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# A Computational Analysis of Ordering in *p-n*-Octyloxy Benzoic Acid – A Nematogen

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## Abstract

A computational analysis of ordering in *p-n*-Octyloxy Benzoic Acid (8OBAC) 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-Schrodinegr perturbation theory along with multicentered-multipole expansion method has been employed to evaluate long-range intermolecular interactions, while a *6-exp* potential function has been assumed for short-range interactions. The possible geometrical arrangements between a molecular pair during the different modes of interactions have been considered. A comparative picture of molecular parameters such as total energy, binding energy, and total dipole moment of 8OBAC with other nematogens 9OBAC (*p-n*-Octyloxy Benzoic Acid) and 10OBAC (*p-n*-Decyloxy Benzoic Acid) has been given. These computations provide information of a dimer complex, the freedom of a molecule in terms of variations in inclination, separation or sliding of one molecule over the other.

**Key words:** CNDO/2 method, interaction energy, quantum chemistry.

## Introduction

Research involving the search for new self-organizing molecular materials such as liquid crystals is an ongoing quest. It has become one of the most intriguing areas of modern science due to pioneer research on rich phase behaviour and applications across a wide spectrum of activities, in the field of soft condensed systems and nano-structured materials [1, 2]. The alkoxy benzoic acids are of structural interest as the molecules in this homologous series represent thermodynamically, one of the groups of materials that form mesophases. The proper understanding of liquid crystalline behavior requires an adequate theoretical background as a precursor to application of new developments and accounting for abnormal properties of the materials [3, 4]. 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 physicochemical properties in these substances [5].

Many LC materials reported based on intermolecular interaction energy calculations using the Rayleigh-Schrodinger perturbation method [6-8]. It has been observed that the interaction energies for a pair of mesogens indicate the preference of a particular configuration over the other depending on their energy values. The intermolecular forces such as van der Waals interaction, hydrogen bonds, electron donor interactions and steric repulsive interactions influences the situation of molecules in a mesophase. Each of these forces separately or together may be responsible for increasing or decreasing the thermal stability of LC phase.

In the present communication, an attempt has been made to interpret the results of intermolecular interaction energy calculations between two 8OBAC molecules at an intermediate distance of 6Å for stacking and 8Å for in-plane interactions. Similarly, a distance of 22 Å has been fixed for terminal 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. The results have been discussed in the light of those obtained for the nematogens 9OBAC and 10OBAC.

The thermodynamic data show that 8OBAC goes to nematic-isotropic melt at 419K [9].

## Computational Approach

The molecular geometry of 8OBAC has been constructed on the basis of the published crystallographic data with standard values of bond lengths and bond angles [9]. 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 [10] 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 provided by Claverie [11] for evaluation of interaction energy between a molecular pair has been used the energy for a fixed configuration. According to the second order of the perturbation theory as modified for intermediate range interactions [12], the total pair interaction energy of molecules ($U_{pair}$) is represented as a sum of several 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.

In turn, electrostatic term is expressed as

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

where $U_{QQ}$, $U_{QMI,}$ and $U_{MIMI}$ 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 involving only the above terms gives a satisfactory result [13]. The evaluation of electrostatic term has, therefore, been restricted by only up to dipole-dipole energy term.

In the present work, the dispersion and short-range repulsion terms are considered together because several semiemperical 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 for hydrocarbon molecules and several other molecules, which finally gave the expression [14]:

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

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

where $Z = R_{\lambda\nu} / R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^w_{\lambda})(2R^w_{\nu})]^{1/2}$, $R^w_{\lambda}$ and $R^w_{\nu}$ are the van der Waals radii of $\lambda$ and $\nu$ atoms respectively. $A$, $B$ and $\gamma$ parameters are independent of particular species. But $R^0_{\lambda\nu}$ 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 [15].

In this case, the origin has been chosen on an atom close to the centre of mass of the molecule. The x-axis along a bond parallel to the long molecular axis, while the y-axis lies in the plane of the molecule, and the z-axis perpendicular to the molecular plane (xy). The origin lies almost at the middle of the molecule.

## Results and Discussion

The molecular geometry of 8OBAC is shown in Fig.1. A comparative picture of molecular parameters such as total energy, binding energy, and total dipole moment of 8OBAC with 9OBAC, and 10OBAC is shown in Fig.2. The results of interaction energy calculations during the different modes of interactions are discussed below:

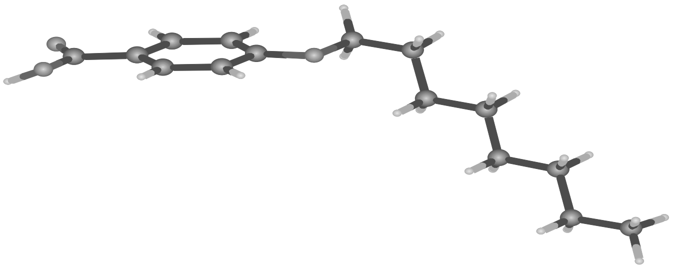
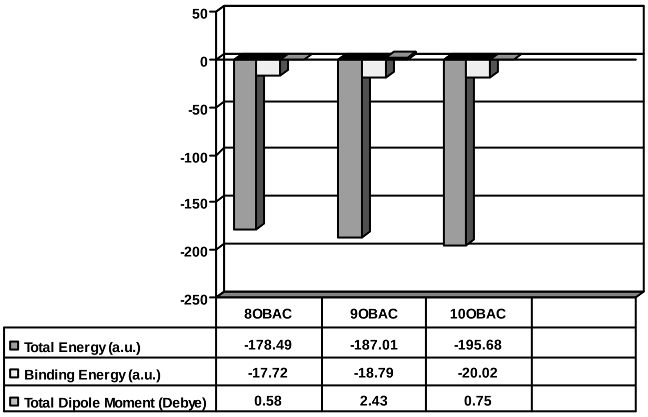


**Figure 1:** Molecular Geometry of 8OBAC.



| | 8OBAC | 9OBAC | 10OBAC | |
|---|---|---|---|---|
| ▨ Total Energy (a.u.) | -178.49 | -187.01 | -195.68 | |
| ☐ Binding Energy (a.u.) | -17.72 | -18.79 | -20.02 | |
| ▨ Total Dipole Moment (Debye) | 0.58 | 2.43 | 0.75 | |

**Figure 2:** A Comparative picture of molecular parameters of 8OBAC, 9OBAC, and 10OBAC.

## Stacking Interactions

The variation of the interaction energy components with respect to the configuration x ($0^0$) y ($0^0$) on the rotation about z-axis is shown in Fig. 3. The interacting molecule has been placed at a separation of 6 Å along the z-axis with respect to the fixed molecule. The distance has been chosen to eliminate Van der Waals contacts and to keep the molecule within the range of short- and medium-range interactions.

Fig. 3 reveals that the dominant component of the total energy is the dispersion energy. The contribution of the polarization energy is negligible. The electrostatic term is much smaller than dispersion term. The repulsion energy component has not been plotted explicitly as it can easily obtained with the help of the dispersion and Kitaigorodsky curves, i.e., the curve showing the sum of dispersion and repulsion energies. The minimum energy so obtained is then taken as starting point and entire process is repeated for 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 $1^0$ in rotation of one molecule with respect to other has been achieved.

The variation of the intermolecular interaction energy components with respect to translation along the long molecular axis corresponding to configuration y ($0^0$) z ($0^0$) is shown in Fig. 4. All components increase with increased overlapping, the increase being small for electrostatic and polarization energy terms. The dispersion energy component is mainly responsible for the attraction between the planes of the 8OBAC molecules, though the exact optimum results always from the Kitaigorodsky energy curve, which has a gross similarity with the total energy curve. Evidently, the stacked pair of 8OBAC molecules can slide one above the other in the range of -16 ± 4 Å without any significant change in the energy and, hence, is capable of retaining molecular order up to 30 Å against increased thermal agitation.

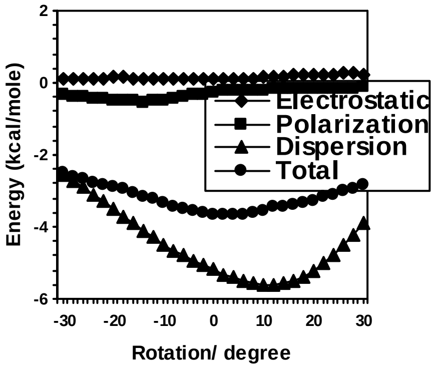


**Figure 3:** Variation of stacking interaction energy components with respect to rotation about z-axis corresponding to configuration x ($0^0$) y ($0^0$).

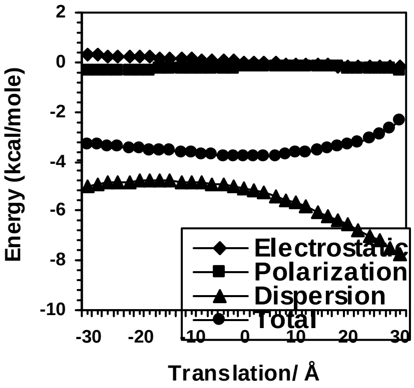


**Figure 4:** Variation of stacking interaction energy components with respect to translation along x-axis corresponding to configuration x ($0^0$) y ($0^0$).

## In-Plane Interactions

An interacting molecule has been kept at a separation of 8Å along the y-axis with respect to the fixed one in order to avoid van der Waals contacts. Similar calculations have been performed for in-plane interactions. Having refined the interacting configuration with respect to rotation about x-axis at an equilibrium condition, the energy is brought down and energy is further investigated with respect to rotation about y-axis corresponding to configuration y ($180^0$). It has been observed that the rotation about y-axis does not alter the configurational energy drastically.

The nematic character of liquid crystals is generally manifested by its translational freedom along the long molecular axis. Therefore, translations have been allowed along x-axis corresponding to configuration y ($0^0$) as shown in Fig. 5. Since, in-plane interactions are weaker than the stacking interactions, a grater freedom corresponding to translation is observed. The dominating role of dispersion is obviously marked here, although the optimum position is always governed by the Kitaigorodsky term.

The total interaction energy is nearly constant in the range of -2 ± 4 Å, which may be correlated with the fluidity of the compound maintaining its alignment in mesophase.

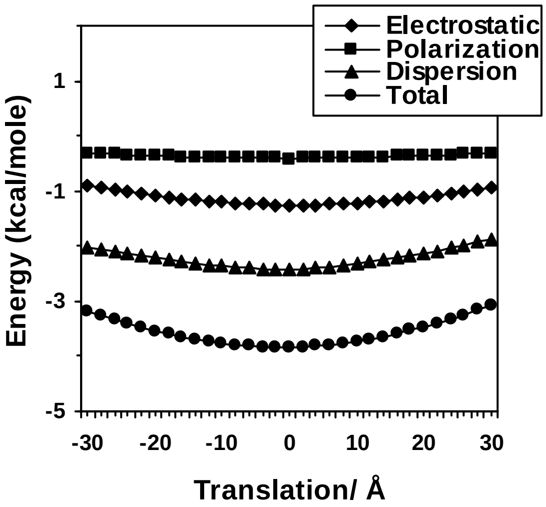


**Figure 5:** Variation of in-plane interaction energy components with respect to translation along x-axis corresponding to configuration y ($0^0$).

## Terminal Interactions

To investigate terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the x-axis by 22 Å with respect to fixed one and allowed to rotate about the x-axis. The interaction energy at such points has been examined. It has been observed that the rotations about the x-axis show absolutely no preferences for angle, i.e., the molecules are free to rotate about their long molecular axis. Further, the observed stacking energies are much larger than in-plane and terminal interaction energies. This supports the basic assumption of molecular field theory [16-18].

## Correlation of the Results

The interaction energy calculation may be reasonably correlated with the mesomorphic behavior of the system. When solid crystals of 8OBAC are heated, thermal vibrations disturb the molecular order of the strongly packed 8OBAC molecules. Consequently, the attraction within a pair of molecules, which largely comprises the dispersion forces, tend to become weaker at higher temperatures and, hence the possibility of relative movement within a molecular pair along the long molecular axis is considerably enhanced. The freedom of molecules in a stacked pair to slide along an axis perpendicular to the long molecular axis (y-axis) is energetically restricted, while terminal interactions are quite insignificant.

The results favor nematic behavior of the system. At a very high temperature, the breaking of all dispersion force occurs and all possible stacking geometries (even perpendicular stacking) become equally probable, which ultimately causes the system to pass on to an isotropic melt.

## Conclusion

It may be concluded that nematogens exhibit a tendency to retain translational order in a small range along with simultaneous orientational freedom. Further, these computations provide information of a dimer complex, the freedom of a molecule in terms of variations in inclination, separation or sliding of one molecule over the other.

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