

Ordering in Nematogenic *p-n*-Heptyloxy Benzoic Acid-A Computational Study

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A computational study of ordering in *p-n*-heptyloxy benzoic acid (7OBAC) has been carried out with respect to translatory and orientational motions. 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 along with a 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. Various possible geometrical arrangements between a molecular pair during different modes of interactions have been considered. A comparative picture of molecular parameters, such as total energy, binding energy and total dipole moment of 7OBAC with 8OBAC (*p-n*-octyloxy benzoic acid) and 9OBAC (*p-n*-nonyloxy benzoic acid) has been given. An attempt has been made to analyze the nematogenic behaviour of 7OBAC at molecular level and develop a simple model by building in realistic features.

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

INTRODUCTION

The liquid crystals (LCs) have captured the attention of numerous studies due to their unique characteristics of behaving as an isotropic liquid or having collective motions in different time scales¹. The exploration of liquid crystallinity is imperative not only from the view point of their technological applications but also from fundamental studies in the field of molecular interactions². The different physical properties of liquid crystals across various phase transition boundaries provides information about the order of transition involved and the strength of the intermolecular interactions accompanying the growth of liquid crystal phase^{3,4}. The ultimate objective of these studies is to determine the macroscopic properties of complex systems, such as liquid crystals from the microscopic quantities.

Many liquid crystal materials reported based on intermolecular interaction energy calculations using the Rayleigh-Schrodinger perturbation method⁵⁻⁷. The computer simulations of interactions are useful in employing molecular models, yield insight

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into general features of phase equilibria, structure and dynamics of liquid crystals. It has been observed that the interaction energies for a pair of mesogens indicate the preference of a particular configuration 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 liquid crystal phase⁸.

The present article deals with the computation of pair interaction energies for 7OBAC molecule at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions. 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. A comparative picture of molecular parameters of 7OBAC with 8OBAC and 9OBAC has been given. The thermodynamic parameter reveals⁹ that the molecule 7OBAC shows nematic-isotropic transition temperature at 420 K.

COMPUTATIONAL DETAILS

The molecular geometry of 7OBAC has been constructed on the basis of the published crystallographic data with standard values of bond lengths and bond angles⁹. 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 method¹⁰ has been 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 Claverie¹¹ for evaluation of interaction energy between a molecular pair has been used to calculate the energy for a fixed configuration. According to the second order of the perturbation theory is modified for intermediate range interactions¹², the total pair interaction energy of molecules (U_{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_{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

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

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 result¹³. The computation of electrostatic term has, therefore, been restricted only up to the dipole-dipole term.

In the 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 for hydrocarbon molecules and several other molecules, which finally gave the expression¹⁴:

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

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

where $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$; $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$, R_{λ}^w and R_{ν}^w are the van der Waals radii of λ and ν atoms, respectively. A , B and γ 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 elsewhere¹⁵.

In this case, the origin of coordinates has been chosen 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 lies in the plane of the molecule and the z-axis perpendicular to the x-y plane of the molecule.

RESULTS AND DISCUSSION

The molecular geometry of 7OBAC is shown in Fig. 1. A comparative picture of molecular parameters, such as total energy, binding energy and total dipole moment of 7OBAC, 8OBAC and 9OBAC are given in Fig. 2. The results of interaction energy calculations during the different modes of interactions are discussed below:

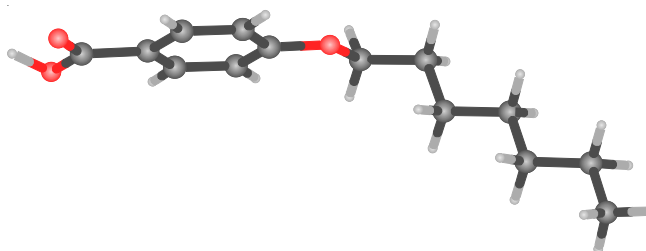


Fig. 1. Molecular geometry of 7OBAC

Stacking interactions: One of the interacting molecules is fixed in the x-y plane such that the x-axis lies along a bond parallel to the long molecular axis, while the other is kept at a separation of 6 Å along the z-axis with respect to the fixed one. The variation of interaction energy components with respect to rotation about the z-axis corresponding to configuration $x(0^\circ)$ $y(0^\circ)$ is shown in Fig. 3. An observation of figure reveals that the dominant component of total energy is the dispersion energy. The contribution of polarization energy is negligible and is almost

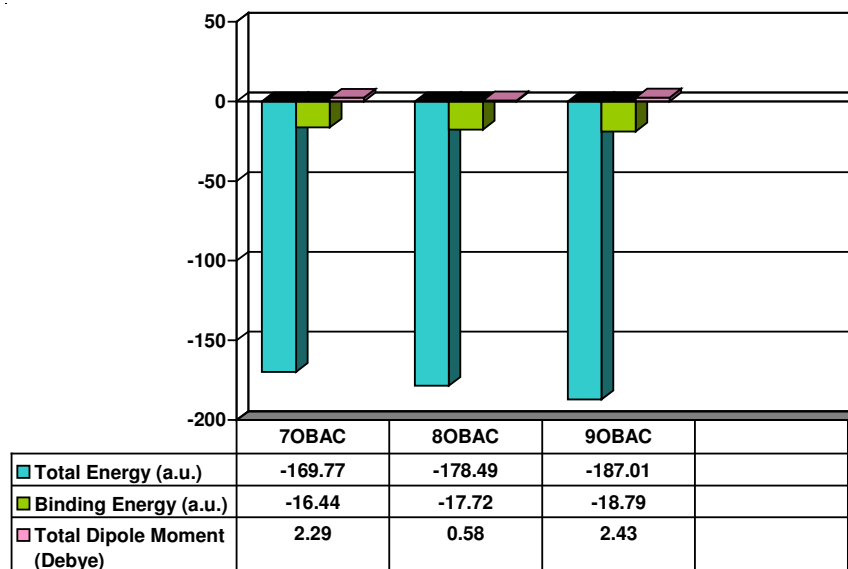


Fig. 2. A comparative picture of molecular parameters of 7OBAC, 8OBAC and 9OBAC

constant through out the entire range, while the dispersion energy is mainly dependent on the extent of overlap during stacking. The magnitude of electrostatic term is much less as compared with the dispersion term but the symmetric fluctuation in the electrostatic term is reflected in the nature of variation in the total energy. The energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 \AA in translation and 1° in rotation of one molecule with respect to other has been achieved. It is important to note here that the path of minimization strictly depends on the objective of computation. The global search for minimum energy configuration or the study of variation of interaction energy under pre-selected condition will have completely different path and, therefore, one has to be careful in choosing the specific route.

Fig. 4 shows the variation of interaction energy components for translation of $\pm 30 \text{ \AA}$ along x-axis corresponding to configuration $y (0^\circ) z (0^\circ)$. It may be observed that all components increase in magnitudes with increased overlapping although the extent of increase is relatively lesser for electrostatic and polarization terms. The variation of energy is almost constant for a region of $-10 \pm 4 \text{ \AA}$, which shows that a sliding of one molecule over the other is energetically allowed for a small range that may be correlated with the fluidity of the compound maintaining its alignment in mesophase.

In-plane interactions: An interacting molecule has been kept at a separation of 8 \AA 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. Again, rotations about the y- and x-axes have been given and the corresponding energy has been minimized with respect to translation and rotation about all axes.

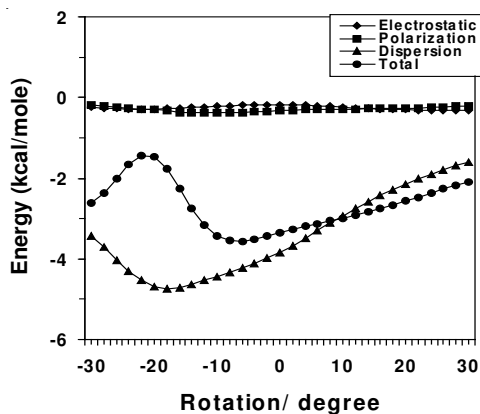


Fig. 3. Variation of stacking interaction energy components with respect to rotation about z-axis corresponding to configuration x (0°) y (0°)

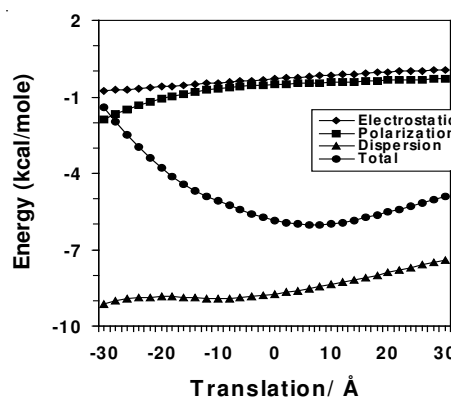


Fig. 4. Variation of stacking interaction energy components with respect to translation along x-axis corresponding to configuration y (0°) z (0°)

The variation of interaction energy components with respect to rotation about the x-axis corresponding to configuration y (0°) has been carried out and it is observed that the main attractive part of the energy comes through dispersion term. Further, the observed in-plane interactions are more pronounced than the stacking interactions. 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°) as shown in Fig. 5. The total interaction energy is nearly constant in the range of -4 ± 4 Å, without any significant change in the energy and, hence is capable of retaining the molecular order up to 30 Å.

Terminal interactions: To investigate terminal interactions, the interacting molecule has been shifted along the x-axis by 22 Å with respect to fixed one. It has been observed that the terminal interactions are much weaker than the stacking or in-plane interactions (after due consideration of short contacts). The variation of interaction energy components with respect to rotation about x-axis corresponding to configuration y (0°) is shown in Fig. 6. It is clear that rotations about the x-axis show absolutely no preferences for angle, *i.e.*, the molecules are free to rotate about their long molecular axis. However, for rotations about y-axis, it has been observed that there is slight preference for the molecular axis being on the same line.

Correlation of results with nematic character: The most prominent energy minima of the above mentioned interactions are further refined and the values thus obtained are listed in Table-1 with all contributing terms to enable comparison. The results indicate that due to the planarity of the molecule, the refinement corresponding to stacking energy is maximum and the ultimate magnitude of stacking energy is much larger than in-plane and terminal interaction energies.

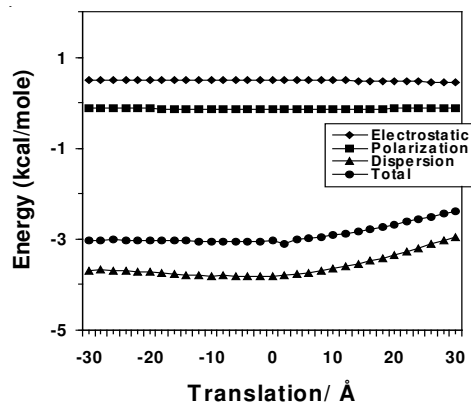


Fig. 5. Variation of in-plane interaction energy components with respect to translation along x-axis corresponding to configuration y (0°)

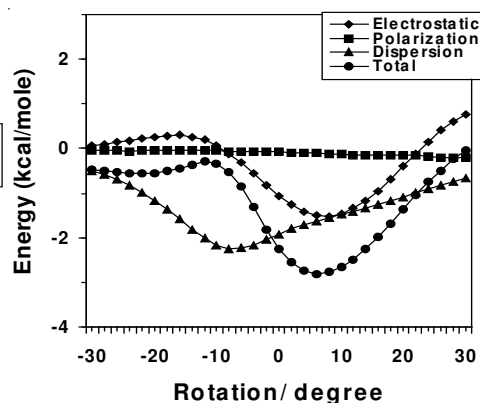


Fig. 6. Variation of terminal interaction energy components with respect to rotation about x-axis corresponding to configuration y (0°)

TABLE-1
MINIMUM ENERGY OBTAINED AFTER REFINEMENT DURING STACKING,
IN-PLANE AND TERMINAL INTERACTIONS BETWEEN A MOLECULAR
PAIR OF 7OBAC. ENERGY IS EXPRESSED IN kcal/mol

Energy terms	Staking energy	In-plane energy	Terminal energy
U_{QO}	-0.216	0.145	-0.845
U_{QMI}	0.031	0.207	-0.018
U_{MIMI}	-0.006	0.149	-0.636
U_{el}	-0.192	0.502	-1.500
U_{pol}	-0.451	-0.144	-0.096
U_{disp}	-8.497	-3.825	-1.620
U_{rep}	3.106	0.409	0.413
U_{total}	-6.035	-3.058	-2.803

U_{QO} : Monopole-monopole; U_{QMI} : monopole-dipole; U_{MIMI} : dipole-dipole; U_{el} : electrostatic; U_{pol} : polarization; U_{disp} : dispersion; U_{rep} : repulsion and U_{total} : total.

The interaction energy calculation may be reasonably correlated with the nematic behaviour of the system. When solid crystals of 7OBAC are heated, thermal vibrations disturb the molecular order of the strongly packed 7OBAC 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 favour with the nematic character of the system. At a very high temperature, the breaking of the dispersion force occurs and all possible stacking geometries (even perpendicular stacking) become equally probable, which ultimately causes the system to pass an isotropic melt.

Conclusion

The present computations are helpful in analyzing the nematogenic behaviour of 7OBAC at molecular level. Further, the possibility also exists of extending this simple model by building in realistic features such as molecular flexibility, complicated anisotropy and electrostatic forces because it is well known that the prime requirement for the formation of a thermotropic liquid crystal is anisotropy in the molecular interaction.

ACKNOWLEDGEMENTS

The financial support rendered by the DST, CSIR, UGC, New Delhi and DAE-BRNS, Mumbai are gratefully acknowledged.

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(Received: 23 December 2009;

Accepted: 3 April 2010)

AJC-8614