

Ordering of fluoro-smectogen in a dielectric medium— a computational approach

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Abstract

A computational analysis of ordering in fluoro-smectogen, 4-propoxyloxyphenyl 4-(4-trifluoromethylbenzoyloxy) benzoate (FLUORO), has been carried out with respect to translatory and orientational motions. The complete neglect differential overlap (CNDO/2) method has been employed to compute the net atomic charge and atomic dipole moment at each atomic centre. The modified Rayleigh–Schrödinger perturbation theory with the multi-centered-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 interaction energy values obtained through these computations were used to calculate the probability of each configuration in a dielectric medium (i.e., non-interacting and non-mesogenic solvent, benzene) at room temperature (300 K), transition temperature (488 K) and above transition temperature (550 K). The flexibility of various configurations has been studied in terms of the variation of probability due to small departures from the most probable configuration. An attempt has been made to develop a new and interesting model of smectogen in a dielectric medium. The present investigation provides theoretical support to the experimental observations.

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1. Introduction

Liquid crystals are an interesting field of soft-condensed matter physics. The progress of research in this material is so rapid due to the great variety of phenomena exhibited by liquid crystals and partly because of enormous commercial interest and importance of liquid crystal displays [1]. In recent years, the focus has been laid on the investigation of new liquid crystal materials with differing molecular chemistry in order to study their viability in technological applications [2–4]. The proper understanding of liquid crystalline behaviour requires an adequate theoretical background as a precursor to application of new developments and to accounting for abnormal properties in the materials [5]. 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 positional and orientational order of the mesomorphic compounds, as well as the type of kinetics of physical and physicochemical processes taking place in these substances [6].

The role of intermolecular forces in mesomorphic behaviour has attracted the attention of several workers [6–9] based on the Rayleigh–Schrödinger perturbation theory. These studies were aimed at establishing the anisotropic nature of the pair-potential, and subsequently finding out the minimum energy configuration of a pair of liquid crystalline molecules. One of the limitations of the work was that the relative preference of different configurations was estimated on the basis of interaction energy. These values, however, do not reflect the actual relative preference. Since mesogenic properties are related to molecular aggregation in specific manner, probability calculation based on interaction energy results will provide valuable information in this respect.

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It is therefore necessary to compute the interaction energy for various configurations by changing the relative positions and orientations of the interacting molecules at different modes of interactions. With the values so obtained and by employing a suitable statistical method, one can determine the relative probability of occurrence of each configuration. Through these computations one is able to obtain information of the dimer complex, the relative freedom of a molecule in terms of variations in inclination, separation or sliding of one molecule over the other, etc.

In the present article, we report the characteristic features of fluoro-smectogen in terms of their energy and configurational probabilities between a molecular pair of 4-propoxyloxyphenyl 4-(4-trifluoromethylbenzoyloxy) benzoate (FLUORO) molecules in a dielectric medium (i.e., the non-interacting and non-mesogenic solvent benzene, the average dielectric constant of which has been taken to be 2.25 for the entire temperature range) at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance 30 Å has been used 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. An examination of thermodynamic data for the compound under study indicates that FLUORO has a smectic-A to isotropic transition temperature at 488 K.

2. The basic formalism and computational technique

The molecular geometry of FLUORO has been constructed on the basis of the published crystallographic data with the standard values of bond lengths and bond angles. Depending on the property interest, a number of following different methodologies have been employed in this work.

2.1. Evaluation of charge and atomic dipole distribution

The simplified formula for interaction energy calculations requires the evaluation of atomic charges and dipole moment components at each atomic centre through an all valence electron method. In the present computation, the complete neglect differential overlap (CNDO/2) method [10] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule. A revised version of the QCPE No. 142 of program, which is an extension of the original program QCPE No. 141 for the third-row elements of the periodic table, has been used. The program language is FORTRAN IV.

2.2. Computation of interaction energy at various configurations

A detailed computational scheme based on a simplified formula provided by Claverie [11] for the evaluation of the interaction energy between a molecular pair has been 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 Fundamental Research, Bombay, India, by Govil and associates has been used for this purpose with further modification. According to the second-order perturbation theory, as modified for intermediate-range interactions [11], the total pair interaction energy of molecules (U_{pair}) is represented as sum of various 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. The electrostatic term can be 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 only up to the dipole–dipole term gives a satisfactory result [12]. The computation of electrostatic term has, therefore, been restricted only up to the dipole–dipole energy term.

In the present computation, the dispersion and short-range repulsion terms are considered together, because several semiempirical approach, viz. the Lennard–Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky [13] introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskaya [14] for hydrocarbon molecules and several other molecules and finally gave the expression:

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

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

where $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$; $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$, where R_{λ}^w and R_{ν}^w are the van der Waals radii of atom λ and ν , respectively. The parameters A , B and γ do not depend on the atomic species. But $R_{\lambda\nu}^0$ and the factor $K_{\lambda} K_{\nu}$ allows the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [15].

2.3. Computation of configurational probabilities

The total interaction energy values obtained through these computations were used as input to calculate the probability of occurrence of a particular configuration i using the Maxwell-Boltzmann formula [16] in order to obtain a better

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