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MODELING OF PHYSICAL CHEMICAL PROPERTIES OF NEW DERIVATIVES OF ARYLPROPARGYL ETHERS OF PHENOL

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This work is devoted quantum-chemical investigations of the structure, dipole moments, and experiments on computer simulation of the behavior of new derivatives of APEP with substituents in the para- positions of the phenyl fragments of molecules (alkylcyclohexyl, NO_2, F, Cl, CN). It was established that it was found that the dipole moments, the heats of formation, and the electronegativity of the new APEP derivatives as a whole correlate with each other. It is shown that their structures have an extended structure that can contribute to the manifestation of liquid crystal properties. The changes in the degree of order with increasing temperature in conjunction with the fluorine atom correspond to this assumption. It is established that parallel annealing is the best approach for such studies. It was found that an increase in the length of the molecules, in the presence of mesogenicity, will have a positive dielectric anisotropy. It is found that the search for phase transition temperatures is better performed by using an annealed cluster at 10 ps as the initial cluster

Keywords: liquid crystals, quantum-chemical calculations, modeling

Introduction

Liquid crystals (LC) are one of the most practically significant materials used in electronic devices. Quantum-chemical methods allow analyzing changes in their physicochemical properties, such as structure, energy and other characteristics of molecules. At the same time, cooperative effects in LCs stimulated the development of Monte Carlo methods and molecular dynamics. The search for suitable intermolecular interaction potentials that determine the existence of long-range orientation ordering in the mesophase is based mainly on mean field theory. The dispersion interaction is actually considered as the main one. Further improvement of the mesogenic properties of the compounds is impossible without detailing the processes occurring in them. The methods of the statistical theory do not allow in most cases to see firsthand the results of the changes occurring in systems of many particles. The cooperative features of molecular processes are very often obscured by the approximations made. The method of molecular dynamics in the approximation of the liquid aggregate state [1-4] proved effective in predicting the experimentally observed physical processes in the LC.

Nematic liquid crystals based on arylpropargyl esters of phenols (APEF) are a promising material for improving the temperature characteristics of liquid crystal devices [5-6]. The results of modeling the behavior of these LCs [1-4] show the efficiency of using the approximation of the liquid aggregate state. The peculiarity of this modeling is the placement of the whole ensemble within a single cell. The initial structures of LC are determined using quantum chemical methods.

It was found that the direction of the dipole moment vectors of p-nitro phenylpropargyl ethers of p-halogen-phenols will have an angle with the longitudinal axis of the order of 20^0 [7-8]. This is less than analogous angles in compounds where the halogen was attached from the opposite side of

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the longitudinal axis [9-10]. The latter are nematic liquid crystals with a dielectric anisotropy $\Delta\varepsilon<0$. Small angles allow us to expect an inversion of $\Delta\varepsilon> 0$ in these compounds.

The purpose of this work was quantum-chemical investigations of the structure, dipole moments, and experiments on computer simulation of the behavior of new derivatives of APEP with substituents in the para- positions of the phenyl fragments of molecules (alkylcyclohexyl, NO_2, F, Cl, CN).

1. The methodology of the analysis

The selection of the optimal simulation parameters (pressure, annealing time, etc.) has been carried out. Input files determined the geometry and force field of compounds are created. The initial clusters of molecules were rectangular parallelepipeds with 13x13x7. The compound structure is optimized by the MOPAC program (MNDO method) from the ChemOffice 8 software package.

The method of investigation is described in detail in [1-4]. The cut-off radius of the dispersion interaction was 2 nm. The simulation was carried out for planar orientation of the molecules relative to the substrate - in the absence of an external electric field. The direction of the director in the original cluster coincided with the OY axis, and the molecules were located in the XYO planes.

2. Results and discussion

The results of the studies are presented in Tables 1-4 and Figures 1-7.

Table 1 - The values of the heat of formation, dipole moments, the distance between molecules in the cluster

N	Substitute	Heat of formation (kcal / mol)	Thedipolemoment (Debye)	The distance between molecules, nm
1	F	33.13919	0.853 1.577 -0.609 Magnitude: 1.893	OX=1, OY=2, OZ=0.5, dY=0.7
2	Cl	71.85598	0.745 1.619 0.763 Magnitude: 1.939	OX=1, OY=2, OZ=0.5, dY=0.7
3	NO_2	94.28028	0.955 5.310 0.228 Magnitude: 5.400	OX=1, OY=2, OZ=0.5, dY=0.7
4	CN	110.80447	-0.175 3.202 -1.078 Magnitude: 3.383	OX=1, OY=2, OZ=0.5, dY=0.7

As can be seen from Table 1, the increase in the heat of formation is accompanied by an increase in the total dipole moment. The influence of the electronegativity of the substituents on these quantities is also observed. A violation of the sequence of influence is observed for the fluorine atom, as was observed in the previously studied APEP [7-8]. In the presence of mesogenicity, these compounds exhibit a positive dielectric constant, as can be seen from the ratio of the components of this component (Dy>Dx, Dz, where Y is the component along the longitudinal axis).

As can be seen in Figure 1, for all the molecules studied, the extended shape is characteristic. This is an essential sign for the manifestation of LC properties [11].

Modeling experiments of the investigated compounds with substituents - F, Cl, NO_2 - were carried out with 3 variants of arrangement of molecules in the cluster: antiparallel rows and layers with displacement dY (t01) (see Table 1), parallel rows and layers without displacement (t02), parallel rows and layers with displacement dY (t03).The annealing was parallel when the same cluster was exposed at different temperatures.

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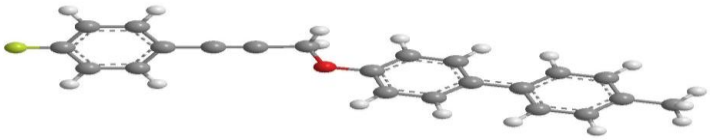
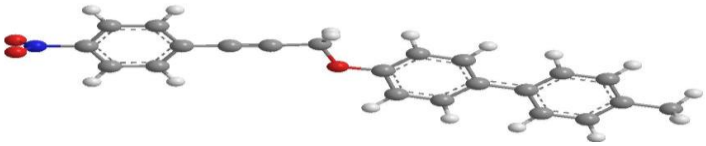
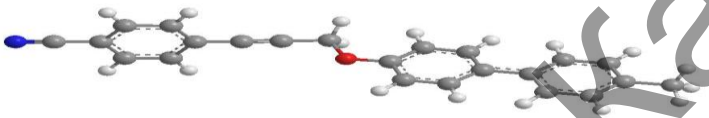


Substitute F

Substitute Cl



Substitute NO_2



Substitute CN

Fig.1. Structure of the investigated derivatives of APEP with differentsubstitutes

Table 2 - Values of the degree of ordering of compound No. 1 (F) with a change in the annealing time (5, 10, 30 ps) and the arrangement of molecules in the cluster

T,K	t01-10ps	t01-5ps	t01-30ps	t02-10ps	t03-10 ps	t03-5 ps
290	0.4603			0.414565	0.539676	0.625948
295	0.454473			0.357874	0.528679	0.617798
300	0.439736			0.398367	0.515938	0.574252
305	0.424764			0.386209	0.518831	0.568593
310	0.411515			0.342858	0.493	0.565473
315	0.417073			0.398274	0.496969	0.567098
320	0.430118			0.400321	0.512865	0.556691
325	0.423978			0.401113	0.467554	0.544459
330	0.40541			0.384984	0.445511	0.527549
335	0.425591			0.431944	0.444893	0.523818
340	0.420068	0.524299	0.280301	0.396473	0.464483	0.531818
345	0.41748	0.49725	0.257127	0.339689	0.44517	0.489777
350	0.382757			0.295655	0.436947	0.499915
355	0.386278			0.293524	0.438562	0.52949
360	0.398996			0.3045	0.410904	0.494142
365	0.359401			0.296869	0.446474	0.516354
370	0.341416			0.330586	0.441468	0.498412
375	0.346756			0.280678	0.431653	0.492156
380	0.369219			0.30969	0.40739	0.493688
385	0.345896			0.298739	0.41767	0.493204
390	0.333011			0.280038	0.372791	0.463736
395	0.314398			0.267934	0.378053	0.468935

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Table 3 - Values of the degree of order of compound No. 2 (Cl) at an annealing time of 10 ps and a change in the arrangement of molecules in the cluster

T,K	t01-10ps	t02-10ps	t03-10ps
335	0.465425	0.13478	0.463834
340	0.494424	0.111805	0.486365
345	0.471234	0.166577	0.441256
350	0.465788	0.159266	0.453947
355	0.465425	0.15067	0.462549
360	0.470781		
365	0.458827		
370	0.453085		
375	0.459482		
380	0.468318		

Table 4 - Values of the order degree of compound No. 3 (NO_2) at an annealing time of 10 ps and a change in the arrangement of molecules in the cluster

T,K	t01-10 ps	t02-10ps	t03-10 ps
335	0.344494	0.087398	0.505176
340	0.350732	0.03595	0.490799
345	0.359339	0.11849	0.48263
350	0.339836	0.102463	0.473093
355	0.349976	0.086798	0.459534
360			0.480804
365			0.45824
370			0.470316
375			0.489867
380			0.510987

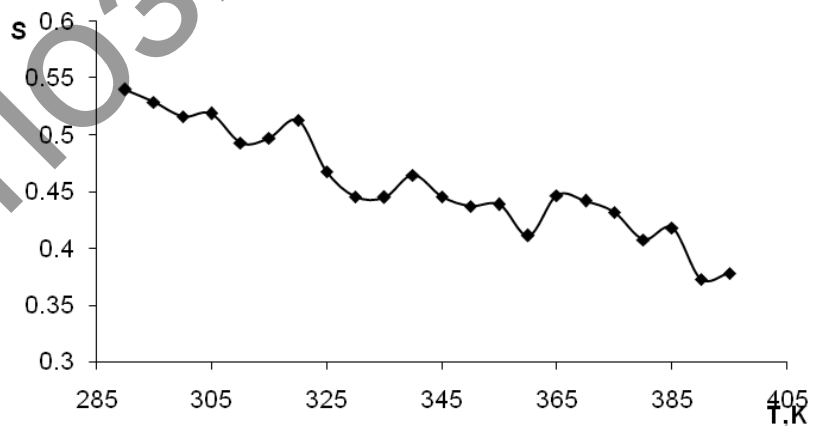

Fig. 2. The values of the order degree S, corresponding to the values from Table 2, the series t03-10ps

As can be seen from Table 2, at low temperatures, the highest order-degree values are observed for all the cases of computer simulation experiments. In this case, the trend of the order degree is observed (see Figure 2) - the order degree decreases when the temperature rises. Experiments in the case of substituents (Cl, NO_2) did not proceed so monotonously. As can be seen from Tables 3-4,

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the mentioned trend is poorly traced, and in some cases the modeling process itself is interrupted (empty fields in the tables).

Preliminary experiments on modeling the behavior of clusters of the investigated molecules show the possibility of mesogenic properties. Accurate determination of the temperature of phase transitions requires further adjustment of the modeling method proposed by us [1-4] .

Experiments to determine the melting point of liquid crystals were carried out. The optimal version of the modeling method was detected simultaneously. A one-component cluster was constructed containing the previously studied APEP-phenylpropargyl ester of cresol (PEK), phenylpropargyl ether of p-chlorophenol (PEC), phenylpropargyl ether of p-fluorophenol (PEF).The initial clusters of molecules were rectangular parallelepipeds with the dimensions - 13x13x17 for PEK and 14x14x17 for PEC, PEF. Sequential annealing of the cluster (1), parallel annealing of the cluster (2), sequential annealing with a 1×10^7 V / m (3) field applied, sequential annealing with the grid (4) simulation parameter (this parameter changes the atomic search function, which in some cases allows reduce simulation time).

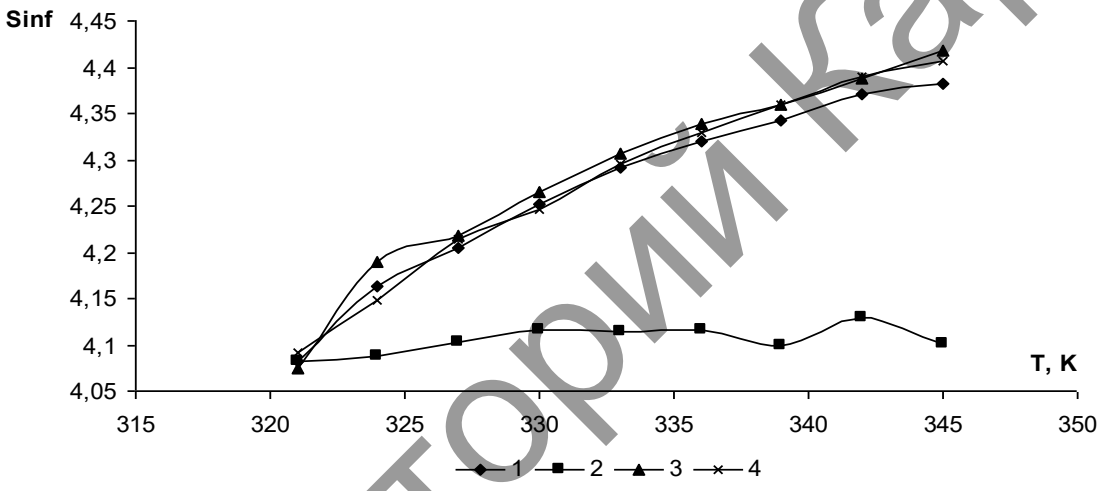

Fig.3. Temperature dependence of the information entropy of the FEK cluster

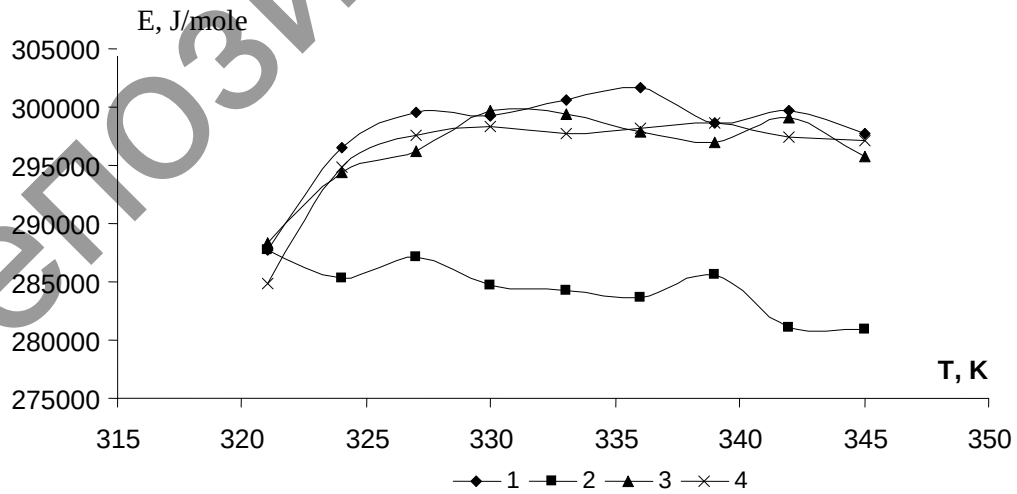

Fig.4. Temperature dependences of the binding energy of the FEK cluster

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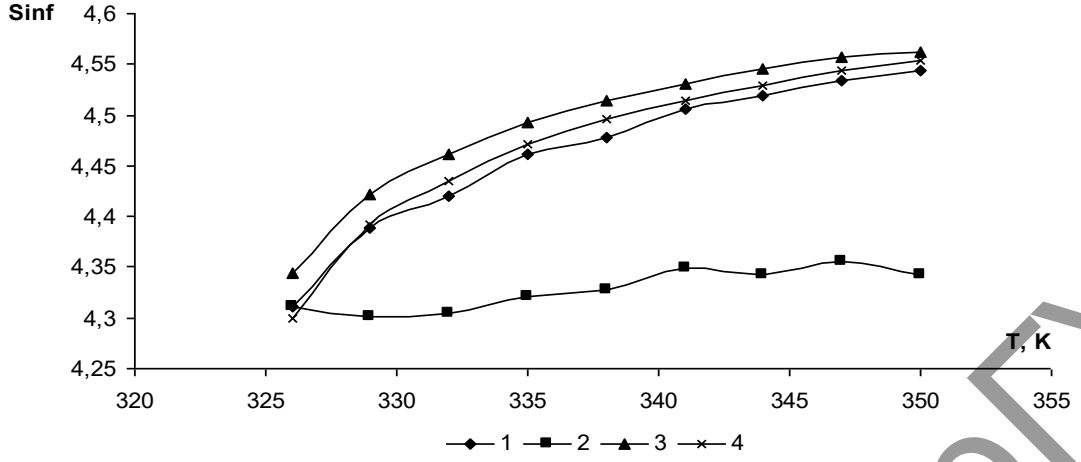

Fig.5. Temperature dependence of the information entropy of the PEC cluster

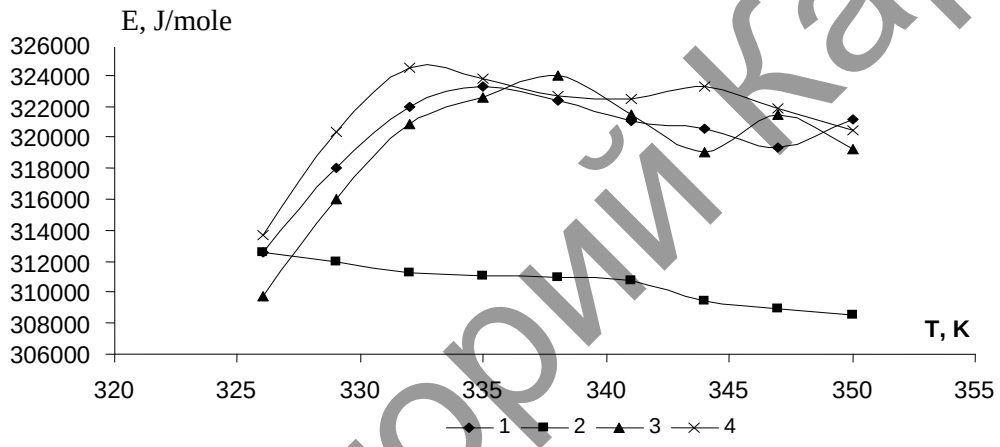

Fig.6. Temperature dependences of the binding energy of an FEC cluster

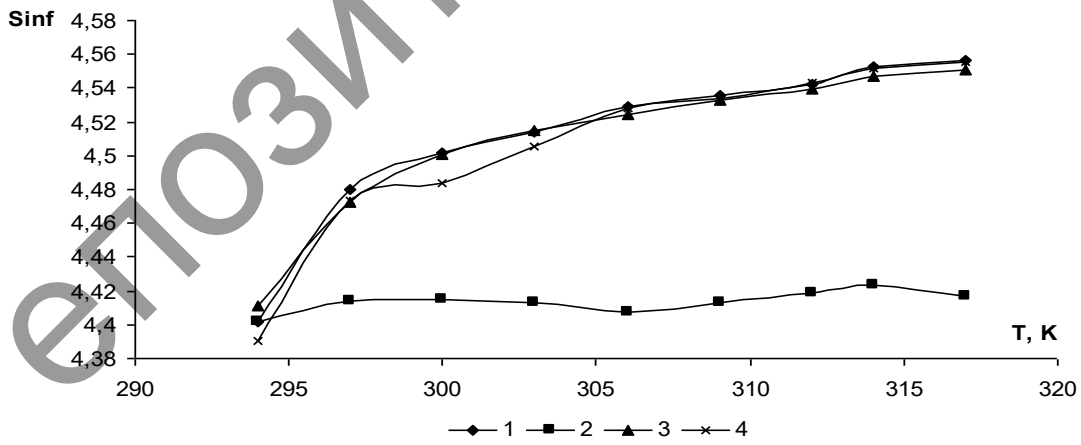

Fig.7. Temperature dependence of the information entropy of the PEF cluster

Based on the temperature dependences of the information entropy and binding energy of the investigated clusters (Figures 3-8), as well as the flexibility of modeling to find the melting point from these methods, method 2 was chosen.

The increase in alkyl chains can lead to the appearance of smectic mesophases [11]. Therefore, quantum-chemical studies of such new derivatives of APEP with substituents in the para- positions of the phenyl fragments of molecules (alkyl radical, NO_2, F, Cl, etc.) were carried out.

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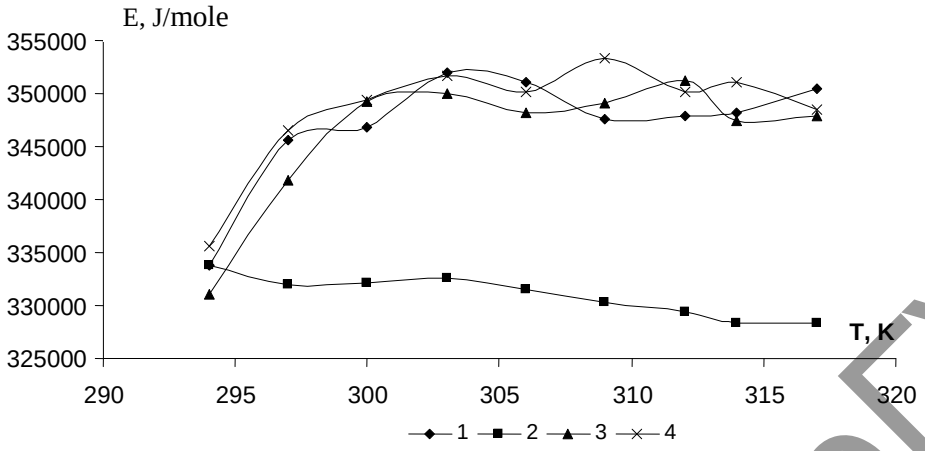
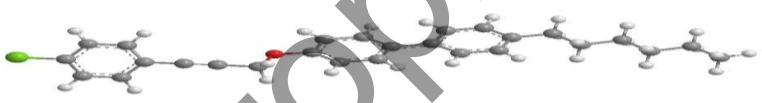


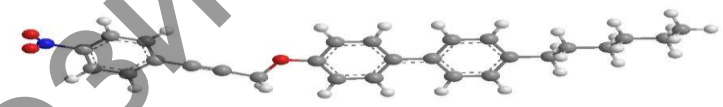
Fig.8. Temperature dependences of the binding energy of the PEF cluster

Research results are shown in Figures 9-12 and Table 5. As can be seen from Table 5, an increase in the heat of formation is accompanied by an increase in the total dipole moment.

Substitute F



Substitute Cl



Substitute NO_2

Fig.9. Structure of the investigated derivatives of APEP with different substitutes

Table 5 - The values of the heat of formation, dipole moments, the distance between molecules in the cluster

№	Substitute	Heat of formation (kcal / mol)	The dipole moment (Debye)	The distance between molecules, nm
1	F	13.83470	0.862 1.638 -0.663 Magnitude: 1.967	OX=1, OY=3, OZ=0.5, dY=0.7
2	Cl	52.85321	0.744 1.634 0.712 Magnitude: 1.931	OX=1, OY=3, OZ=0.5, dY=0.7
3	NO_2	75.00224	0.861 5.427 0.391 Magnitude: 5.509	OX=1, OY=3, OZ=0.5, dY=0.7

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The influence of the electro-negativity of the substituents on these quantities is observed. A violation of the sequence of influence is observed for the fluorine atom, as was observed in the previously studied APEF [5-6]. In the presence of mesogenicity, these compounds have a positive dielectric constant, as can be seen from the ratio of the component components of this quantity (Dy>Dx, Dz, where Y is the component along the longitudinal axis). It has been established that increasing the length of molecules leads to a decrease in the heat of formation (Tables 1 and 5). It is shown that for all the molecules studied, the extended shape is characteristic (Figure 9).

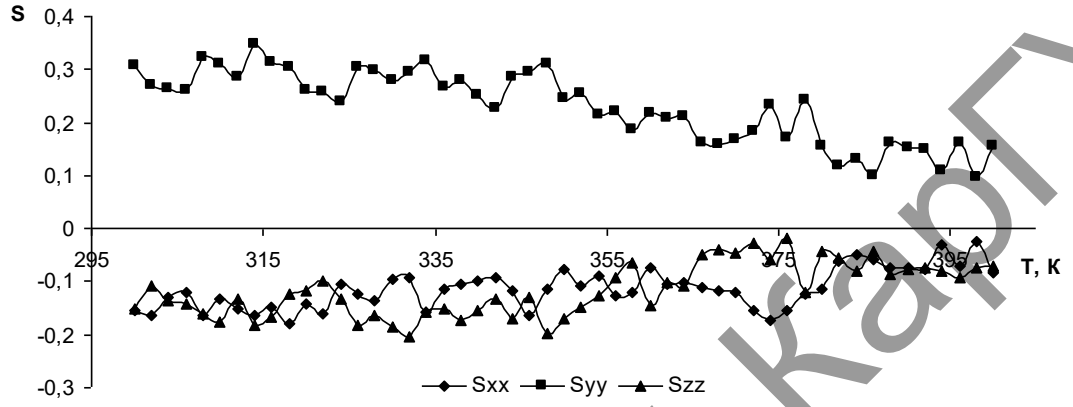

Fig.10. Values of the order degree of compound No. 1 (F). The cluster size is 13x13x3, the interval of parallel annealing temperatures is from 300 to 400 K in steps of 2 K.

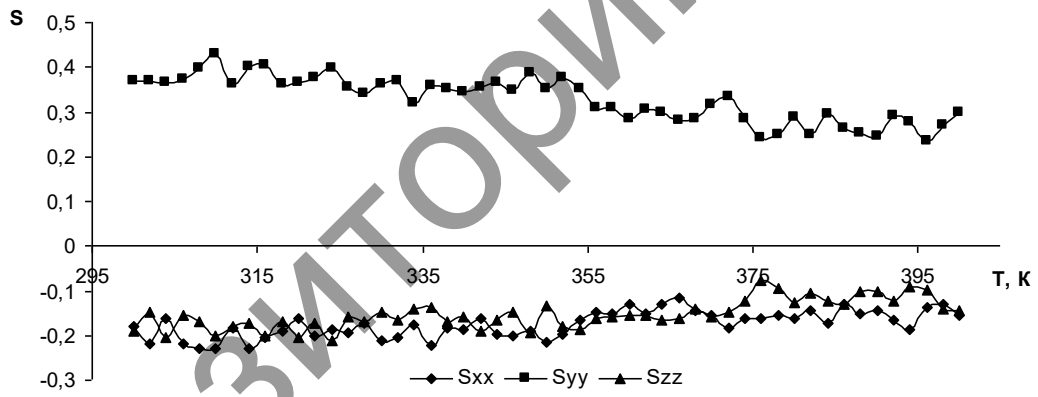

Fig.11. Values of the order degree of compound No. 1 (F). The cluster size is 13x13x4, the interval of parallel annealing temperatures is from 300 to 400 K in steps of 2 K.

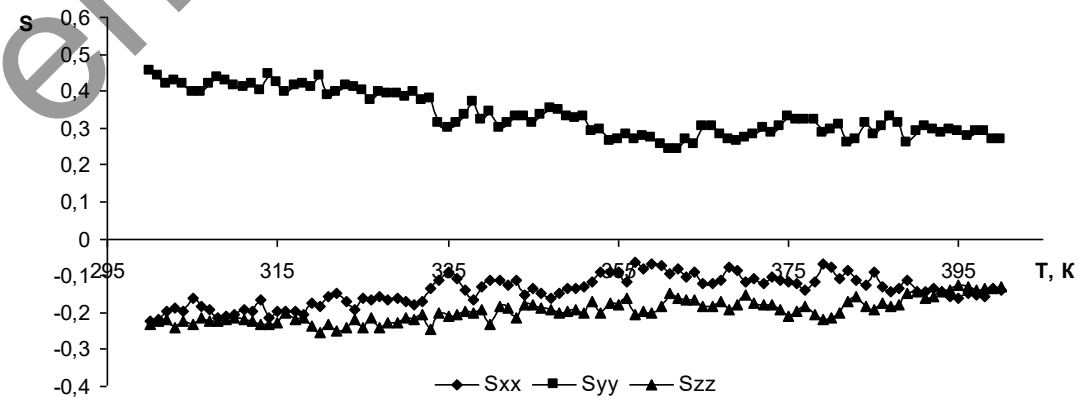

Fig.12. Values of the order degree of compound No. 1 (F). The cluster size is 13x13x7, the interval of parallel annealing temperatures is from 300 to 400 K in steps of 2 K.

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Preliminary experiments on modeling the behavior of clusters (substituent-fluorine atom, Figures 10-12) show a high probability of manifestation of LC properties of the molecules under study. However, a more accurate prediction of the values of the temperatures of the phase transitions requires further studies on the correlation of the method used.

Conclusion

Thus, on the basis of the investigations carried out, it was established that it was found that the dipole moments, the heats of formation, and the electro-negativity of the new APEP derivatives as a whole correlate with each other. It is shown that their structures have an extended structure that can contribute to the manifestation of liquid crystal properties. The changes in the degree of order with increasing temperature in conjunction with the fluorine atom correspond to this assumption. It is established that parallel annealing is the best approach for such studies. It was found that an increase in the length of the molecules, in the presence of mesogenicity, will have a positive dielectric anisotropy. It is found that the search for phase transition temperatures is better performed by using an annealed cluster at 10 ps as the initial cluster.

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