

Molecular Ordering in Liquid Crystalline EMBAC. A Quantum Mechanical Study

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Z. Naturforsch. **55a**, 923–928 (2000); received September 28, 2000

Molecular ordering in a liquid crystal, ethyl 4-(4'-methoxybenzylidene amino) cinnamate (EMBAC) has been studied by intermolecular interaction energy calculations. The CNDO/2 method has been employed to compute the atomic charge and atomic dipole at each atomic centre. The modified Rayleigh-Schrödinger perturbation theory along with the multicentered-multipole expansion method have been employed to evaluate the long-range intermolecular interactions, while a '6-exp' potential function has been assumed for the short-range interactions. On the basis of stacking, in-plane, and terminal interaction energy calculations all possible geometrical arrangements of a molecular pair have been considered, and the most favourable configuration of the pair has been obtained. Molecular parameters like total energy, binding energy and total dipole moment have been given. Results are discussed in the light of those obtained for the nematogens 4-(4'-ethoxyphenylazo) phenyl valerate (EPPV) and 4,4'-di-*n*-propoxy-azoxybenzene (DPAB). An attempt is made to explain the liquid crystalline behavior of these liquid crystals and thereby develop a molecular model for liquid crystallinity.

Key words: Liquid Crystal; Multicentered-multipole; CNDO/2 Method; Intermolecular Interactions; EMBAC.

Introduction

The science of liquid crystals has considerable interest because of the numerous applications of this material [1, 2]. The peculiar changes occurring at phase transitions are primarily governed by the interactions occurring between the sides, planes, and ends of a pair of molecules [3]. The role of the interaction energy between a molecular pair of mesogenic compounds has been studied by Sanyal and coworker for a number of systems [4–6] using quantum mechanical methods such as CNDO (Complete Neglect of Differential Overlap) and perturbation techniques. It has been observed that the stability of molecular packing stems solely from the dispersion forces. In these calculations the energy was optimized for various possible configurations and ultimately a stable molecular packing geometry was obtained.

Recently computer simulations of liquid crystals have become a tool for understanding liquid crystal phases [7–10]. It is essential to study simple models in some depth in order to understand the forces responsible for mesophase formation. The possibility also exists of extending these simple models by building in realistic features such as molecular flexibility, complicated structural anisotropy and electrostatic forces. It is generally agreed that the prime requirement for the formation of

thermotropic liquid crystals is an anisotropy in the molecular interactions [11]. In the present paper, an attempt has been made to interpret the results of interaction energy calculations for molecules at an intermediate distance of 6 Å for stacking, 10 Å for in-plane interactions and 25 Å for terminal interactions.

The computations have been carried out on ethyl-4-(4'-methoxybenzylideneamino) cinnamate (EMBAC). A possible explanation of its liquid crystallinity is furnished. The results are discussed in the light of those obtained for the nematogens EPPV [12] and DPAB [13]. The thermodynamic parameters reveal that EMBAC shows a nematic mesophase at 118 °C and exhibits an isotropic melt at 140 °C [14].

Computational Details

Crystallographic data from literature [14] have been used to construct the molecular geometry of EMBAC. The crystal packing makes the two phenyl rings nearly coplanar and the central C–CH=N–C group non-planar. The molecules are oriented approximately along a unique direction [14].

In the second order perturbation theory, as modified for intermediate range interactions [15], the total inter-

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action energy (E_{total}) between a pair of molecules is given by

$$E_{\text{total}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}},$$

where E_{el} , E_{pol} , E_{disp} , E_{rep} represent electrostatic, polarization, dispersion and repulsion component, respectively. According to the multicentered-multipole expansion method [16], the electrostatic energy may be expressed as the sum of interaction terms between atomic multipoles of successively higher order:

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

where E_{QQ} , E_{QMI} , E_{MIMI} etc. are the monopole-monopole, monopole-dipole, dipole-dipole and other interaction terms caused by higher multipoles. In general, for most of the molecular systems the evaluation of the electrostatic energy up to the dipole-dipole term has been found to be adequate [16]. Therefore, the computation was performed up to the dipole-dipole term. Dispersion and short-range repulsion energy terms are considered together because several semiempirical expressions, viz. the Lennard-Jones or Buckingham type approach, actually proceed in this way. Kitaigorskii [17] introduced a Buckingham formula whose parameters were later modified by Kitaigorskii and Mirskay for hydrocarbon molecules and several other molecules [17]. The CNDO/2 method [18] has been used to compute the net atomic charge and dipole moment components at each atomic centre of the molecule.

Energy Minimization

In the present work, computations have been carried out for a pair of EMBAC molecules. One of these molecules has been treated as fixed while the distance of the other has been varied with respect to the fixed molecule, and the minimum energy point has been obtained. The molecule is then rotated about the axis perpendicular to the long molecular axis in an interval of 10° , and the corresponding energies are calculated. The minimum energy so obtained is taken as starting point and the entire process is repeated for smaller intervals. The final configuration is refined through very small variations in distance and angle. The whole process of optimization is carried out with computer programs run on a CDC 'Cyber-170' computer.

The X -axis has been chosen along the long molecular axis, while the Y -axis lies in the plane of the molecule and Z -axis perpendicular to the molecular plane. The origin has been chosen at almost the mid point of the mole-

cule. As mentioned earlier, the aim of the investigation is to calculate the intermolecular interaction energy of different configuration allowing free rotation and translation of one molecule in the presence of another molecule at a fixed position. Terms like stacking, in-plane or terminal interactions will be used to maintain continuity with my previous work [12, 13, 19–21].

Results and Discussion

The molecular geometry of EMBAC is shown in Figure 1. Table 1 presents a comparative picture of the total energy, binding energy and dipole moments of EMBAC with the similar systems EPPV and DPAB. As evident from Table 1, the total energy and binding energy of these nematogens exhibit the order

$$\text{EMBAC} > \text{EPPV} > \text{DPAB}$$

while the dipole moments exhibit the order

$$\text{EMBAC} > \text{DPAB} > \text{EPPV}.$$

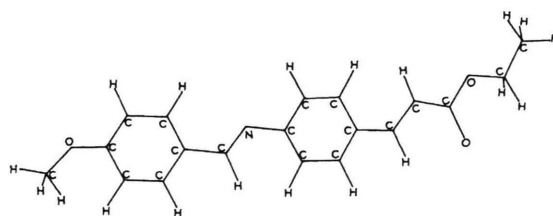


Fig. 1. Molecular geometry of EMBAC molecule.

Table 1. Total energy*, binding energy** and total dipole moment of EMBAC, EPPV, and DPAB molecules.

Molecule	Total energy (A.U.)	Binding energy (A.U.)	Total dipole moment (Debyes)
4-(4'-methoxybenzylidene amino) cinnamate (EMBAC)	-232.62	-23.93	2.26
4-(4'-ethoxyphenylazo) phenyl valerate (EPPV)	-230.55	-22.96	0.68
4,4'-di- <i>n</i> -propoxy-azoxybenzene (DPAB)	-223.57	-22.15	1.46

* Total energy corresponds to the sum of atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

** Binding energy of a molecule is the difference between the total energy of the equilibrium molecular geometry and the sum of atomic energies of the constituent atoms.

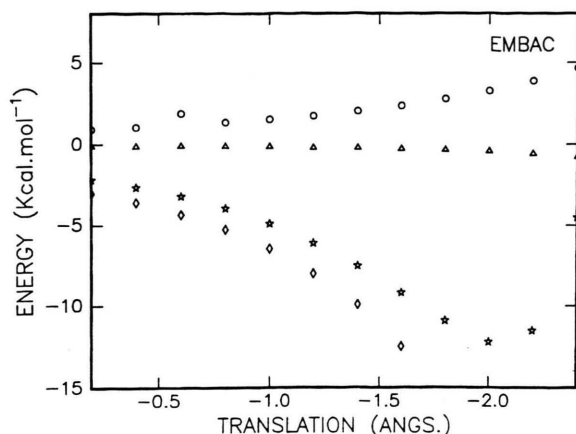


Fig. 2. Variation of various interaction energy components with respect to translation along the Z-axis during stacking interactions. (○ – electrostatic, △ – polarization, ◇ – dispersion, ☆ – total)

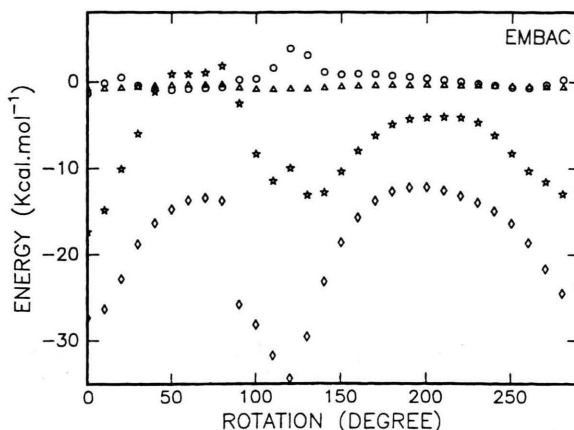


Fig. 3. Variation of the stacking interaction energy components with respect to rotation about the Z-axis corresponding to the configuration X(0°) Y(0°). Notations are the same as in Figure 2.

Stacking Interactions

The interacting molecule has been placed at a separation of 6 Å along the Z-axis with respect to the fixed one. This distance has been chosen to eliminate the possibility of van der Waals contacts and to keep the molecule within the range, of short and medium range interactions. The variation of various energy components with respect to translations along Z-axis is shown in Fig. 2, corresponding to the configuration X(0°) Y(0°). The figure reveals that the dominant component of the total energy is dispersion energy. The contribution of polarization energy is negligible and is almost constant throughout the entire range, while the dispersion energy is mainly dependent on the extent of overlap during stacking. The electrostatic energy, on the other hand, is mainly responsible for the selection of the minimum energy configuration for the molecular pair. The variation of the interaction energy components on rotation about the Z-axis is shown in Fig. 3, corresponding to the configuration X(0°) Y(0°). It is clear from this figure that the electrostatic energy term is smaller than the dispersion term, but the symmetric fluctuation in the electrostatic term is reflected in the nature of the variation in the total energy. Thus, minima of the total energy are observed at 130° and 280°. The total energy curve exhibits a gross similarity with the Kitaigordskii curve, i.e. the curve shows the sum of dispersion and repulsion energies. This indicates that only short-range forces such as dispersion and repulsion bring about the stability of the interactions in

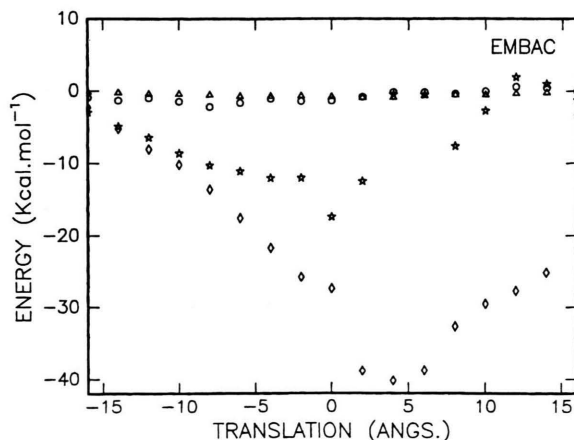


Fig. 4. Variation of the stacking interaction energy components with respect to translation along the X-axis. Notations are same as in Figure 2.

a pair of EMBAC molecules. Further, it is obvious that dispersion forces are the only major attraction acting between the planes of EMBAC molecules and accounting for the specific stacked geometry. The repulsion component has not been plotted explicitly as it can easily be obtained with the help of the Kitaigordskii curves. Having refined the equilibrium configuration with respect to translation along and rotation about the Z-axis, the energy is calculated and the probability is further investigated with respect to translation along the X-axis. Figure 4 shows the variation of the energy components for trans-

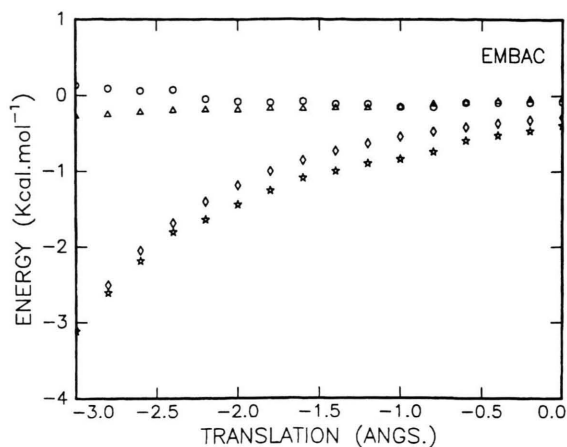


Fig. 5. Variation of the in-plane interaction energy components with respect to translation along the Y -axis corresponding to the configuration $X(0^\circ)$. Notations are the same as in Figure 2.

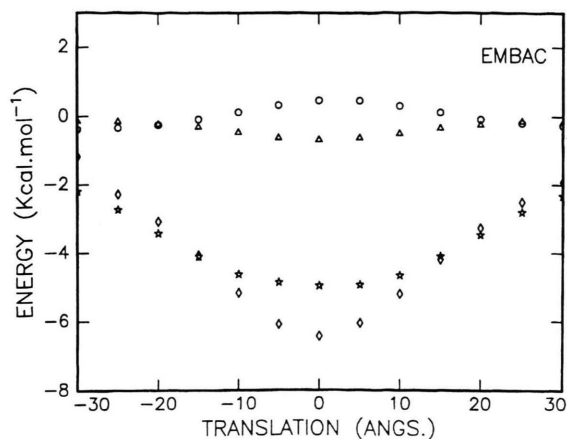


Fig. 6. Variation of the in-plane interaction energy components with respect to translation along the X -axis. Notations are the same as in Figure 2.

lations of $\pm 16 \text{ \AA}$. It may be observed that all the components increase with increasing overlapping, and that the increase is smaller for the electrostatic and polarization terms. The variation of energy almost vanishes for a region $-4 \text{ \AA} \pm 2 \text{ \AA}$, which shows that a sliding of one molecule over the other is energetically allowed for a small range which may be correlated with the fluidity of the compound maintaining its alignment in the mesophase.

In-plane Interactions

The interacting molecule has been kept at separation of 10 \AA along the Y -axis with respect to the fixed one. The distance chosen for these calculations is such that van der Waals contact is avoided. Figure 5 shows the variation of the energy components on translation along the Y -axis corresponding to the configuration $X(0^\circ)$, which indicates clearly that a minor translation along the Y -axis does not alter the total energy drastically. It may be seen from the total energy curve that an energy barrier of approximately 2.28 kcal/mole exists for translations within the range of 1 \AA to 3 \AA . This implies that the sliding of the molecular pair along the Y -axis is very restricted. Since, the in-plane interactions are much weaker than the stacking interactions, relatively greater freedom of translation is observed. The effect of translation along the X -axis is shown in Fig. 6, where it may be observed that translational freedom is much more pronounced than freedom of stacking.

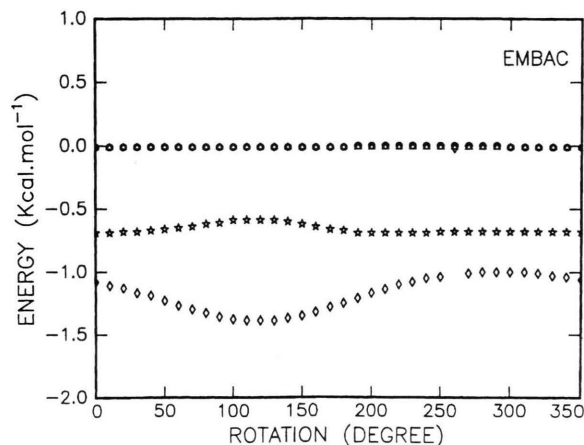


Fig. 7. Variation of the terminal interaction energy components with respect to rotation about the X -axis. Notations are the same as in Figure 2.

Terminal Interactions

To investigate the terminal interactions far from van der Waals contacts, the interacting molecule has been shifted along the X -axis by 25 \AA with respect to the fixed one. The terminal interactions are much weaker than the stacking or in-plane interactions. A plot representing the angular dependence of various interaction energy components with respect to rotation about the X -axis is shown in Figure 7. It is obvious from the figure that the electrostatic and polarization energies

Table 2. Minimum energy values obtained after refinement during stacking, in-plane and terminal interactions. The energy is expressed in kcal/mole.

Energy terms	Stacking energy	In-plane energy	Terminal energy
E_{QQ}	0.19	0.01	0.01
E_{QMI}	-0.03	0.41	-0.06
E_{MIMI}	-1.22	0.05	0.05
E_{el}	-1.06	0.47	-0.00
E_{pol}	-0.69	-0.73	-0.01
E_{disp}	-23.90	-8.73	-0.99
E_{rep}	-8.39	3.15	0.25
E_{total}	-17.26	-5.84	-0.74

are independent of rotations. The dispersion energy curve contributes more to the total energy curve. In this case, the energy is almost constant for a region of $300^\circ \pm 50^\circ$, which shows that sliding of one molecule over the other is energetically allowed to a large extent, which may be correlated with the fluidity of compounds maintaining their alignment in the meso-phase.

These results support the nematogenic behaviour of the system at higher temperatures because the molecules of EMBAC are capable of sliding along the long molecular axis with constant relative orientation. Similar results have been observed in for the nematogens EPPV [12] and DPAB [13].

The energy corresponding to the optimum angle has been further refined with an accuracy of 1° in rotation and 0.1 \AA in translation. The details of stacking, in-plane and terminal interactions are listed in Table 2. The results indicate that the largest attractive contribution in stabilizing the stacking, in-plane and terminal interacting of a pair of EMBAC molecules comes from the dispersion forces. This supports the earlier observations [4–6, 12, 13, 19–21] and also the basic assumptions of molecular field theory [22–24].

Correlation of the Results

The intermolecular interaction energy calculations may be reasonably correlated with the mesomorphic behaviour of the system. When solid crystals of EMBAC are heated, thermal vibrations disturb the molecular ordering of the strongly packed geometrical arrangement of EMBAC molecules. Consequently, the attraction within a pair of molecules, largely comprising the dispersion forces, tend to get weaker at higher temperatures, and hence the possibility of relative movement within a molecular pair along the long axis is considerably enhanced (Figure 4). As indicated in Fig. 5, the freedom of molecules in a 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 the nematic behaviour of the system at higher temperatures because the molecules of EMBAC are only capable of sliding along the long molecular axis with a simultaneous orientation. Similar results have been obtained for EPPV and DPAB. At very high temperatures, allround breaking of the dispersion forces results and all possible stacking geometries are equally favoured, which ultimately causes the system to pass on to an isotropic melt.

Conclusion

Intermolecular interaction energy calculations are helpful in analysing the liquid crystalline behaviour of EMBAC in terms of molecular forces.

Acknowledgements

The financial support rendered by the Department of Science and Technology, New Delhi, India is gratefully acknowledged. The author is thankful to Dr. V. G. K. M. Pisipati, Director of CLCRE for providing the facilities and helpful discussion.

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