

## Molecular Ordering in Nematogens Based on Quantum Mechanics and Intermolecular Forces: A Computational Analysis

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A computational analysis of ordering in nematogens *trans-trans*-4'-alkyldicyclohexyl-4-carbonitriles cyclohexanes (CCHs) with alkyl group, propyl (CCH3), pentyl (CCH5) and heptyl (CCH7) has been carried out based on quantum mechanics and intermolecular forces. The evaluation of atomic net charges and dipole moments at each atomic center has been carried out using the Complete Neglect Differential Overlap (CNDO/2) method. The modified Rayleigh-Schrodinger perturbation theory and the multicenter-multipole expansion method were employed to evaluate long-range intermolecular interactions, while a 6-exp potential function was assumed for short-range interactions. Various possible geometrical arrangements of molecular pair with regard to different modes of interactions were considered. A comparative picture of molecular parameters, such as total energy, binding energy and total dipole moment of CCH3 with CCH5 and CCH7, are given. The results are discussed in the light of other theoretical observations.

**Key Words:** CNDO/2 method, Interaction energy, Quantum chemistry.

### INTRODUCTION

The liquid crystal technology has had a major effect in many areas of science and engineering, as well as device technology. Applications for this kind of materials are still being discovered and continue to provide effective solutions to many different problems<sup>1,2</sup>. The proper understanding of liquid crystalline behaviour requires an adequate theoretical background as a precursor to application of new developments and accounting for abnormal properties of the materials<sup>3,4</sup>. The potential energy of interaction of two molecules is considered as a prime requirement in theoretical investigation of molecular interactions. This interaction determines the physical properties of liquid crystals, as well as the type of kinetics of physical and physico-chemical properties in these substances<sup>5,6</sup>.

The role of molecular interactions in mesogenic compounds has attracted attention of several workers based on the Rayleigh-Schrodinger perturbation theory<sup>7-9</sup>. These studies were aimed at computing the interaction energy of a molecular pair depending on the angle and distance, but efforts were made directed toward explaining the aligned structure or, at best, correlating the minimum energy with the

observed crystal structures. It has been observed that the interaction energy of a pair of mesogens indicates the preference of a particular configuration, depending on the relative energies.

The present article deals with the computation of pair interaction energies for CCH3, CCH5 and CCH7 molecular pairs but detailed results are reported only for CCH3 at an intermediate distance of 8 Å for stacking and 10 Å for in-plane interactions. Similarly, a distance of 22 Å was set for terminal interactions. However, the salient features of the residual molecules (CCH5 and CCH7) are also given. The choice of distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the short- and medium-range interactions. Further, 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.

### COMPUTATIONAL DETAILS

**Computational details:** The geometry of CCHs molecules (CCH3, CCH5 and CCH7) was constructed on the basis of the published crystallographic data with standard values of bond lengths and bond angles<sup>10</sup>. In order to find the interaction energy of two molecules, it is necessary to compute atomic net charges and dipole moments with an all valence electron method. Hence, in the present work, the CNDO/2 method<sup>11</sup> was used to compute the net atomic charges and dipole moments at each atomic centre of the molecule.

A detailed computational scheme based on simplified formula given by Claverie<sup>12</sup> for evaluating the interaction energy of a molecular pair was used when calculating the energy at fixed configurations. According to the second order of the perturbation theory is modified for intermediate range interactions<sup>13</sup>, the total pair interaction energy of molecules ( $U_{\text{pair}}$ ) is represented as a sum of several terms contributing to the total energy:

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

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

In turn, electrostatic term is expressed as

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

where  $U_{\text{QQ}}$ ,  $U_{\text{QMI}}$  and  $U_{\text{MIMI}}$  *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 involving only the above terms gives satisfactory results<sup>14</sup>. The evaluation of electrostatic term was, therefore, restricted by the dipole-dipole energy term.

In present work, the dispersion and short-range repulsion terms are considered together because several semiempirical approach, *viz.*, the Lennard-Jones or Buckingham approach, actually proceed in this way. Kitaygorodsky introduced a

Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay<sup>15</sup> for hydrocarbon molecules and several other molecules, which finally gave the expression:

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

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

where  $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$ ;  $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$ ,  $R_{\lambda}^w$  and  $R_{\nu}^w$  are the van der Waals radii of  $\lambda$  and  $\nu$  atoms, respectively.  $A$ ,  $B$  and  $\gamma$  parameters are independent of particular species. But  $R_{\lambda\nu}^0$  and  $K_{\lambda} K_{\nu}$  factor, which determine the energy minimum, have different values according to the atomic species involved. The necessary formulae may be found elsewhere<sup>16</sup>.

In this case, the origin was set on an atom close to the centre of mass of the molecule. The  $x$ -axis was directed along a bond parallel to the long molecular axis, while the  $y$ -axis lied in the plane of the molecule and the  $z$ -axis was normal to the molecular plane.

## RESULTS AND DISCUSSION

The molecular geometries of CCH3, CCH5 and CCH7 are shown in Fig. 1. A comparative picture of molecular parameters, such as total energy, binding energy and total dipole moment of CCH3, CCH5 and CCH7 is given Fig. 2. As evident from Fig. 2, the total energy and binding energy of these molecules are arranged in a series:

$$\text{CCH7} > \text{CCH5} > \text{CCH3}$$

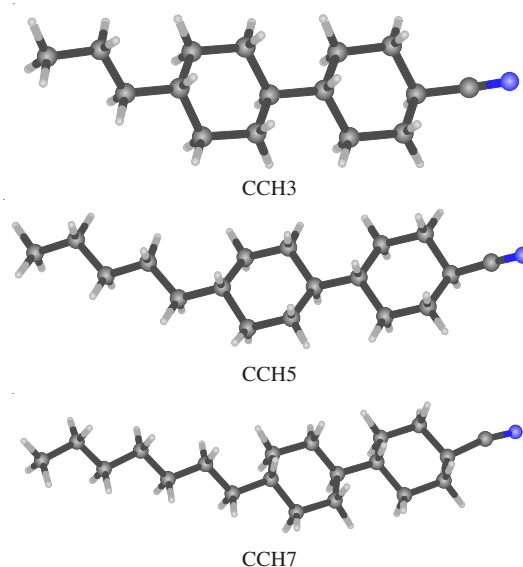


Fig. 1. Molecular geometry of CCH3, CCH5 and CCH7 molecules

while the dipole moments change as follows:

$$\text{CCH5} > \text{CCH7} > \text{CCH3}$$

The results of interaction energy calculations with regard to the different modes of interactions are discussed below.

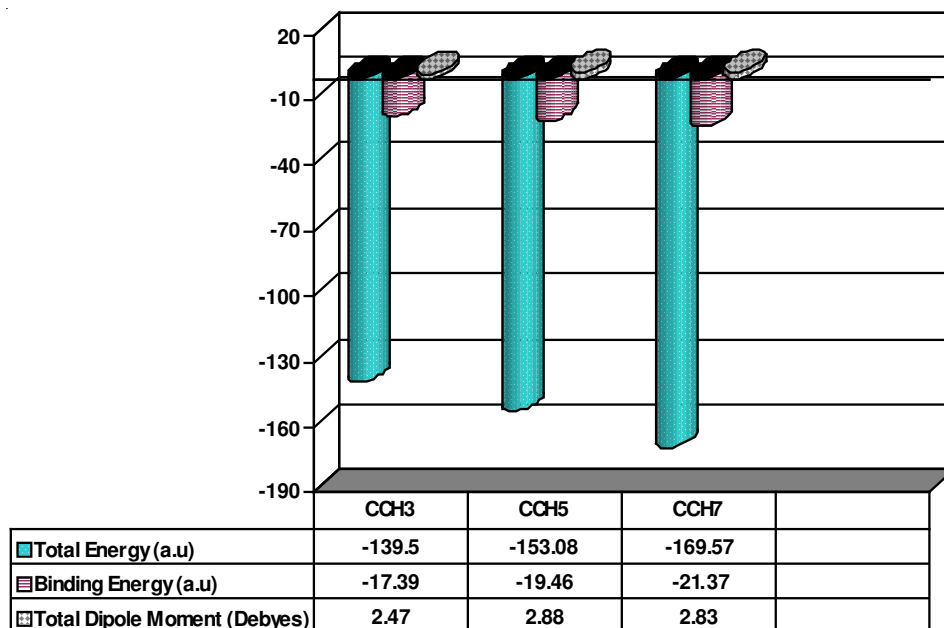


Fig. 2. A comparative picture of molecular parameters of CCH3, CCH5 and CCH7

**Stacking interactions:** One of the interacting molecules is fixed in the x-y plane in such a manner that the x-axis is directed along a bond parallel to the long molecular axis, while the other molecule is kept at a distance of 8 Å along the z-axis from the fixed one. The variation of interaction energy components with respect to rotation about the z-axis corresponding to the configuration  $x(0^0) y(0^0)$  has been carried out. It has been observed that the dispersion energy is mainly responsible for the attraction between CCH3 molecules, although the exact minimum is estimated always from the Kitaygorodsky energy curve, which is generally similar to the total energy curve.

The nematic character of liquid crystals is manifested in their translational mobility along the long molecular axis. Therefore, translations were considered at a step of 0.2 Å and the corresponding changes in various interaction energy components are reported in Fig. 3. All components increase with an increase in overlapping, the increase being smaller in the case of electrostatic and polarization energies. Evidently, molecules in a stacked pair can slide in a range of  $0.2 \pm 0.4$  Å with no significant change in the energy and, hence, molecular order can be kept up to 2.8 Å at the thermal agitation.

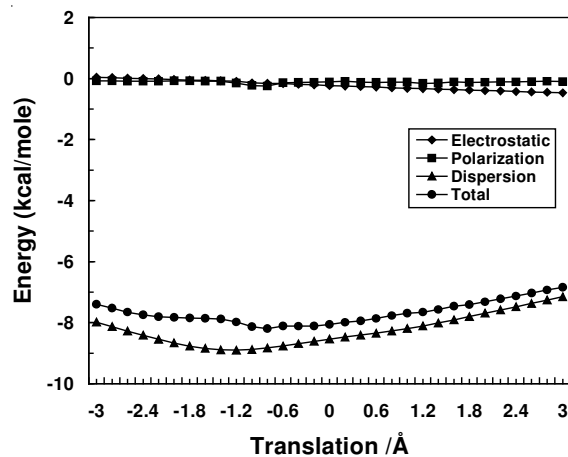


Fig. 3. Variation of stacking interaction energy components with respect to translation along x-axis

**In-plane interactions:** An interacting molecule was kept at a distance of  $10 \text{ \AA}$  along the y-axis from the fixed other one to avoid van der Waals contacts. Similar calculations were carried out for in-plane interactions. Again, rotations about the y- and x-axes were considered and the energy was minimized with respect to the translation and rotation about x, y and z-axes.

The variation of interaction energy components depending on the rotation about the x-axis with respect to configuration y ( $0^\circ$ ) was carried out (Fig. 4). The main attractive part of interaction energy comes from the dispersion term. Evidently, the

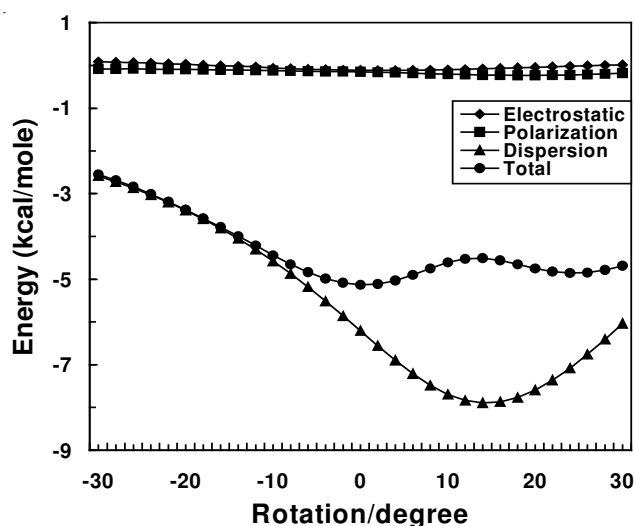


Fig. 4. Variation of in-plane interaction energy components with respect to rotation about x-axis

interaction shows a clear preference, though the difference in energy at different values of rotation angle is very small. Thus, generally, the molecule may be assumed to be able to rotate freely except at a lower temperature, when the two molecules being prefer to be in the same plane. The effect of translations along the x-axis with respect to configuration  $y(0^0)$  is shown in Fig. 5. It can be seen that the translational freedom is much more pronounced than the stacking interactions. The total interaction energy is nearly constant in the energy of  $1.8 \pm 0.4 \text{ \AA}$ , which may be correlated with the fluidity of the compound preserving its alignment in mesophase.

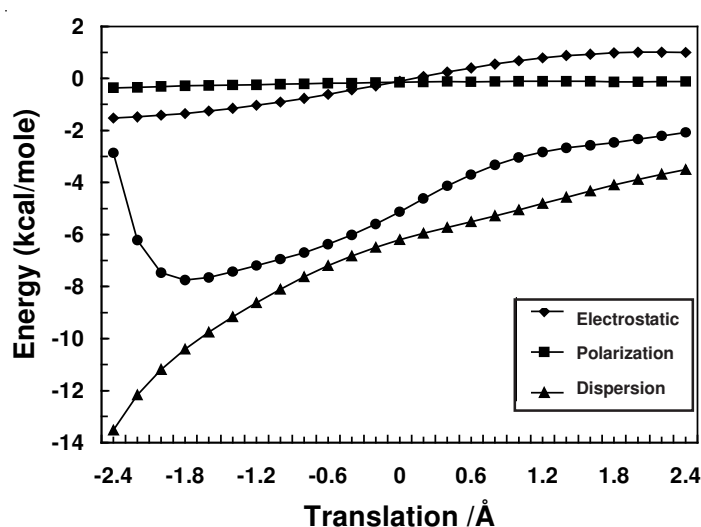


Fig. 5. Variation of in-plane interaction energy components with respect to translation along x-axis

**Terminal interactions:** To investigate the terminal interactions beyond the van der Waals contacts, the interacting molecule was shifted along the x-axis by  $22 \text{ \AA}$  with respect to the fixed one and allowed to rotate about the x and y-axes (Fig. 6). The terminal interactions are much weaker than the stacking or in-plane interactions. Rotations about the x-axis show absolutely no preference of any angle, *i.e.*, molecules are completely free to rotate about their long molecular axis. Furthermore, all possible geometrical arrangements in a molecular pair were considered.

**Correlation of the results:** The interaction energy calculations may reasonably be related to the mesomorphic behaviour of the system. When solid crystals of CCH3 are heated, thermal vibrations disturb the molecular order of strongly packed CCH3 molecules. Consequently, the attraction of molecules within a pair, which largely comprises the dispersion forces, tends to weaken at higher temperatures and, hence, the possibility of relative motion of paired molecules along the long molecular axis is considerably enhanced. The freedom of molecules in a stacked pair to slide along the axis normal to the long molecular axis (y-axis) is energetically restricted, while terminal interactions are quite insignificant.

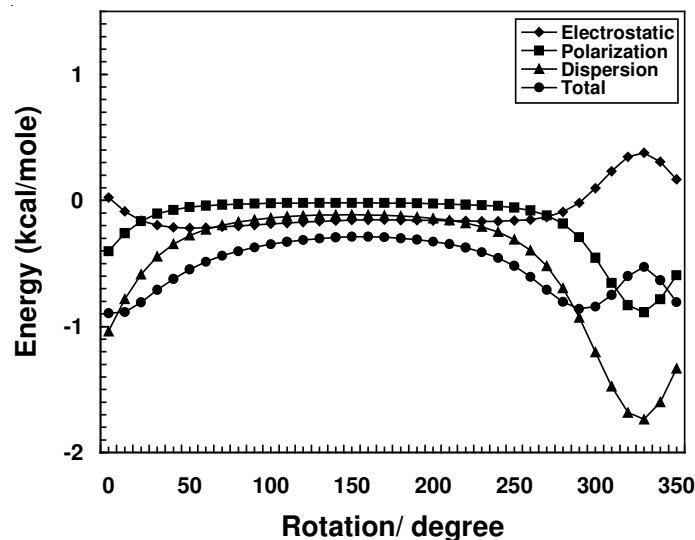


Fig. 6. Variation of terminal interaction energy components with respect to rotation about x-axis

The results favor nematic character of the system. At a very high temperature, the dispersion forces play negligible role and all possible stacking geometries (even T-shape stacking) become equally probable, which ultimately causes the system to become an isotropic melt.

### Conclusion

It may, therefore, be concluded from the above discussion that intermolecular interaction energy calculations are helpful in analyzing the liquid crystalline behaviour of CCH<sub>3</sub> molecules in terms of molecular forces accounting for mesomorphism. The study may be extended to predict the effect produced by the addition of a suitable functional group of higher homologues of CCH<sub>3</sub>.

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