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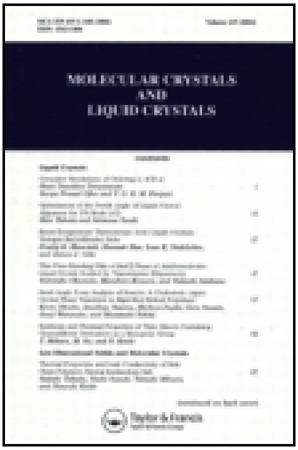

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A Theoretical Study of Molecular Ordering of Some Smectic Liquid Crystals

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A Theoretical Study of Molecular Ordering of Some Smectic Liquid Crystals

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A theoretical investigation of molecular ordering of smectic *C* liquuid crystals $C_8H_{17}O$-C_6H_4-C_6H_4-COO-C_6H_4-OC_8H_{17} {*A*}, $C_9H_{19}O$-C_6H_4-COO- C_6H_4-COO-C_6H_4-NO_2 {***B***} and its binary mixtures {***A+B***} has been carried out by the method based on the Rayleigth-Schrodinger perturbation theory. The mutual arrangement of two molecules corresponding to the minimum of the total interaction energy between them U_{pair} has been established. The curves of the dependence of U_{pair} and its various contributions on displacement of molecules from each other along the molecular long *X*-axis and angle θ between molecules' long axes has been also computed in the minimum point vicinity. The obtained results make it possible to determine the peculiarities of the structural organization of molecules, as well as to construct a model of the structure of *A* and ***B*** compounds in different phases taking into account the most probable packing of molecules.

Keywords: smectic liquid crystals; interaction energy; molecular packing

INTRODUCTION

Molecular interaction plays substantial role in liquid crystal structures' characterization. This interaction determines the physical properties of liquid crystals (LC), as well as the type and kinetics of physical and physicochemical processes taking place in these substances [1-3].

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Therefore, it is quite natural that a lot of attention is paid in the literature to this problem. The potential energy of interaction of two molecules is considered as a prime issue in theoretical investigations on intermolecular interactions. Only in rare cases it is possible to obtain the full intermolecular potential from the experimental data. Therefore, the theoretical approaches applying such kind of approximations and methods, as an atom-atom potentials model [4-7] as well as various models of semi-empirical (*CNDO/2, MINDO/3* etc.) and non-empirical (*ab initio*) quantum mechanical characterizations have been widely applied [8-11].

In this paper a theoretical investigations of molecular ordering of smectic *C* LC

$C_8H_{17}O\text{-}C_6H_4\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}OC_8H_{17}$ (*A*)

$C_9H_{19}O\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}NO_2$ (***B***)

and its binary mixtures {*A*+***B***} has been carried out by the method based on the Rayleight–Schrodinger perturbation theory. The geometric structure of *A* and ***B*** molecules are represented in Figure 1.

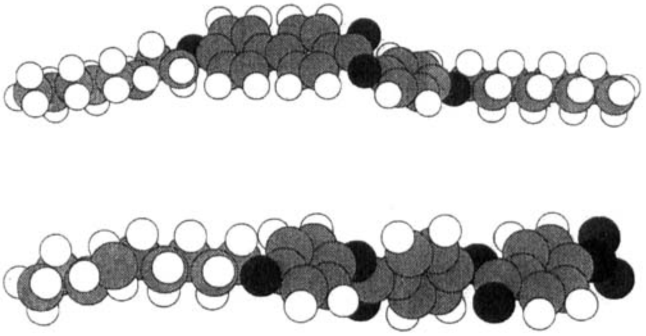

FIGURE 1. Geometrical structures of *A* and ***B*** molecules

CALCULATION TECHNIQUE

The calculations were made in two stages. In the first stage, the data of the conformation of the *A* and ***B*** molecules (see Figure 1), ionization potentials, net atomic charges and the dipole moments at each atomic centre have been computed by molecular orbital method in the **AM1**

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approximation (an improvement of the **MNDO** method). In the second stage, on the basis of the obtained data, the intermolecular interaction has been studied by using perturbation theory with multicentered-multipole expansion method. The total pair interaction energy of molecules, U_{pair}, is represented as a sum of various terms contributing to the total energy:

$$U_{pair} = U_{el} + U_{pol} + U_{disp} + U_{rep}, \qquad (1)$$

where U_{el}, U_{pol}, U_{disp}, U_{rep} are the electrostatic, polarization, dispersion and repulsion energy terms respectively. A Lennard Jones ("6-12") type potential represents Van der Waals interactions ($U^{*}_{pair} = U_{disp} + U_{rep}$) [6,7]. The U_{pol} expression is taken from [12]. The electrostatic term expressed as:

$$U_{el} = U_{qq} + U_{qd} + U_{dd} \qquad (2)$$

where U_{qq}, U_{qd} and U_{dd} are the monopole-monopole, monopole-dipole and dipole-dipole terms respectively.

RESULTS AND DISCUSSION

The mutual arrangement of two molecules corresponding to the minimum of U_{pair} of the interaction between them has been established (see Table and Figure 2).

TABLE Minimum magnitudes of pair interaction energy of molecules, U_{min}, and the distribution of various energy components (in kcal/mole)

Interaction	U_{min}	U_{el}	U_{qq}	U_{qd}	U_{dd}
AA	-25,03	-2,68	0,89	-1,32	-2,25
BB	-22,49	-3,94	-0,52	-1,05	-2,37
AB	-23,51	-2,63	0,74	-1,18	-2,19

The curves of the dependence of U_{pair} on displacement of molecules from each other along the molecular long X-axis (at the different distances R between axes) (Figure 3) and angle θ between molecules' long axes (Figure 4) has been also computed in the minimum point vicinity. Several deep local extrema in the curve of the dependence of U_{pair} on displacement along X-axis were revealed (see Figure 3), this is

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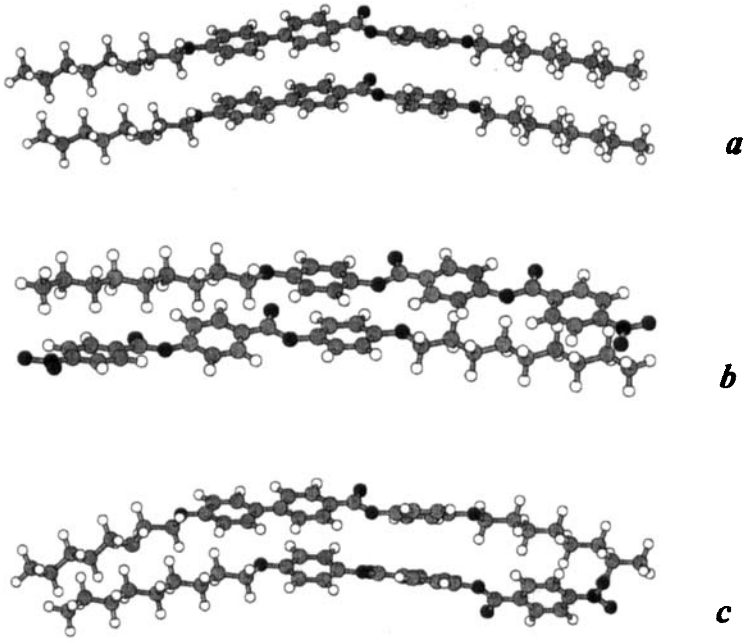

FIGURE 2. Packing of molecules corresponds to a minimum of U_{pair} function: *a* - ***AA***, *b* – ***BB***, *c* – ***AB***.

one of the basic causes of the existence of various types of local ordering in smectic phases. It is shown, in particular, that at the short-range interactions of molecules a slight horizontal displacement of molecules from each other (at the minimum point vicinity) leads to the abrupt decrease in the interaction energy (at $R=3.8Å$ *and* $\Delta X=\pm 1Å$, $\Delta U_{pair} \approx 3 \div 4$ *kcal/mole*). At the large values of R the same qualitative features are observed. The only difference is that at large R the range of the horizontal translation of molecules at the thermal motion is increased (see Figure 3).

The behaviour of the U_{pair} potential function (1) without the allowance for the contribution of U_{el} electrostatic interaction is completely different (Figure 5). Here the energy barriers are essentially different and their variation with the increasing intermolecular distance R proceeds non-uniformly, that leads to essential change of packing of

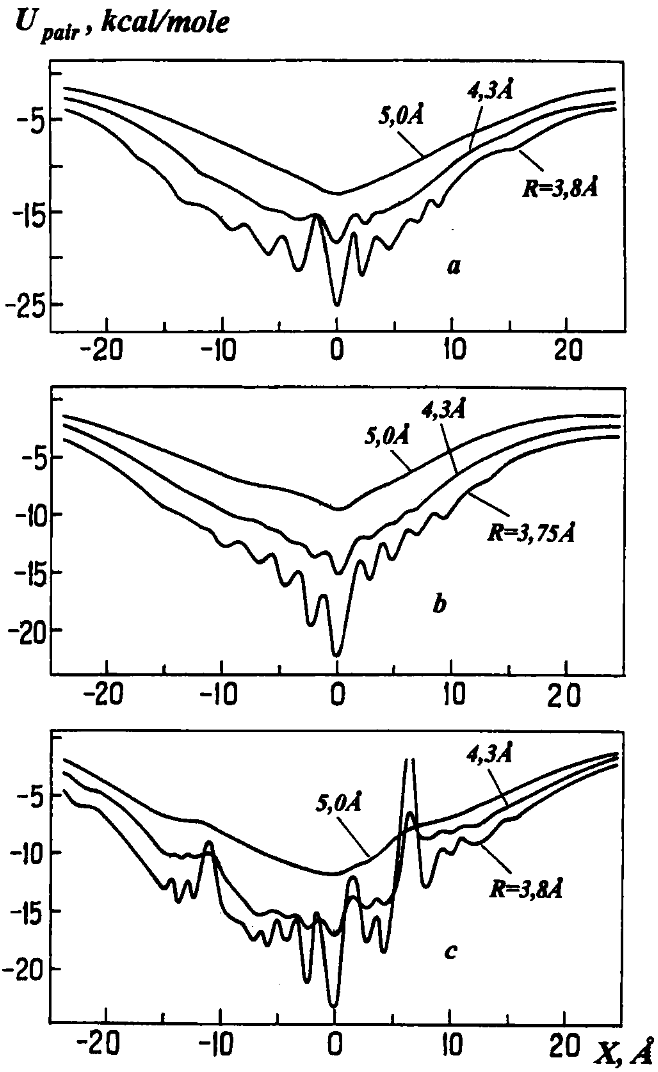

FIGURE 3. Dependence of U_{pair} energy of pair interactions on displacement of molecules from each other along the long X axis: *a* - ***AA***, *b* – ***BB***, *c* – ***AB***.

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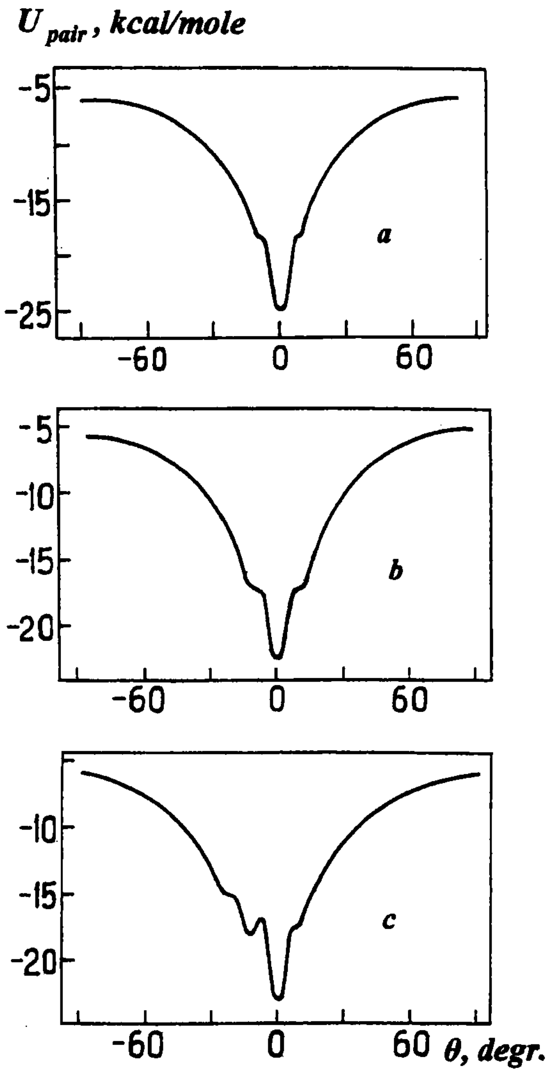

FIGURE 4. Dependence of U_{pair} energy of pair interactions on θ angle between molecules' long axes: *a* - ***AA***, *b* – ***BB***, *c* – ***AB***.

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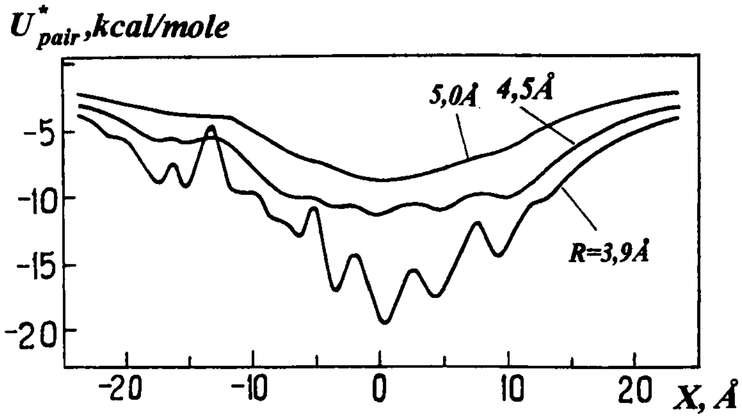

FIGURE 5. Dependence of energy of pair interactions (without the allowance for the contribution of U_{el}), U^*_{pair}, on displacement of molecules from each other along the long X axis. For case of ***AB*** interaction.

molecules. Besides, the displacement of molecules from each other along the long X-axis does not give any notable change in the interaction energy U^*_{pair} (e.g., at R=4,5Å and ΔX=±5Å, $\Delta E \leq 1,0$ *kcal/mole*). Moreover, it should be noted (see Table) that the general (main, essential) contribution into U_{el} is come from U_{dd}. These results enable one to suppose, that the presence of the strongly polar groups -O-, -NOO- and -COO- leads to the essential changes of packing of molecules, although the contribution of U_{dd} dipole-dipole interaction to the U_{pair} total energy is not so large (see Table). Here it should be also noted that -O-, -NOO- and -COO- polar groups contribute mainly to the perpendicular orientational component of polarization ($\mu_{\parallel}$=1,9; $\mu_{\perp}$=3,6 *Debye*,. where μ is the dipole moment of A molecule).

On basis of the results discussed in this paper, it may be reasonably concluded that interaction energy studies based on semi-empirical quantum mechanical calculation methods are helpful for a quantitative evaluation of mutual influence of intermolecular field forces on equilibrium mutual packing of molecules. These calculations provide an insight of the molecular arrangements inside a bulk of materials.

The obtained results make it possible to determine the peculiarities of the structural organization of molecules, as well as to construct a model of the structure of *A* and *B* compounds in different phases taking into account the most probable packing of molecules.

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