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# ARTICLE

# Vacuum and Solvent Dynamics of a Cyanobiphenyl Molecule: Mesophase Estimation from Thermodynamic View

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**Abstract:** Thermodynamic view has been presented to analyze the vacuum, solvent dynamics and mesophase behaviour of a cyanobiphenyl compound named *p-n*-butyl cyanobiphenyl (4CB). The different modes of interaction energy values under vacuum in a dielectric medium (benzene) during translation and rotation have been calculated. The corresponding Helmholtz free energy and entropy have been analyzed at room temperature (300K) and transition temperature (389.5K) and the stability of the molecule at definite translation, rotation and temperature has been concluded. The change of thermodynamic characteristics and compound stability at nematic-isotropic temperature has been observed. The observed results have been analyzed to obtain an insight into the process of mesophase formation. This study may guide in establishing the other molecular models with transition temperature.

Keywords: Liquid crystal, 4CB, Mesophase, Free energy, Entropy.

# Introduction

The transition from an ordered crystal to the liquid usually disordered happens via mesophases in several organic compounds that are labelled as liquid crystalline (LC) phases [1]. In these phases, the crystalline order is lost partially and some degree of flexibility exists between the molecules. The research studies for the structure-phase correlation at molecular level are the progressing quest of LC science [2, 3]. The interplay among molecular interactions and motions is decisive for phase organization [4, 5]. The molecular motions directly impact the configurational entropy of a compound through which the free energy is controlled that governs the stability of a given phase. Generally, phase transition occurs with a subtle variation of molecular electronic energy that is sufficiently larger than the intermolecular potential energy at intramolecular level. This causes an unchanged molecular structure in spite of phase transitions.

Variation of intermolecular interaction energy that relies on the structure of the compounds has a firm dependence on anisotropy of properties [6-8]. This understanding arises from the tricky play between energy estimations, positional and orientational distributions which induce entropy data. significance of intermolecular The interactions in liquid-crystal compounds has involved many reports using the Rayleigh-Schrödinger perturbation method [9-14]. These studies are mainly focused on the establishment of anisotropic potential of the molecular pair and attempt to obtain the configuration with minimum energy. Further, the interaction energies of numerous configurations in different interaction modes indicate the inclination of a configuration over the other. In general, this data does not disclose the definite relative flexibility to explain the existence of mesostate. Further, multipole interactions show enough variations among the configurational energies, which ultimately have an impact on thermodynamic parameters. Therefore, these relative energy values have been chosen as input to compute the thermodynamic parameters to explicate the stability of 4CB mesophase.

In the present work, an attempt has been made to explain the phase stability of 4CB from a thermodynamic view. The relative energies of 4CB molecular pair in benzene have been computed using the below methodology and compared with values of vacuum [15]. The pair interaction energy computations of 4CB have been performed at a stacking intermediate distance of 10Å and an in-plane intermediate distance of 8Å. These intermolecular distances have been chosen so as to permit molecular freedom during translation and rotation relative to each other. The literature data shows the nematic-isotropic temperature of 4CB at 389.5K [16].

#### Methodology

The structure of 4CB molecule has been figured using published crystallographic data [16]. The atomic net charges and dipole moments are necessary for the calculation of the interaction energy of molecular pair. For this calculation, the CNDO/2 approach has been implemented [17]. The comprehensive computational methodology using the formula proposed by Claverie has been utilized to estimate the pair interaction energy of a molecular configuration [18]. In accordance with the second order of the perturbation theory, the pair interaction total energy of molecules  $(U_{pair})$ for intermediate range interactions is expressed as [19]:

$$U_{pair} = U_{el} + U_{pol} + U_{disp} + U_{rep} \tag{1}$$

where  $U_{el}$  is electrostatic,  $U_{pol}$  is polarization,  $U_{disp}$  is dispersion and  $U_{rep}$  is repulsion energy terms. The electrostatic term is:

$$U_{el} = U_{QQ} + U_{QMI} + U_{MIMI} + \dots$$
(2)

where  $U_{QQ}$  is monopole-monopole,  $U_{QMI}$  is monopole-dipole and  $U_{MIMI}$  is dipole-dipole terms, respectively. The evaluation of electrostatic term has been limited up to the dipole-dipole energy term as the calculation provides satisfactory results [19]. The detailed methodology finally gave the expression [19, 20]:

$$U_{disp} + U_{rep} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} U(\lambda, \nu)$$
(3)

$$U(\lambda, \nu) = K_{\lambda} K_{\nu} (-A/Z^{6} + B e^{-\gamma Z})$$
(4)

where  $Z = R_{\lambda\nu} / R^{0}_{\lambda\nu}$ ;  $R^{0}_{\lambda\nu} = [(2R^{w}_{\lambda}) (2R^{w}_{\nu})]^{1/2}$ ,  $R^{w}_{\lambda}$ and  $R^{w}_{\nu}$  are the van der Waals radii of  $\lambda$  and  $\nu$ atoms, respectively. *A*, *B* and  $\gamma$  parameters do not depend on particular species. But  $R^{0}_{\lambda\nu}$  and  $K_{\lambda} K_{\nu}$ factor that establish the energy minimum have various values according to the atomic species involved. The essential formulae and the orthogonal coordinate system details may be found elsewhere [20]. The total interaction energy data attained *via* these estimations has been utilized as input for the calculation of the thermodynamic parameters, as given below [21]:

$$A = -kT \ln \Sigma_i \exp\left(-\beta \varepsilon_i\right) \tag{5}$$

$$S = k \ln \Sigma_i \exp \left(-\beta \varepsilon_i\right) + (U/T) \tag{6}$$

$$U = \sum_{i} \varepsilon_{i} \exp(-\beta \varepsilon_{i}) / \sum_{i} \exp(-\beta \varepsilon_{i})$$
(7)

where A represents the Helmholtz free energy, U represents the internal energy and S represents the entropy.  $\beta = 1/kT$ , k represents the Boltzmann constant. T represents the absolute temperature and  $\varepsilon_i$  is the energy of the configuration i to the minimum energy value.

#### **Results and Discussion**

The structure of 4CB compound is presented in Fig. 1. The interaction energy calculations in vacuum and in dielectric medium (benzene) during the various modes of interactions are given below to analyze the physical and mesophase behaviour of the molecule.



FIG. 1. Structure of 4CB molecule.

#### **Stacking Interactions**

In this mode, one molecule has been arranged in the x-y plane in a molecular pair. The x-axis is chosen along a bond that is parallel with respect to the long molecular axis. The second molecule has been considered along z-axis with a distance of 10Å from the fixed molecule. For x  $(0^0)$  y  $(0^0)$ configuration, rotational operation about the zaxis have been performed in  $10^{0}$  intervals, to calculate the interaction energies (Fig. 2). It has been understood that the dispersion forces are the factor for the attractive interaction between

4CB molecules. The trend of estimating the exact minimum from the total energy curve is followed, as it is similar to the Kitaygorodsky energy curve [22, 23].



FIG. 2. Variation of total interaction energy depending on the rotation angle about z-axis.

The configuration y  $(\theta_1^{0})$  z  $(\theta_2^{0})$  means that the molecule has been rotated from its initial position by  $\theta_1^{0}$  about the y-axis and by  $\theta_2^{0}$  about the z-axis. Configurational probability has been calculated after displacing the molecule to a specified distance from the molecule initial position [24, 25]. Further, translational operations have been considered at 0.2Å interval. The variation of total interaction energy is reported in Fig. 3 for vacuum and dielectric medium. The translational study is essential as the nematic appeal of liquid crystals is understood from the translational mobility along the selected molecular axis. The pair of stacked molecules is expected to slide in a range of -0.4Å to 0.2Å for vacuum and -0.8Å to 0.4Å in dielectric medium with almost no difference in the total energy and hence, the higher region of translation has been observed in the dielectric medium for the molecules to preserve the order against the increment of thermal scale.



FIG. 3. Variation of total stacking interaction energy depending on the translation along x-axis.

#### **In-plane Interactions**

One molecule under interaction has been arranged at a separation of 8Å from the prefixed molecule along the y-axis to keep away from van der Waals contacts. The akin steps of computations have been repeated during in-plane mode interactions. The rotational variations about the x- and y-axes have been studied to minimize the energy during the translational and rotational motions about all (x, y and z) axes.

The interaction energy during the rotational motion about the x-axis for the configuration y  $(0^0)$  has been examined (Fig. 4). The dispersion term has been identified as the prime attractive component of interaction energy. One may observe that the apparent inclination of interaction has been exhibited although the energy difference at different rotations is quite lower. Therefore, in this configuration, the molecules in general may exhibit rotational

flexibility freely with the exception of lower scale of temperature, when the pair of molecules desires to exist in one molecular plane. Further, the translational effect along the x-axis for the y  $(0^{0})$  configuration is given in Fig. 5. The translational flexibility of molecules has been noticed to be greater in the in-plane mode in comparison with the stacking mode. The net interaction energy is observed to be nearly the same in the energy region of -2.6A to -2A in vacuum and -2.8A to -1.8A in benzene. These regions may be understood as favourable regions for exhibiting the fluidity property of the molecule by preserving the mesophase orientation. Further, the lengthy energy region of similarity has been found in the dielectric medium. The standard procedure for obtaining the minimum energy configurations has been followed [26-30].



FIG. 4. Variation of total in-plane interaction energy depending on the rotation angle about the x-axis.



FIG. 5. Variation of total in-plane interaction energy depending on the translation along the x-axis.

#### **Terminal Interactions**

A separating distance of 22Å has been selected between a pair of molecules away from the van der Waals contacts to explore the terminal mode interactions. The free molecule in the pair has been allowed for rotational motion about the x- and y-axes. The x-axis rotations exhibit no angular preference, which means that these molecules are totally flexible for rotational motion about their long-molecular axis. This indicates that these interactions are enough feebler compared to the above two modes of interactions.

### Vacuum and Solvent Dynamics

These calculations may plausibly be linked to the mesophase behaviour of the compound. Upon heating the 4CB crystals, the thermal vibrations perturb the ordering of closely packed molecules. Hence, the molecular attractive interaction in a pair becomes weaker with increment in temperature. This enhances the opportunity of relative molecular motion along the molecular long axis. From the above analysis, it may be understood that the stacked molecular flexibility to glide with respect to the axis normal to the elongated molecular axis (yaxis) is controlled. Further, the terminal mode data is trivial. These calculations support nematic behaviour. However, to explore the nematic behavior, the following thermodynamic analysis has been reported.

## **Helmholtz Free Energy**

The Helmholtz free energy estimation offers a better consideration of phase ordering and molecular-level stability. A relative analysis of Helmholtz free energy during translational motion along x-axis in stacking, in-plane mode interactions of 4CB molecule at room temperature (300K) and transition temperature (389.5K) in vacuum and benzene is given in Table 1. Evidently, in case of vacuum, the translational free energy of 4CB in stacking mode interactions is -1.06 kcal/ mol at 300K and has been found to be diminished to -1.52 kcal/ mol at 389.5K. In this way, a difference of free energy -0.46 kcal/ mol has been observed during phase transition. The free energy of 4CB molecule in solvent (benzene) during the stacking mode interactions under translation is -1.39 kcal/mol at 300K has been found to be diminished to -1.93 kcal/mol at 389.5K. A difference of -0.54 kcal/ mol has been observed. Similarly, a difference free energy of -0.59 kcal/ mol has been observed during the in-plane mode interactions under vacuum, while a value of -0.60 kcal/ mol has been observed in solvent (benzene).

From the rotational free energy data (Table 1), one may notice a free energy difference of -0.08 kcal/ mole and -0.26 kcal/ mol in vacuum and solvent during stacking interactions. Similarly, free energy difference of -0.39 kcal/mol, and -0.55 kcal/mol has been observed in vacuum and solvent, respectively, during inplane interactions. The negative value of freeenergy increment approves the mesophase stability at transition temperature. The compared values of difference amount of free energy in stacking and in-plane mode interactions discloses that the molecules show a higher amount of in-plane mode free energy difference. Hence, the molecules have enough choice to move along-long molecular axis, which confirms the phase stability in this mode of interactions. Moreover, in the presence of dielectric medium (benzene), the higher difference of free energy from transition to room temperature discloses that the stability of meso phase is higher in solvent (benzene) compared to vacuum [31].

TABLE 1. Helmholtz free energy (A) corresponding to various configurations during stacking and inplane interactions at room temperature (300K) and transition temperature (389.5K) of 4CB molecule.

Mode of Interactions	Vaccum			Benzene			
	300K	389.5K	$\Delta F$	300K	389.5K	$\Delta F$	
Stacking	-0.07	-0.15	-0.08*	-0.28	-0.54	-0.26*	
	-1.06	-1.52	-0.46**	-1.39	-1.93	-0.54**	
In-plane	-0.56	-0.95	-0.39*	-1.06	-1.61	-0.55*	
	-1.51	-2.10	-0.59**	-1.78	-2.38	-0.60**	
* Detation ** Translation							

<sup>\*\*</sup>Translation.

#### **Configurational Entropy**

The estimated configurational entropy during translation and rotation operations during the stacking and in-plane modes of interactions for 4CB molecule is shown in Table 2. The translational entropy in stacking interactions is observed to be  $5.35 \times 10^{-3}$  kcal mol<sup>-1</sup> k<sup>-1</sup> at 389.5K and  $5.02 \times 10^{-3}$  kcal mol<sup>-1</sup> k<sup>-1</sup> at 300K. The roomtemperature data reveals higher binding (less disorder) at lower temperatures. Upon increasing the temperature, these molecules attain necessary flexibility to glide along the long-molecular axis. Hence, larger entropy difference  $(0.33 \times 10^{-3} \text{ kcal})$  $mol^{-1} k^{-1}$ ) from transition to room temperature has been observed. The translational entropy data during in-plane interactions for 4CB molecules is descripted in Table 2. A less entropy difference of 0.22x10<sup>-3</sup> kcal mol<sup>-1</sup> k<sup>-1</sup> indicates that the molecule prefers in-plane structure which offers more translational

freedom. Similar calculations in benzene during the above two modes indicate that the molecule possesses higher translational freedom. This data favours the nematic appeal of the molecule.

The translational entropy favours parallel molecular orientation as this orientation offers minimum excluded volume. Hence, the higher available enough space for the molecules causes the jostling around. Further, the parallel orientation designates a lower orientational entropy state (Table 2). The same trend has been noticed during the rotational motion for the molecule. However, the comparative picture of configurational entropy in both modes of interactions in vacuum and benzene indicates that the molecule exhibits lesser z-axis ordering (*i.e.*, stacking) and greater y-axis ordering (*i.e.*, in-plane) that authorizes the nematic appeal of the molecule.

TABLE 2. Entropy x  $10^{-3}$  (S) of various configurations during stacking and in-plane interactions at room temperature (300K) and transition temperature (389.5K) of 4CB molecule.

Mode of Interactions	Vaccum			Benzene			
	300K	389.5K	$\Delta S$	300K	389.5K	$\Delta S$	
Stacking	0.73	1.11	0.38*	2.41	3.45	1.04*	
	5.02	5.35	0.33*	5.85	6.02	0.17**	
In-plane	3.54	4.42	0.88*	5.84	6.38	0.54*	
	6.40	6.62	0.22**	6.74	6.78	0.04**	
** ** Tronglation							

Rotation. Translation.

## Conclusions

The estimation of phase behaviour and phase stability of a nematic liquid crystal (4CB) leads to the following conclusions:

1. The negative free energy increment approves the mesophase stability at transition temperature. The compared values of difference amount of free energy in both interactions disclose that the molecules illustrate a higher amount of in-plane free energy difference. Hence, the molecules have enough choice to move along the long molecular axis, which confirms phase stability in this mode of interaction.

- 2. The higher free energy difference in the dielectric medium (benzene) discloses that the meso-phase stability is higher in solvent (benzene) compared to vacuum.
- 3. The comparative configurational entropy view in vacuum and benzene indicates that the molecule exhibits lesser z-axis ordering (*i.e.*, stacking) and greater y-axis ordering (*i.e.*, in-plane) that authorizes the nematic appeal of the molecule.

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