular arrangements inside a bulk material.

It may, therefore, be concluded 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 (or maximum probability) configuration. Also, each configuration has its own minimum energy structure for every degree of freedom. Thus in a molecular assembly, a number of local minimum energy configurations exist. All of them have their own importance, as in case of closed 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 coming down from very high temperature where the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy, and the others have a sequential preference depending on their individual relative probabilities.

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