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Molecular Organization of 4-Cyano-4'-nonylbiphenyl in a Dielectric Medium: A Statistical Analysis

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Abstract—The molecular organization of 4-cyano-4'-nonylbiphenyl (CNBP) in a dielectric medium has been explored using a statistical model based on quantum mechanics and computer simulation. The complete neglect differential overlap (CNDO/2) method has been employed to evaluate the net atomic charge and atomic dipole components at each atomic centre of the molecule. The modified Rayleigh–Schrodinger perturbation theory along with multicentered multipole expansion method has been employed to evaluate the long-range intermolecular interactions, while the 6-exp potential function has been assumed for short-range interactions. The total interaction energies obtained through these computations were used as input to calculate the probability of occurrence of each configuration in a dielectric medium, benzene, at room temperature (300 K) using the MB formula. The various possible geometrical arrangements between a molecular pair during the different modes of interactions have been considered. This provides theoretical support to the experimental observations.

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Liquid crystal displays (LCDs) become, in recent years, the most significant and fastest growing type of display technology. The operation efficiency of LCDs is essentially determined by the liquid crystalline material properties [1]. The thermotropic liquid crystals containing terminal cyano groups are especially important for the development of commercial liquid crystalline materials for display applications [2].

The proper understanding of liquid crystalline behavior requires an adequate theoretical background as precursor to application of new developments and to accounting for abnormal properties in materials. The liquid crystalline materials are known for their anomalous physical properties near the phase transitions and maintain orientational order in 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 potential energy of interaction of two molecules is considered as a prime requirement in the theoretical investigation on molecular interactions. This interaction determines the physical properties of liquid crystals, as well as the type of kinetics of a physical and physicochemical process taking place in these substances [4, 5].

Recently Oiha reported [6] the smectogenic behavior of compounds in a dielectric medium using a statistical model based on quantum mechanics and computer simulation that motivated us to extend the similar investigation to nematogenic homologous series of 4-cyano-4'-alkylbiphenyls with a nonyl alkyl group (CNBP) in terms of pair energy and configurational probabilities in a dielectric medium (i.e. a non-interacting and non-mesogenic solvent benzene whose average dielectric constant is 2.25) fully for a molecular pair at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å was kept for terminal interactions. The interacting molecules were kept within short- and medium-range interactions in order to avoid the possibility of van der Waals contacts completely.

The molecular geometry of CNBP is shown in Fig. 1. The results of probability distribution based on the interaction energies of different modes of interactions are discussed below.

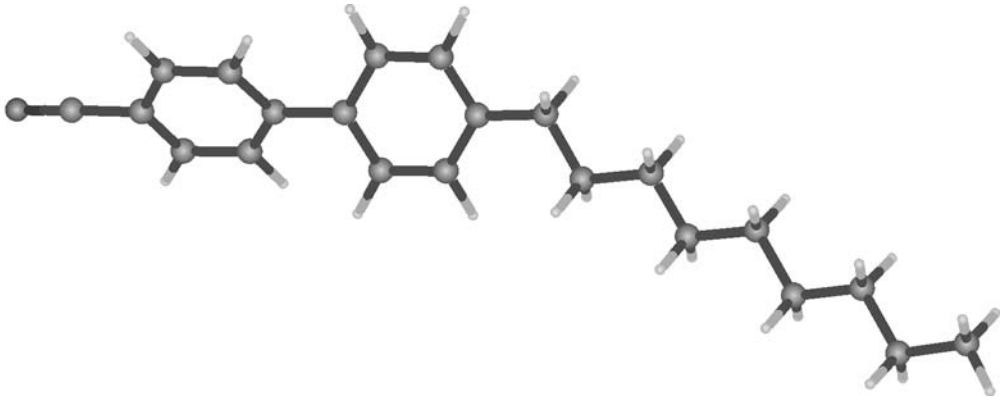

Fig. 1. Molecular geometry of CNBP.

Stacking interactions in a dielectric medium. The variation of the probability with respect to rotation about the *z* axis, corresponding to the $x(0^0)y(0^0)$ configuration was carried out at room temperature (300 K). The maximum probability was found to correspond to CNBP at an equilibrium position. Thus obtained energy minimum was then taken as the starting point, and the entire process was repeated for smaller intervals. The energy was minimized with respect to translation and rotation about the *x, y,* and *z* axes. An accuracy of 0.1 Å in translation and 1^0 in rotation of one molecule with respect to other was achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. Global search for minimum energy configuration or study of interaction energy variations under preselected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route**.**

The variation of probability with respect to translation along the long molecular axis (*x* axis), corresponding to the $y(0^0)z(180^0)$ configuration is shown in Fig. 2. As seen, the configuration shows a sharp preference towards the minimum energy point at room temperature (300 K). The variation of probability is almost constant in the region of 1.6 ± 0.2 Å, which shows that sliding of one molecule over the other is energetically allowed for a small range, which can be correlated with the fluidity of a compound maintaining its alignment in the mesophase.

Figure 3 shows the variation of probability with respect to rotation about the *x* axis corresponding to the $y(0^0)$ configuration at room temperature (300 K). The maximum probability corresponds to an equilibrium position indicating a slight preference for an aligned structure of this configuration. Further, it can be observed that the rotational rigidity about the

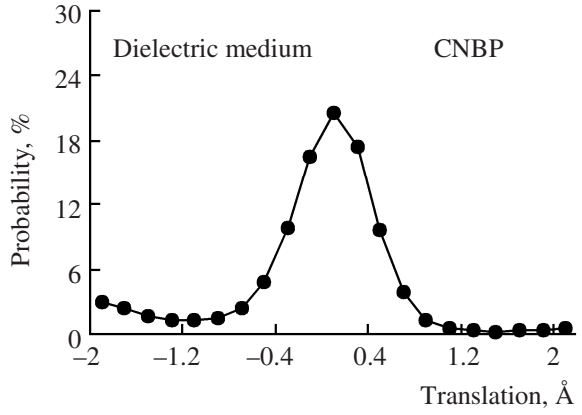

Fig. 2. Variation of the probability with respect to translation along the *x* axis, corresponding to the $y(0^0)z(0^0)$ configuration during stacking interactions at room temperature (300 K).

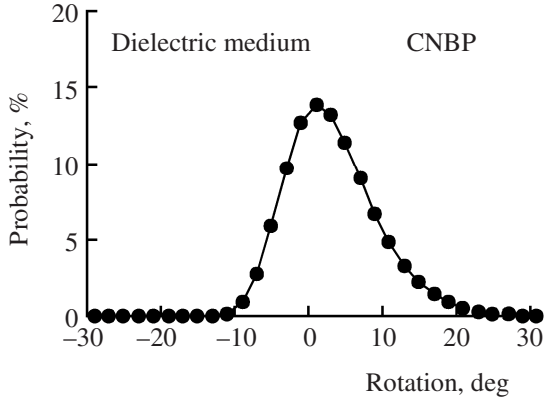

Fig. 3. Variation of the probability with respect to rotation about the *x* axis, corresponding to the $y(0^0)$ configuration during stacking interactions at room temperature (300 K).

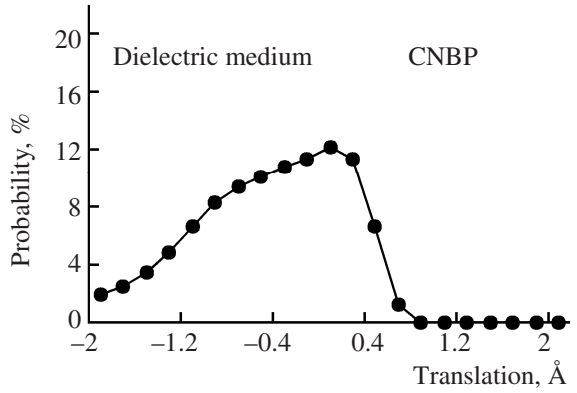

Fig. 4. Variation of the probability with respect to translation along the *x* axis, corresponding to the $y(0^0)$ configuration during in-plane interactions at room temperature (300 K).

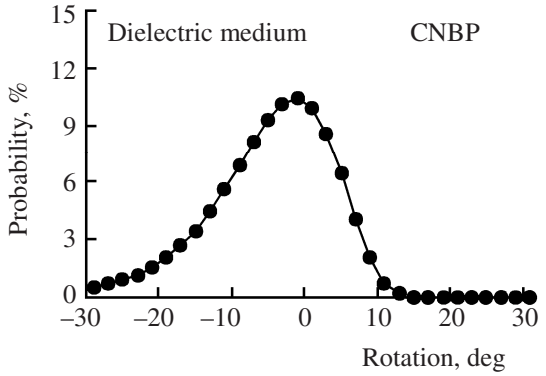

Fig. 5. Variation of probability with respect to rotation about the *x* axis, corresponding to the $y(0^0)$ configuration during in-plane interactions at room temperature (300 K).

long molecular axis is less at the nematic–isotropic transition temperature. However, the observed value at room temperature (300 K) suggests strong binding, but, as the temperature increases, the molecules obtain sufficient freedom to rotate about the long molecular axis.

In-plane interactions in a dielectric medium. Similar calculations were performed for in-plane interactions. The effect of translation along the x axis, corresponding to the $y(0^0)$ configuration, at room temperature (300 K) is shown in Fig. 4. Since in-plane interactions are weaker than stacking interactions, a greater freedom corresponding to translation is observed. It is also evident from the figure that the maximum probability occurs at an equilibrium position.

Relative probabilities of different minimum energy configurations, obtained for stacking, in-plane, and terminal interactions in a vacuum and a dielectric medium at room temperature

Configuration	Energy in a vacuum, kcal mol^{-1}	Energy in dielectric medium, kcal mol^{-1}	Probability at 300 K, %	
			A	B
$x(0°)y(0°)$[a]	–12.71	–5.65	47.7	39.3
$y(0°)z(180°)$[a]	–12.22	–5.43	20.9	27.3
$y(0°)z(0°)$[a]	–12.46	–5.54	31.3	32.6
$y(0°)$[b]	–6.87	–3.05	0.0	0.5
$y(180°)$[b]	–6.29	–2.80	0.0	0.3
$y(0°)$[c]	–2.32	–1.03	0.0	0.0

[a] The average dielectric constant of benzene was taken to be 2.25.
[b] Stacking interactions.
[c] In-plane interactions. Terminal interactions; (A) probability in a vacuum and (B) probability in a dielectric medium.

Figure 5 shows the variation of probability with respect to rotation about the *x* axis, corresponding to the $y(0^0)$ configuration. A pronounced peak exists at room temperature (300 K) and all the remaining regions have negligible probabilities as compared to this configuration. Thus, generally, molecules can be assumed to be capable of free rotations, where they prefer to reside in the same plane. Further, it can be seen that the rotational freedom is much more pronounced as compared to stacking interactions.

Having refined the interacting configuration with respect to rotation about the *x* axis at an equilibrium condition, the energy is brought down, and the probability is further investigated with respect to rotation about the *y* axis, corresponding to the $x(180^0)$ configuration. As seen, rotation about the *y* axis does not alter the configurational probability drastically.

Terminal interactions in a dielectric medium. End-to-end interactions are the weakest but become important when a molecule possesses a polar group at either or both of the ends or if there is a possibility of hydrogen bonding. Terminal interactions are much weaker than stacking and in-plane interactions. The observed rotations about the *x* axis corresponding to the $y(0^0)$ configuration show no preference for any angle, i.e. the molecules are completely free to rotate about their long molecular axis.

In order to examine the effect on molecular organization in a dielectric medium, various possible geometrical arrangements between a molecular pair were considered. Table 1 shows the relative probabilities of different minimum energy configurations calculated for a vacuum and a dielectric medium during the different modes of interactions. The most

favorable stacked configuration $x(0^0)y(0^0)$ of paring was obtained with a 39.3% probability in a dielectric medium at room temperature

It is clear from the above discussion that in a molecular assembly a number of local minimum energy configurations exist. Each of them have their own importance, as in the case of a closed molecular packing any molecule, depending on its own spatial position, can be forced to assume a local minimum energy configuration. The global minimum is, however, of paramount importance, because, while coming down from a 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.

Furthermore, the energies are redistributed in a dielectric medium and there is considerable rise in the probabilities of interactions, although the order of preference remains the same. This offers theoretical support to experimental findings [12, 13] and provides a new and interesting way of looking at liquid crystalline molecules in a dielectric medium.

EXPERIMENTAL

The molecular geometry of CNBP was constructed on the basis of published crystallographic data of 4-cyano-4'-heptylbiphenyl with the standard values of bond lengths and bond angles [7]. The calculations were carried out in three stages.

Computation of atomic net charges and dipole moments. The simplified formula for interaction energy calculations requires evaluation of atomic net charges and dipole moment components at each atomic center through an all-valence-electron method. In the present computation, the CNDO/2 method [8] was employed to compute the net atomic charge and dipole moment at each atomic center of the molecule. A revised version of the QCPE No. 142 of program, which is an extension of the original QCPE No. 141 program for the third-row elements of the periodic table, was used. The program language is FORTRAN IV.

Computation of interaction energy at various configurations. A detailed computational scheme based on the simplified formula provided by Claverie [9] for the evaluation of interaction energy between a molecular pair was used to calculate the energy for a fixed configuration. The computer program INTER, originally developed by Claverie and later on modified at the Chemical Physics Group, Tata Institute of Fundamental Research, Bombay, India, by Govil and associates was used for this purpose with further modifications. According to the second-order perturbation theory as modified for medium-range interactions [9], the total pair interaction energy of molecules (U_{pair}) is represented as a 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.

The electrostatic term is expressed as

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

where U_{QQ}, U_{QMI}, and U_{MIMI} are the 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 a satisfactory result [10]. The computation of the electrostatic term was, therefore, restricted only up to the dipole–dipole energy term.

In the present computation, the dispersion and short-range repulsion terms were considered together, since the applied semiemperical approach, viz. a Lennard–Jones- or Buckingham-type approach, actually proceeds in this way. Kitaygorodsky introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay for hydrocarbon and some other molecules, and finally gave the expression [10]:

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

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

where $Z = R_{\lambda\nu}/R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^w_\lambda)(2R^w_\nu)]^{1/2}$, where R^w_λ and R^w_ν are the van der Waals radii of the λ and ν atoms, respectively. The parameters A, B and γ do not depend on the atomic species, but R^w_λ and the $K_\lambda K_\nu$ factor allow the energy minimum to have different values, according to the atomic species involved. The necessary formulas can be found elsewhere [11].

***C*omputation of configurational probabilities.** The total interaction energies obtained through these computations were used as input to calculate the

probability of occurrence of a particular configuration i, using the Maxwell–Boltzmann formula [11] 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; $\beta = 1/kT$, k is the Boltzmann constant; T, absolute temperature; and ε_i, energy of the configuration i relative to the minimum energy for which the probability distribution is computed.

An orthogonal coordinate system was considered to facilitate the above calculation. The origin on an atom was chosen close to the center of mass of the molecule. The x axis was directed along a bond parallel to the long molecular axis, while the y axis was in the plane of the molecule, and the z axis was perpendicular to the molecular plane (xy).

The aim of the present investigation was to calculate the probability distribution of different configurations allowing free rotation and translation of one molecule in the presence of another molecule at a fixed position.

Stacking interactions. One of the interacting molecules was fixed in the xy plane, while the second was kept at a distance of 6 Å along the z axis with respect to the fixed one. The choice of the distance was 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. Rotations about the z axis were given at an interval of 1^0, and the probability at each point was calculated.

In-plane interactions. One of the interacting molecules was kept at a distance of 8 Å along the y axis with respect to the fixed one. The distance chosen for these calculations was such that the possible van der Waals contacts are avoided. Again, translations along the x axis were given, and the corresponding probabilities were reported.

Terminal interactions. To investigate the terminal interactions away from the van der Waals contacts, one of the interacting molecules was shifted along the x axis by 22 Å with respect to the fixed one, and rotations were allowed along the x axis. The probability at each point was examined.

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