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Ordering of a Monotropic Nematic Liquid Crystal in Dielectric Medium at Phase Transition Temperature: a Computational Analysis

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Abstract—Ordering in a monotropic nematic liquid crystal, 4'-*n*-butyl-4-cyanobiphenyl, was examined by the methods of quantum mechanics and intermolecular forces. The atomic charges and dipole moment at each atomic center were evaluated by the CNDO/2 method. The configurational energy was computed using the Rayleigh–Schrödinger perturbation method. The total interaction energies obtained by these computations were used to calculate the probability of each configuration in a dielectric medium (noninteracting and nonmesogenic solvent, benzene) at the phase transition temperature using the Maxwell–Boltzmann formula. In the dielectric medium, the energies/probabilities are redistributed, and there is a considerable rise in the probability of interactions, although the order of preference remains the same. An attempt was made to develop a new and interesting model of nematogen in a dielectric medium. A theoretical support is offered to the experimental observations.

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INTRODUCTION

In recent years, the focus has been laid on the investigation of new liquid crystal materials with differing molecular chemistry in order to study their viability in technological applications [1, 2]. The liquid crystalline materials are known for their anomalous physical properties near the phase transitions; they maintain orientational order in the mesophase [3]. The phase transitions of these liquid crystals are primarily governed by the intermolecular interactions acting between sides, planes, and ends of a pair of molecules. The proper understanding of liquid crystalline behavior requires an adequate theoretical background as a prerequisite for developing new materials and for understanding abnormal properties of materials.

The potential energy of interaction of two molecules is considered as a prime requirement in theoretical studies of molecular interactions. This interaction determines the physical properties of liquid crystals, as well as the type of kinetics of physical and physicochemical process taking place in these substances [4, 5]. Further, the simulation of the phase behavior represents a major challenge despite a substantial increase in the availability of computer processing time [6, 7].

The intermolecular interactions of liquid crystalline compounds in solution (noninteracting and nonmesogenic solvent, benzene) have been examined in several studies [8, 9] by analyzing the temperature dependences of the ultrasonic velocity and specific volume. Solutions of liquid crystalline substances show interesting trends in temperature dependences of such physical parameters as the adiabatic compressibility, molar sound velocity, molar compressibility, and intermolecular free lengths, and there is a considerable increase in the intermolecular interactions in the dielectric medium. In order to confirm the experimental findings, a quantitative theoretical study of the configurational probability distribution pattern in a dielectric medium has been carried out. These computations furnish information on the probability of the formation of dimers and on the relative freedom of a molecule in terms of variation of inclination, separation or sliding of one molecule over another, etc.

This paper deals with the characteristic features of 4'-*n*-butyl-4-cyanobiphenyl in dielectric medium (benzene; average dielectric constant taken to be 2.25) for a molecular pair at an intermediate distance of 7 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance 20 Å has been kept for terminal interactions. The distances were chosen so as to eliminate the possibility of van der Waals contacts and to keep the molecule within the short and medium-range interactions. The thermodynamic parameter shows that 4'-*n*-butyl-4-cyanobiphenyl undergoes nematic to isotropic transition at 389.5 K [10].

BASIC FORMALISM AND COMPUTATIONAL TECHNIQUE

The molecular geometry of 4'-*n*-butyl-4-cyanobiphenyl has been constructed on the basis of the published crystallographic data with the standard values of bond lengths and bond angles [10]. The calculations have been carried out in three stages as given below.

A. Computation of atomic net charges and dipole moments. The interaction energy calculations require the evaluation of atomic charges and dipole moment components at each atomic center by an all-valence electron method. Here we used the CNDO/2 method [11] to compute the net atomic charge and dipole moment at each atomic center of the molecule. A revised version QCPE no. 142 of the program, which is an extension of the original program QCPE no. 141 for the third-row elements of the periodic table, has been used. The program language is FORTRAN IV.

B. Computation of interaction energy at various configurations A detailed computational scheme based on simplified formula provided by Claverie [12] for the evaluation of interaction energy within a molecular pair has been used to calculate the energy for fixed configuration. The computer program INTER, originally developed by Claverie and later modified at the Chemical Physics Group, Tata Institute of Fundamental Research, Bombay, India by Govil and associates has been used for this purpose with further modification. According to the second-order perturbation theory as modified for intermediate-range interactions [13], the total pair interaction energy of molecules (U_{pair}) is represented as the 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.

In turn, the electrostatic term is expressed as

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

where U_{QQ}, U_{QMI}, 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 [14]. The computation of electrostatic term has, therefore, been restricted only to dipole–dipole energy term.

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

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

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

where $Z = R_{\lambda\nu}/R^{0}_{\lambda\nu}$; $R^{0}_{\lambda\nu} = [(2R^{\mathrm{w}}_{\lambda})(2\mathrm{R}^{\mathrm{w}}_{\nu})]^{1/2}$, where R^{w}_{λ} and $\mathrm{R}^{\mathrm{w}}_{\nu}$ are the van der Waals radii of atoms λ and ν, respectively. The parameters *A*, *B*, and γ are independent of the atomic species, but $R^{0}_{\lambda\nu}$ and factor $K_{\lambda}K_{\nu}$ allow the energy minimum to have different values depending on the atomic species involved. The necessary formulas can be found elsewhere [17].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin has been chosen close to the center of gravity of the molecule. The *x* axis has been chosen along a bond parallel to the long molecular axis, while the *y* axis lies perpendicular to it and *z* axis perpendicular to the molecular plane.

C. Computation of configurational probabilities. The total interaction energy values obtained by these computations were used as input data to calculate the probability of occurrence of a particular configuration *i* using the Maxwell-Boltzmann formula [17] in order to obtain a better insight:

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

where P_i stands for 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* relative to the minimum energy value in a particular set for which the probability distribution is computed.

RESULTS AND DISCUSSION

The molecular geometry of 4'-*n*-butyl-4-cyanobiphenyl is shown in Fig. 1. The total energy, binding energy, and total dipole moment along with its components are listed in Table 1. The results of probab-

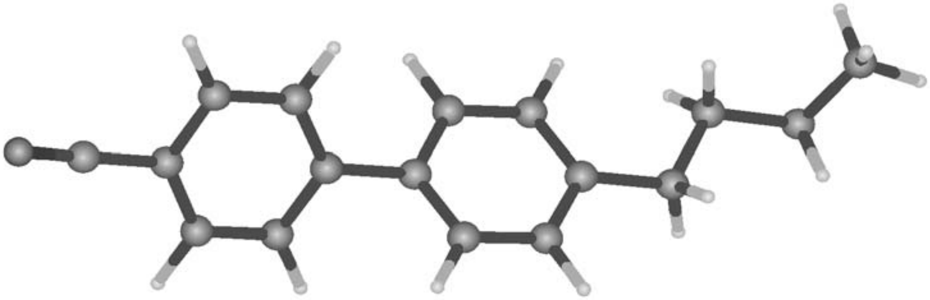

Fig. 1. Molecular geometry of 4'-*n*-butyl-4-cyanobiphenyl.

ility distribution based on interaction energy are discussed below.

A. Stacking interactions in dielectric medium. In a molecular pair, one of the interacting molecules is fixed in *x*–*y* plane while the second is kept at a distance of 7 Å from the fixed molecule. The variation of the stacking energy with respect to rotation about *z*-axis corresponding to configuration *x*(0°)*y*(0°) was examined at an interval of 10°, with calculation of the interaction energy at each point. The energy minimum thus obtained is then taken as starting point and the entire process is repeated at smaller intervals. The energy has been minimized with respect to translation and rotation about *x*, *y*, and *z* axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to another has been achieved.

The nematic character of liquid crystal is generally manifested in its translational freedom along the long molecular axis. Therefore, translations have been allowed at an interval of 0.2 Å corresponding to configuration *y*(0°)*z*(180°); the probability distributions are shown in Fig. 2. Evidently, in the stacked pair 4'-*n*-butyl-4-cyanobiphenyl molecules can slide one above the other in the range from –1.6 ± 0.4 Å without any significant change in the energy and hence are capable of retaining molecular order at a distance of up to –2.2 Å at thermal agitation.

B. In-plane interactions in dielectric medium. The interacting molecule was kept at a distance of 8 Å along *y* axis with respect to the fixed molecule. The variation of the probability with respect to translation along the *x* axis corresponding to the configuration *y*(180°) is shown in Fig. 3. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to the translation is observed. It is evident that the maximum probability occurs at 1.4 Å separation. The variation of probability is almost constant for the range –1.6 ± 0.6 Å, which may be correlated with the fluidity of the compound maintaining the molecular alignment in the mesophase.

C. Terminal interactions in dielectric medium. To examine the terminal interactions apart from van der Waals forces, the interacting molecule was shifted along the *x*-axis by 20 Å with respect to the fixed molecule, and rotations were allowed about the *x*-axis. The rotations about the *x*-axis corresponding to the configuration *y*(0°) show no preference for any angle, i.e., the molecules are completely free to rotate about their long molecular axis.

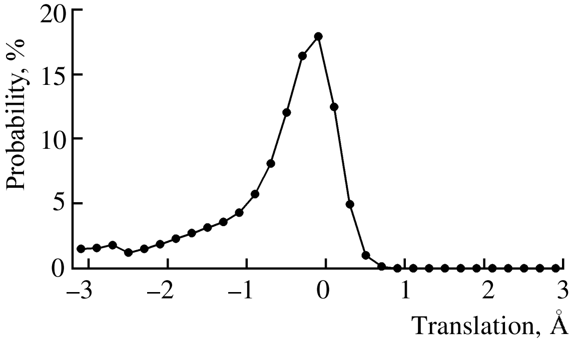

Fig. 2. Probability distribution at translation along the *x* axis for the case of stacking interactions at nematic–isotropic transition temperature (398.5 K, dielectric medium).

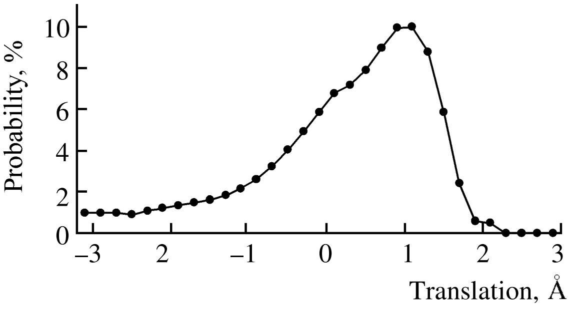

Fig. 3. Probability distribution at translation along the *x* axis for the case of in-plane interactions at nematic–isotropic transition temperature (398.5 K, dielectric medium).

Table 1. Components (D) of the dipole moment of 4'-*n*-butyl-4-cyanobiphenyl[a]

Component	μ_X	μ_Y	μ_Z
Density[b]	0.58	1.00	–0.15
sp[c]	0.79	1.13	–0.24
pd[c]	0.00	0.00	0.00
Total[d]	1.37	2.13	–0.39

[a] Total energy (sum of atomic and electronic energies of all the constituents of the molecule in the equilibrium geometry) –145.30 au, binding energy (difference between the total energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms) –18.56 au, total dipole moment 2.56 D. [b] Contribution to dipole moment components due to electron densities. [c] Hybridization moment. [d] Sum of electron density and hybridization contributions to dipole moment components.

Table 2. Relative probability of different minimum energy configurations obtained for stacking, in-plane, and terminal interactions in vacuum and dielectric medium at 300 K[a]

Configuration	Energy, kcal mol^{-1}		Probability, %	
	in vacuum	in benzene	in vacuum	in benzene
$x(0°)y(0°)$[b]	–11.82	–5.25	54.2	41.7
$y(0°)z(180°)$[b]	–11.32	–5.03	23.1	28.5
$y(0°)z(0°)$[b]	–11.30	–5.02	22.6	28.2
$y(0°)$[c]	–6.21	–2.76	0.0	0.6
$y(180°)$[c]	–6.47	–2.87	0.0	0.7
$y(0°)$[d]	–2.43	–1.08	0.0	0.0

[a] The average dielectric constant of benzene is taken as 2.25. [b] Stacking interactions. [c] In-plane interactions. [d] Terminal interactions.

ROLE OF DIELECTRIC MEDIUM

In order to examine the role of dielectric medium more closely, various possible geometric arrangements between a molecular pair have been considered. Table 2 shows the relative probabilities of different minimum energy configurations calculated for vacuum and dielectric medium at different modes of interactions. Evidently, the energies/probabilities are redistributed in the dielectric medium and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same. This is in agreement with the experimental observations [8, 9]. Further, the most favorable stacked configuration $x(0°)y(0°)$ of pair has been obtained for 4'-*n*-butyl-4-cyanobiphenyl with 41.7% (Fig. 4) probability in dielectric medium at room temperature (300 K).

Thus, isolated consideration of any particular degree of freedom shows, in general, a preference for an aligned structure with some allowance of deviation from its minimum energy (or maximum probability) configuration. In a molecular ensemble, a number of local minimum energy configurations exist. The global minimum is, however, of paramount importance, because, while descending from a very high temperature where the molecules have a completely

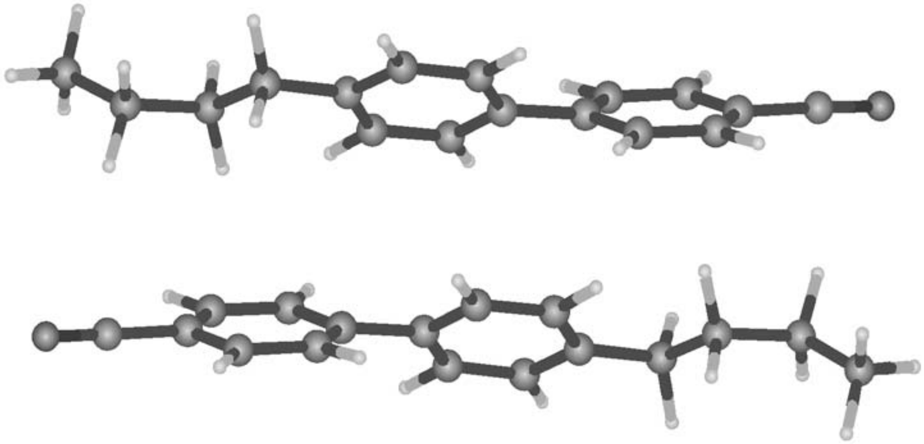

Fig. 4. The most favorable stacked configuration of a pair of 4'-*n*-butyl-4-cyanobiphenyl molecules at an interplanar spacing separation of 4 Å (energy –5.25 kcal mol^{-1}) in benzene.

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

CONCLUSION

The present calculations are helpful in characterizing the nematogenic behavior of 4'-*n*-butyl-4-cyanobiphenyl in terms of the relative order. The energies are redistributed in a dielectric medium, and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same. This offers theoretical support to the experimental observations as well as a new and interesting way of looking at the liquid crystalline molecules in a dielectric medium.

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