Nematic Behaviour of a Compound EBBA – A Compuational Analysis

Durga Prasad Ojha and V. G. K. M. Pisipati

Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar-522 510, A. P., India

Reprint requests to Dr. D. P. O.; E-mail: durga_ojha@hotmail.com

Z. Naturforsch. **57 a,** 977–981 (2002); received September 11, 2002

A computational analysis has been carried out to determine the configurational preferences of a pair of *p*-ethoxybenzylidine-*p*-*n*-butylaniline (**EBBA**) molecules with respect to translatory and orientational motions. The **CNDO/2** method has been employed to evaluate the net atomic charge and atomic dipole components at each atomic centre of the molecule. The configurational energy has been computed using the Rayleigh-Schrödinger perturbation method. The interaction energies obtained through these computations were used to calculate the probability of each configuration at 300 K. The energy of a molecular pair during stacking, in-plane, and terminal interaction has been calculated. The results are discussed in the light of other experimental and theoretical results.

Key words: EBBA, CNDO/2 Method; Quantum Chemistry; Computer Simulation.

1. Introduction

The widespread use of liquid crystals has attracted the attention of theoretical workers [1 - 4]. The phase transitions of these crystals are primarily governed by the intermolecular interactions between the sides, planes and ends of the molecules [5]. There have been many attempts to measure the long-range orientational order of liquid crystals and to explain it [6]. Anisotropy in the molecular interactions is required for the formation of thermotropic liquid crystals [7]. Calculations of the intermolecular interactions of mesogenic compounds, based on the Rayleigh-Schrödinger perturbation theory, have been reported by several workers [8 - 10]. These studies were aimed at explaining the aligned structure or at best, correlating the minimum energy with the observed crystal structure. It is therefore still important to investigate the relative freedom of the molecules to depart from the minimum energy configuration in terms of a) variation in orientation, and b) translation along the long molecular axis.

In the present communication an attempt is made to find the characteristic features of liquid crystallinity in terms of the energy and configurational probabilities of a molecular pair of **EBBA** molecules at a distance of 10 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 and to keep the molecule within the short and medium range interactions.

EBBA is a typical nematic having sometimes staggered but always approximately parallel molecules. The aliphatic and aromatic carbons show typical tetrahedral and trigonal angles. The angle between the two-phenyl rings is 57.6 ° [11].

2. Simplified Formula and Computational Details

In order to find the interaction energy between two molecules, it is necessary to compute atomic net charges and dipole moments through an all valence electron method. In the present computation, the **CNDO/2** method [12] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule. The calculations have been carried out in two stages:

2.1. Computation of Interaction Energy at Various Configurations

A simplified formula for the evaluation of the interaction energy of a molecular pair has been used to calculate the energy for fixed configurations. According to the second order perturbation theory as modified

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for intermediate range interactions [13], the total pair interaction energy of molecules U_{pair} is represented by

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

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

The electrostatic erergy is expressed as

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

where U_{QQ}, U_{QMI} and U_{MIMI} are the monopole-monopole, monopole-dipole and dipole-dipole terms, respectively. The inclusion of higher order multipoles does not affect significantly the electrostatic interaction energy, and the calculation upto dipole-dipole term only gives satisfactory results [14].

In the present computation the dispersion and short-range repulsion terms are considered together because several semiemperical approaches, viz. the Lennard-Jones or Buckingham type approach, actually proceed in this way. Kitaigorodskii introduced a Buckingham formula whose parameters were later modified by Kitaigorodskii and Mirskay for hydrocarbon molecules, and several other molecules and finally gave the expression

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

with

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

where $Z = R_{\lambda\nu}/R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^w_{\lambda})(2R^w_{\nu})]^{1/2}$. Where R^w_{λ} and R^w_{ν} 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 $R^0_{\lambda\nu}$ and the factor $K_{\lambda}\mathrm{K}_{\nu}$ allow the energy minimum to differ according to the atomic species involved. The necessary formulae may be found in [15].

An orthogonal coordinate system facilitates the calculation. For the origin an atom close to the centre of mass of the molecule has been chosen. The *X*-axis of a bond lies parallel to the long molecular axis, while the *Y*-axis lies in the plane of the molecule and the *Z*-axis perpendicular to it.

2.2. Computation of Configurational Probabilities

The total interaction energies obtained through these computations were used as input to calculate the intrinsic probability of each configuration by means of the Maxwell-Boltzmann formula [16]

$$P_i = \frac{\exp(-\beta\varepsilon_i)}{\sum_i \exp(-\beta\varepsilon_i)}, \; \beta = \frac{1}{kT},$$

where P_i is the probability of the occurrence of a particular configuration and ε_i is the energy of the configuration i relative to the minimum energy configuration.

Table 1. Total energy[a], binding energy[b], total dipole moment and its components of the **EBBA** molecule. Total energy = –182.09 atomic units, Binding energy = –21.11 atomic unit, Total dipole moment = 2.91 Debyes.

Components	μ_X	μ_Y	μ_Z
Densities^{+}	0.21	0.44	–0.06
sp*	–1.15	2.27	0.56
pd**	0.00	0.00	0.00

[a] The total energy corresponds to the sum of the atomic and electronic energies of all constituents of the molecule in equilibrium geometry. [b] The binding energy of a molecule is the difference between the energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms. [+] Contribution to dipole moment components due to electron densities. sp*-hybridization moment; pd**-hybridization moment. [++] Sum of electron density and hybridisation contribution to the dipole moment component.

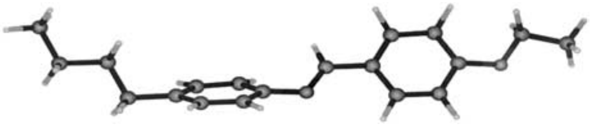

Fig. 1. Molecular geometry of *p*-ethoxynenzylidene-*p*-*n*-butylaniline (EBBA).

3. Results and Discussion

The molecular geometry of **EBBA** is shown in Figure 1. The total energy, binding energy and total dipole moments along with its components are listed in Table 1.

3.1. Stacking Interactions

One of the interacting molecules is fixed in the X-Y plane, while the second molecule is kept at separation of 10 Å along the Z-axis with respect to the fixed one. The selection of intermolecular separation

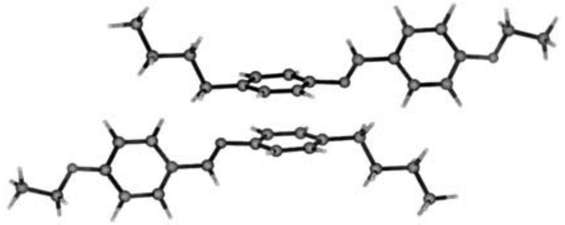

Fig. 2. The lowest stacking energy configuration obtained with energy –8.17 kcal/mole at intermolecular separation of 3.45 Å.

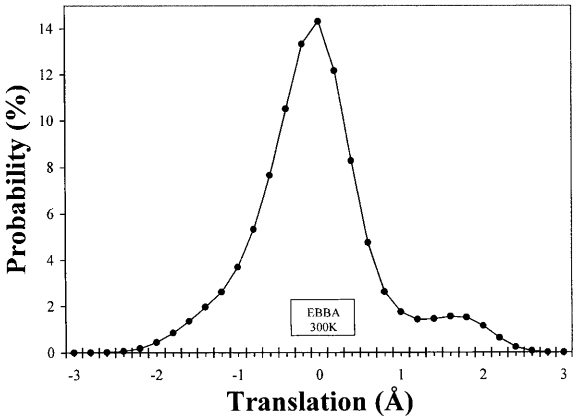

Fig. 3. Variation of the probability on translation along the *X*-axis during stacking interactions at room temperature.

has been made to allow the molecule to have full freedom corresponding to rotation and translation relative to each other.

The angular dependence of stacking interaction energy with respect to rotation about Z-axis corresponding to configuration $X(0°)Y(0°)$ has been carried out at an interval of 10 ° and the interaction energy at each point has calculated. The minimum energy so obtained is then taken as starting point and the entire process is repeated at smaller intervals. The minimum energy has been minimized with respect to translation and rotation about the X, Y and Z-axis. An accuracy of 0.1 Å in translation and 1 ° in rotation of one molecule with respect to the other has been achieved. The final lowest stacked geometry was obtained at an interplanar separation of 3.45 Å with energy –8.17 kcal/mole (Fig. 2). This configuration agrees with those obtained from crystallographic studies [11].

Variation of the stacking interaction energy components with respect to rotation about the X-axis corresponding to configuration $Y(0°)Z(0°)$ has been carried out, and it has been observed that the dominant component of the total energy is the dispersion energy. The contribution of the polarization energy is almost constant throughout the entire range. The electrostatic energy term is much smaller that the dispersion term.

The nematic character of a liquid crystal is generally manifested by its translational freedom along the X-axis. Therefore, the translational freedom along the X-axis has been allowed at interval of 0.2 Å. The corresponding change of the probability is shown in Figure 3. It is evident from the figure that a stacked pair of **EBBA** molecules with the configuration $Y(0°)Z(0°)$ can slide one above the another in the range of (1.6±0.4) Å without any significant change in the energy / configurational probability, and hence conforming the nematic character.

3.2. In-plane Interactions

The interacting molecule has been kept at separation of 8 Å along Y-axis with respect to fixed one to avoid the possibility of van der Waals contacts. Similar calculations have been performed for in-plane interactions. Again, the energy on rotation about the Y- and X- axis has been calculated. This energy has been minimized with respect to translation and rotation about the X, Y, and Z-axis. The lowest in-plane geometry, obtained at separation of 3.5 Å with an energy of –6.21 kcal/mole is shown in Figure 4.

The variation of the in-plane interaction energy on rotation about the X-axis corresponding to configuration $Y(0°)$ has been calculated. The main attractive part of the energy was formed to come through the dispersion term. The electrostatic energy term is much smaller than the dispersion term, but its symmetric fluctuation is reflected in the variation of the total energy.

Fig. 4. The lowest in-plane energy configuration obtained with an energy of –6.21 kcal/mole at intermolecular separation of 3.50 Å.

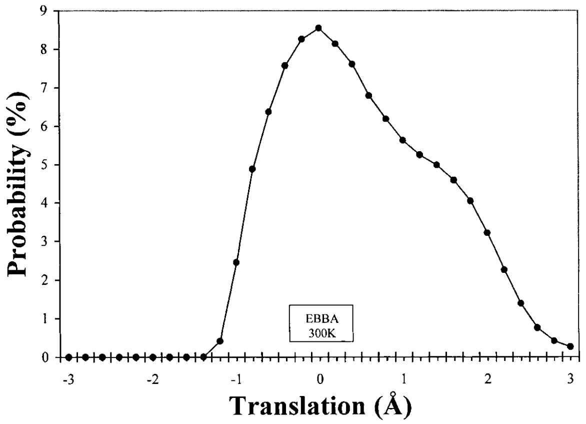

Fig. 5. Variation of probability on translation along *X*-axis during in-plane interactions at room temperature.

The effect of translation along X-axis corresponding to the configuration $Y(0°)$ is shown in Figure 5. Since, the in-plane interactions are weaker than the stacking interactions, a greater freedom for translation is observed. The maximum probability occurs at an equilibrium position. The variation of the probability is almost constant at zero to 2.8 Å ± 0.2 Å, which may be correlated with the fluidity of the compound maintaining its alignment in the mesophase.

3.3. Terminal Interactions

To investigate the terminal interactions away from van der Waals contacts, the interacting molecule was shifted along X-axis by 22 Å with respect to the fixed one and was allowed to rotate about the X-axis. The terminal interactions are much weaker than the stacking or in-plane interactions. A graphical representation of the probability distribution with respect to rotation about the X-axis (Fig. 6) shows no preference for any angle, i. e. the molecules are completely free to rotate about their long molecular axis. Although, a minimum energy configuration has been marked in this case too, it has not been included in the results. However, a salient feature has been reported in Table 2: Evidently, the largest attractive contribution in stabilizing the stacked, in-plane and terminal interacting pair of **EBBA** molecules comes from dispersion forces. This supports the earlier observations [7 - 9] and also the basic assumption of the molecular field theory [17 - 19].

Table 2. Minimum energy values obtained between a pair of **EBBA** molecules during stacking, in-plane and terminal interactions after refinement. Energy is expressed in kcal/mole.

Energy terms	Stacking energy	In-plane energy	Terminal energy
U_{QQ}	0.006	–0.053	–0.004
U_{QMI}	–0.001	–0.258	–0.004
U_{MIMI}	0.006	–0.186	–0.004
U_{el}	0.011	–0.497	–0.011
U_{pol}	–0.167	–0.267	–0.008
U_{disp}	–12.851	–7.145	–1.199
U_{rep}	4.838	1.694	0.429
U_{total}	–8.169	–6.215	–0.789

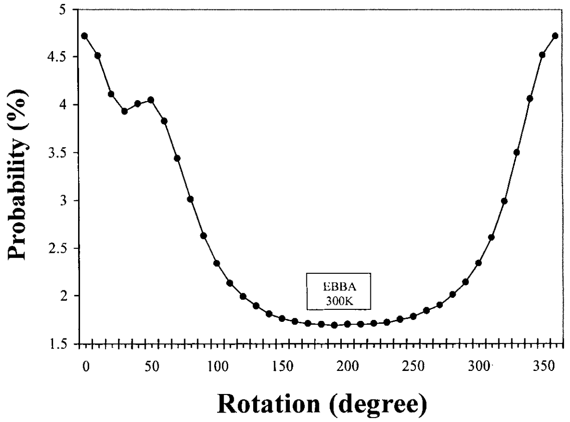

Fig. 6. Variation of probability on rotation about *X*-axis during terminal interactions at room temperature.

4. Conclusion

Various possible geometrical arrangements of a molecular pair during the different modes of interactions (i. e. stacking, in-plane and terminal interactions) have been considered and provide an insight in the molecular arrangements in the bulk material. It may be concluded from the above discussion that in a molecular assembly a number of local minimum energy configurations exist, all of which having their own importance i. e. in the case of close molecular packings one may be forced to assume local minimum energy configurations. The global minimum is, however, of paramount importance because, when coming from a very high temperature where the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy and the others have a preference depending on their individual relative probabilities.

Acknowledgements

The financial support rendered by the Department of Science & Technology (Grant No. SP/S2/M-34/ 2000) and the Council of Scientific & Industrial Research (Grant No. 03 (0932)/ 01/ EMR-II), New Delhi, India is gratefully acknowledged.

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