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INTERMOLECULAR INTERACTION IN LIQUID CRYSTALS

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The analysis of possible mechanisms for the implementation of orientational ordering in the mesophase of liquid crystals has been carried out. It has been shown that benzene rings in the structure play a major role in the existence of the mesophase. Van-Vlecky paramagnetism, due to ring currents in benzene rings, seems to be one of the reasons for such ordering. Apparently, this explains the high degree of order of liquid crystals when exposed to a magnetic field. In this regard, the intermolecular interaction in the case of π-stacking may have a magnetic component. A type of possible intermolecular interaction potential is proposed when simulating the behavior of an ensemble of liquid crystal molecules. It is shown that the ordering of molecules of liquid crystals is associated with the different nature of intermolecular interactions, but having the same order.

Keywords: liquid crystals, aromatic compounds, the potential of intermolecular interaction, modeling

Introduction

Intermolecular interactions in their energy are noticeably weaker than chemical (from tenths to ten kJ/mol, for chemical bonds, of the order of tens and hundreds kJ / mol). Typical dependence of the interaction energy between particles on the distance *r*, similar to the potential energy curve for diatomic molecules. Some common properties of [1] intermolecular forces acting in different systems are observed:

1. At large distances, these forces are mainly forces of attraction;
2. They decrease faster with distance than Coulomb forces;
3. The repulsive forces are more short-range than the forces of attraction;

The main value, which is trying to calculate theoretically, is the total potential energy of interaction U (g). The exact form of this function determines the success of modeling processes in the molecular system.

Computer simulation using Monte Carlo and molecular dynamics methods is a tool for studying the behavior of systems of condensed matter of varying complexity. The first works on simulating simple atomic liquids were started in 1950. The methods were successfully extended to simulate more complex systems: molecular liquids, polymer and liquid crystal (LC) systems. Computer modeling at the atomistic level is a difficult task, and the size of particles in an ensemble has essentially small values in comparison with other models. As shown in [2], it is reasonable to conduct oscillations of molecular bonds and intramolecular motion at times of 1 fs and 10 fs, respectively; diffusion within the molecular fluid requires simulation of at least 1 ns; growth of orientational order and uniform arrangement of a nematic director for several hundred molecules may require more than 10 ns

The effectiveness of such studies is related to the accuracy of the potential of intermolecular interaction. Understanding the nature of orientational ordering in LCs is a cornerstone in the synthesis of such compounds with desired properties. Therefore, the purpose of this work was to analyze the features of intermolecular interaction in LCs to determine the processes that determine orientational ordering.

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1. Features of liquid crystals

Considering a liquid crystal as a continuous medium, one can investigate many physical phenomena - unusual properties in the flow, response to electric and magnetic fields - in NLCs. The foundations of the continuum theory were laid in the late 20s of the 20th century on the basis of a static theory. The formulation of the general conservation laws and the fundamental equations describing the mechanical behavior of the nematic state belong to Eriksen and Leslie [3-4].

In contrast to a normal liquid, a nematic LC (NLC) consists of rod-like molecules, in which the long axes of neighboring molecules are approximately parallel to each other. A vector n, called a director, is introduced to describe the direction of the preferential orientation of molecules in the vicinity of a point. Its orientation in the medium can vary continuously and systematically from point to point (with the exception of singularities). External forces and fields acting on the liquid crystal, can cause the translational movement of the fluid, as well as the orientational movement of the director.

Studies using continual theory on the basis of the balance equations study the behavior of the director during various effects on NLC. Thus, in [5], when considering the Poiseuil flow, the existence of domain structures parallel to the flow, separated by singular lines, was established. The method of numerical simulation established an increase in time as the fixing on the substrate [6] weakened and the texture twist was due to the presence of sycotactic groups [7] when studying the twist-deformation dynamics induced by an electric field. In [8], it was found that the deformation is accompanied by the rotation of the director around an axis perpendicular to the plane of the layer. In [9], the flexo-optic effect for the case of cholesteric LCs with short pitch of a helix, in [10], the fleco-electric effect in NLCs was considered. In [11] the behavior of NLCs depending on the geometry of the electro-optical cell, in [12] the reorientation dynamics of the director in bipolar NLC droplets, in [13] the planar layer of NLC under the action of electric and magnetic fields, in [14] - elastic deformations in NLC using additive potential, in [15] - the microstructural and macrostructural properties of LC polymers with a strong anisotropy of the elastic coefficients are investigated. In [16], a phenomenological theory for axial and biaxial nematic phases using a two-component tensor of degree of order, in [17] the theory of dielectric permeability of NLC molecules with an arbitrarily directed dipole moment, in [18] is a model for describing a pretransition state in antiferroelectric LCs providing the union of the inner layers of the dipole-dipole interaction was developed. In [19], the phase behavior of achiral banana-shaped molecules and in [20] — the behavior of ferroelectric LCs using a quantum-mechanical potential was investigated.

On the basis of the continuum theory, phase diagrams of LCs are investigated using various types of potentials, which are based on the mean field approximation [2-4]. The development of the theory does not require the specification of the exact form of intermolecular forces [4, 21]. However, initially, Mayer and Zaupe suggested that the cause of the stability of the nematic phase is the dipole-dipole component of the anisotropic dispersion forces. It is believed that the rotational motion of molecules is independent of their translational motion.

When the temperature T is less than the temperature of the nematic – isotropic liquid phase transition (T_{NI} bleaching temperature), there is only one minimum in the free energy dependence on the degree of order s, which corresponds to a stable ordered phase. At $T > T_{NI}$, there are two minima, but the minimum at $s = 0$ is the absolute minimum. At $T = T_{NI}$, two minima are again observed: one at $s = 0$, the other at $s = s_c$, but both states have the same free energy, i.e. at this temperature it has a critical transition without a change in volume, but with a sharp change in the order parameter [3-4, 21]. This is defined if the change in volume объема ΔV is known. However, ΔV is usually so small that s_c is 1-2% different. As a result, the theory predicts a universal value $s = 0.44$ for all nematic substances. Although this value is in satisfactory agreement with the data obtained for a number of compounds, there are statistical deviations. Despite this, theoretical studies are being actively carried out on the properties of the compounds themselves, as well as mixtures based on them.

A prerequisite for substantial progress in the management of the mesogenic properties of such compounds is an understanding of the nature of the intermolecular interaction. Numerous studies [21-23] state the importance of the presence of cyclic groups, the need for the length, and rigidity of the structure of LC molecules. The liquid phase does not allow obtaining exact structures from X-ray diffraction studies [21,23]. The difficulty in understanding the general questions of mesogenicity is associated with the diversity of the studied classes of LC [24]. The same structural transformations lead to different results in different classes of LC molecules. So while studying the effect of the structure of nematic LCs based on arylpropargyl ethers of phenols on their electrophysical properties, a number of unexpected results were obtained:

- most of the compounds have a negative sign on the anisotropy of the dielectric constant, despite the expected positive value [6];
- was predicted from geometry studies using molecular mechanics and confirmed experimentally the fact that the sign of this magnitude inverted when attached to the ortho-position of the NO_2 functional group [24]. The cause of the observed inversion is a change in the direction of the dipole moment of the molecules as a result of the rotation of the benzene ring. Such a structural transformation usually leads to the opposite result [25].

The important role of benzene rings in the presence of order in the mesophase is confirmed by their presence in most LC structures [21]. The concepts of the structure of the LC phases are based on a simplified model. In more detailed analysis it is necessary to take into account the conformation of the molecules. As in the molecular crystal, molecules with different conformation, environment, orientation can coexist in the LC phase. One of the most typical complications of the structure of LCs is the formation of dimers and so-called bilayers [22]. The approximation of the mean field, continual theory is not enough to predict mesogenic properties, depending on their structure.

Here are some facts about the benzene rings that exist in the physical chemistry of the liquid crystal:

- rigidity of the benzene ring as a fragment in the structure of LC compounds [21];
- plane-parallelism of rings in the crystalline state [23,26];
- it is known that LC molecules are almost 100% oriented in a magnetic field [27,28];
- benzene rings have a bright anisotropy of magnetic susceptibility [29];
- it was found that with an increase in the number of benzene rings in LC molecules, the anisotropy of magnetic susceptibility increases [30];
- effects with chlorine-containing compounds [31]: the aggregation of chlorine atoms is due to the “chlorophobic” effect - the interaction of benzene rings with each other is energetically more advantageous than their interaction with chlorine; chlorine atoms are pushed out of the interaction region of the benzene rings, which leads to the formation of C1 ... C1-aggregates;.
- it is known that aromatic solvents (benzene and its substituted), despite their low dielectric constant, affect many chemical processes as strongly polar liquids. The cause of the "benzene" effect is the large anisotropy of the polarizability of the aromatic rings. As a result, the polarizability significantly depends on the orientation of the solvent molecules to the dipole moments of the molecules of the solute [32].
- π-stacking, non-covalent interaction, determining the self-organization of various molecular systems, including discotic LCs [33-39].

2. Results and discussion

Let's analyze the given data. Indeed, like most organic substances, LCs, as a rule, are diamagnetic. Diamagnetism is due to Larmor precession of electrons. This leads to the appearance of an induced magnetic moment directed opposite to the external field, and therefore the magnitude of the magnetic susceptibility is negative.

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Since the atomic susceptibility is isotropic, it can be expected that the anisotropy of the magnetic susceptibility is also small. However, the aromatic systems have a large anisotropy [40]. This can be explained by the fact that the π-electrons of the benzene ring are delocalized and form a "ring current". When the magnetic field is perpendicular to the plane of the ring, one can expect the appearance of a large induced moment directed against the field creating it. In the case of NLC, the susceptibility anisotropy must be positive and proportional to the number of aromatic rings [21]. With each replacement of the benzene ring by cyclohexane, the anisotropy of susceptibility decreases. If there are no aromatic rings in the compound, this value becomes negative. The value of the bridge –C≡C–C≡C– is especially lowered. Qualitatively, this effect can be associated with ring currents, which in the case of triple bonds can occur in a plane perpendicular to the long axis of the molecule. The presence of a triple bond in the compounds studied by us [24] may be, apparently, one of the reasons for the presence of small values of the anisotropy of the dielectric constant.

It is known that the location of LC molecules in the crystalline state occurs mainly when the antiparallel position of nearby molecules is either head-to-head or overlapped [23]. Therefore, it can be assumed that, given the known "spacing" of the benzene rings of the LC molecules, the far orientational ordering will be determined by the possibility of the formation of interacting parallel pairs of benzene rings of neighboring molecules. Such a mechanism is easy to implement because of its good mobility, due to the small energy barriers of rotation [41]. An increase in temperature in the region of the mesophase leads to a decrease in the degree of order [21], which can be explained by the breaking of bonds between the benzene rings. T_{NI} will increase with increasing binding energy between these rings. The steric factor will play an important role in the orderliness of the molecules and determine the amount of repulsion of other fragments of nearby LC molecules. Apparently, the excess of the energy of such an interaction over the binding energy of the benzene rings makes it impossible for the mesophase to exist in this compound.

As is known [23], in order for a separate crystalline phase to become a precursor of the classical nematic phase, two conditions are required. First of all, it is a parallel or approximately parallel arrangement of molecules. The second condition is the requirement that the forces of intermolecular interaction were not large enough and allowed only translational movement of molecules at such thermal energies, when rotational movement around all three axes is possible.

There are few prerequisites for the existence of ionic and covalent bonds due to non-fulfillment of the second condition. The most frequently considered van der Waals interaction appears to be present, but not dominant. The observed nonfulfillment of the principle of dense packing, which characterizes the isotropy of the van der Waals interaction, in the case of orthorhombic crystalline benzene and its derivatives, is the reason for this statement [42].

As the analysis shows, the unusual properties of benzene rings are due to the anisotropy of the magnetic susceptibility, determined by the existence of ring currents. Apparently, the interaction of the magnetic fields of the benzene rings of neighboring molecules is the main mechanism for the realization of orientational ordering in NLCs. It is easily realized due to the small size of the energy barrier of rotation of the benzene rings, a characteristic arrangement already in the crystalline phase of the LC molecules (head to head or overlapped). This can lead to a parallel arrangement of the benzene rings of neighboring molecules in the presence of a translational motion in the liquid phase. It can be assumed that such a bond can be enhanced by cooperative effects in the direction perpendicular to the long axis of the LC molecules.

In the processes of self-organization of large molecular systems, one of the main factors is the π-stacking process. It is carried out through non-covalent interaction between the aromatic rings of neighboring molecules. However, the nature of these considerations is electrical. Different arrangements of interacting aromatic rings are usually studied (Fig. 1).

Stacking interactions between p systems play a major role in molecular recognition [33-39], in shaping the structure and the functionality of nucleic acids and in determining the tertiary and quaternary structure of proteins. Vertical stacking between planar molecular systems is favored in polar environment, mainly due to entropic reasons, while electrostatic forces are in general determinant for planar or T-shaped structures in non polar media.

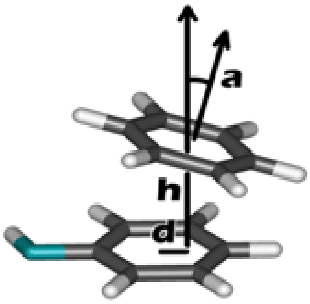

Fig.1. Type of the investigated system of interacting aromatic rings

In this respect, the traditional terminology ‘‘p–p’’ stacking is somewhat misleading since it is suggestive of some kind of special interaction between p molecular orbitals. The calculations presented in [33] revealed that a H_2O molecule accelerates the time of π-stacking formation in a benzene molecular system. The times of stacking formation in the benzene dimer (n = 2) and trimer (n = 3) cations were calculated to be 594 fs (H_2O) and 922 fs (*no*-H_2O), and 566 fs (H_2O) and 1155 fs (*no*-H_2O), respectively.

Molecular self-assembly and self-organization are Nature’s methods for the creation of dynamic and complex materials necessary for life on earth. These non-covalent interactions include hydrogen bonding, π-stacking, polar-nonpolar interactions, metal coordination, ionic interactions, etc.[34-35]. One particularly interesting example of a selfassembled material is a liquid crystalline phase [36]. The interactions that are crucial for the formation of liquid crystals are very similar to those of biologically relevant interactions: van der Waals forces, π-stacking, dipolar interactions, charge transfer interactions and hydrogen bonding [34-38]. These forces in effect control the properties of liquid crystals. Since these interactions are weak, it allows for partial dissociation to repair disordered units and obtain a uniform and more stable system; this is also known as self-healing. A better understanding of how the structure and morphology of a molecule will affect the self-assembly of supramolecular materials will allow for an efficient and effective design of these building blocks so that their properties can be utilized.

The binding between molecules is in most cases mainly due to van der Waals forces [38-39]. The core–core and tail–tail van der Waals interactions are responsible for the formation of the columnar phase. These packing structures are a function of the symmetry of columns and also intracolumnar van der Waals forces. An introduction to DLCs and the powerful potential it possesses in molecular electronics, as 1D molecular wires due to stacking of its π–π orbitals. The potential of such an interaction in [1] is

$$U = -\frac{A}{r^3} + \frac{B}{r^6}.$$

The non-potential nature of magnetic interaction is a major problem in the development of modeling software. At the same time, the presented potential represents an opportunity to take into account its contribution to some extent. At the same time, there is a possibility that the influence of paramagnetism is manifested not only on such a functional group as aromatic rings [43]. The

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potential of intermolecular interaction in the LC should include dispersion, Coulomb and magnetic interactions. The Coulomb is not dominant due to the neutrality of the LC molecules. Therefore, two other interactions are decisive. By the strength of the interaction, they are comparable.

Conclusion

The analysis performed shows the main role of benzene rings in the existence of orientational ordering in nematic liquid crystals. One of the mechanisms that implements this process may be the interaction of the magnetic fields of the ringless rings of neighboring molecules. Van-Vlecky paramagnetism, due to ring currents in benzene rings, seems to be one of the reasons for such orderliness. Apparently, this explains the high degree of orderliness of liquid crystals when exposed to a magnetic field. In this regard, the intermolecular interaction in the case of staking may have a magnetic component. A type of possible intermolecular interaction potential is proposed when simulating the behavior of an ensemble of liquid crystal molecules. It is shown that the ordering of molecules of liquid crystals is associated with the different nature of intermolecular interactions, but having the same order.

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