POLARIZABILITY ANISOTROPY OF $C_NH_{2N+1}OC_6H_4C(O)OH$ LIQUID CRYSTAL MOLECULES

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INTRODUCTION

The anisotropy of liquid crystals is their fundamental feature. In the liquid crystals we can find the anisotropy of refractive indices, dielectric permittivity and the viscosity. These parameters are connected with the axial symmetrical arrangement of liquid crystal molecules. Because of their physical properties, liquid crystals have found great number of applications in technique and in everyday life. These properties are connected with the shape and properties of liquid crystal molecule too. Therefore, the mentioned above information about liquid crystal molecules is very important for a study of liquid crystal properties. There are many data in the literature, characterising the liquid crystal molecules: the trace of polarizability tensor, polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$, moment of inertia, polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ belong to those. In this work we are interested in the temperature dependence of polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$, and in the polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ of $C_nH_{2n+1}O\text{-}C_6H_4C(O)OH$ liquid crystals. In the works [1-3] it was proved that the trace of polarizability tensor α_s of liquid crystal sample is equal to the α_s of liquid crystal molecule. As follows: $(\alpha_1 + 2\alpha_2) = (\alpha_{\parallel} + 2\alpha_{\perp}) = \alpha_s$ where α_1, α_2, $\alpha_{\parallel}$, $\alpha_{\perp}$ are the polarizability tensor components of liquid crystal sample and molecule, respectively. Having the additional equation with the unknown expressions of $\alpha_{\parallel}$, $\alpha_{\perp}$, one can find from the results of Saupe and Maier theory of molecular arrangement in liquid crystal the new equations as below:

$$\alpha_{\parallel}=(M/N)[(n^2-1)/d+2(n_e+n_o)/3k_Ad]$$

$$\alpha_{\perp}=(M/N)[(n^2-1)/d-(n_e+n_o)/3k_Ad]$$

$$(\alpha_{\parallel}-\alpha_{\perp})=(M/N)[(n_e+n_o)/k_Ad] \tag{1}$$

where: M – the molecular weight, N – Avogadro number, d – density of liquid crystal, and $n^2=(n_e^2+2n_o^2)/3$.

Knowing the values of refractive indices, density and k_A coefficient of investigated liquid crystal, one can calculate the polarizability tensor components using the above mentioned equations.

EXPERIMENTAL

In this work we use the new method of calculating $\alpha_{\parallel}$ and $\alpha_{\perp}$ of four liquid crystal molecules, which chemical formulas are $C_nH_{2n+1}OC_6H_4C(O)OH$. The number n changes from n=6 to n=9. In order to calculate the polarizability tensor components of mentioned liquid crystal molecules, we can use the values of their refractive indices, density and constant coefficient k_A. The values of refractive indices and density come from the literature [5]; they are collected in the Tables 1-4.

Table 1. Refractive indices, density, polarizability anisotropy $(\alpha_\parallel - \alpha_\perp)$, polarizability tensor component $\alpha_\parallel$ and order parameter S of $C_nH_{2n+1}OC_6H_4C(O)OH$ liquid crystal for n=6. Transition temperature to the isotropic liquid crystal $T_o=152.5\ C^o$.

ΔT	d g/cm^3	n_e	n_o	$(\alpha_\parallel - \alpha_\perp)$ 10^{-23}cm^3	$\alpha_\parallel$ 10^{-23} cm^3	S
20	1.0108	1.6100	1.4520	33.180	68.478	0.532
17.5	1.0084	1.6070	1.4519	33.225	68.494	0.523
15	1.0060	1.6036	1.4516	33.264	68.476	0.512
12.5	1.0033	1.5990	1.4516	33.303	68.446	0.497
10	0.9994	1.5950	1.4520	33.394	68.558	0.482
7.5	0.9964	1.5890	1.4521	33.430	68.493	0.461
5	0.9934	1.5820	1.4530	33.464	68.444	0.435
2.5	0.9892	1.5730	1.4549	33.527	68.467	0.398
1.75	0.9873	1.568	1.4560	33.548	68.454	0.377
1	0.9867	1.5650	1.4570	33.546	68.436	0.364
-1	0.9752		1.4880	33.154	68.237	
-3	0.9733		1.4865	33.185	68.178	
-5	0.9711		1.4853	33.233	68.179	
-7	0.9693		1.4840	33.266	68.139	
-10	0.9655		1.4820	33.352	68.150	

Table 2. Refractive indices, density, polarizability anisotropy $(\alpha_{\parallel}-\alpha_{\perp})$, polarizability tensor component $\alpha_{\parallel}$ and order parameter S of $C_nH_{2n+1}OC_6H_4C(O)OH$ liquid crystal for n=7. Transition temperature to the isotropic liquid crystal $T_o=147.5\ C^o$.

ΔT	d g/cm^3	n_e	n_o	$(\alpha_{\parallel}-\alpha_{\perp})$ $10^{-23}cm^3$	$\alpha_{\parallel}$ 10^{-23} cm^3	S
30	1.0075	1.6110	1.4530	33.180	67.893	0.525
25	1.0031	1.6065	1.4522	33.268	67.922	0.513
20	0.9975	1.6000	1.4520	33.381	67.988	0.492
17.5	0.9950	1.5955	1.4518	33.413	67.935	0.477
15	0.9919	1.5905	1.4516	33.461	67.902	0.461
12.5	0.9894	1.5855	1.4516	33.490	67.843	0.445
10	0.9863	1.5800	1.4520	33.539	67.834	0.425
7.5	0.9838	1.5745	1.4521	33.564	67.760	0.406
5	0.9800	1.5690	1.4530	33.643	67.840	0.385
2.5	0.9747	1.5594	1.4550	33.741	67.924	0.347
1.75	0.9729	1.5566	1.4560	33.784	68.001	0.334
1	0.9717	1.5500	1.4570	33.762	67.860	0.309
-1	0.9638		1.4840	33.597	67.603	
-3	0.9614		1.4830	33.659	67.645	
-5	0.9592		1.4819	33.711	67.660	
-7	0.9570		1.4806	33.759	67.650	
-10	0.9538		1.4790	33.836	67.672	

Table 3. Refractive indices, density, polarizability anisotropy $(\alpha_\parallel{-}\alpha_\perp)$, polarizability tensor component $\alpha_\parallel$ and order parameter S of $C_nH_{2n+1}OC_6H_4C(O)OH$ liquid crystal for n=8 Transition temperatureto the isotropic liquid crystal T_o=148.5 C°.

ΔT	d g/cm³	n_e	n_o	$(\alpha_\parallel{-}\alpha_\perp)$ 10^{-23}cm³	$\alpha_\parallel$ 10^{-23} cm³	S
30	0.9967	1.6080	1.4510	32.970	74.757	0.608
25	0.9948	1.6056	1.4506	33.003	74.740	0.600
22.5	0.9896	1.5985	1.502	33.095	74.728	0.574
20	0.9867	1.5950	1.4500	33.152	74.747	0.561
17.5	0.9843	1.5911	1.4497	33.187	74.700	0.547
15	0.9813	1.5866	1.4496	33.238	74.684	0.530
12.5	0.9789	1.5821	1.4489	33.262	74.570	0.515
10	0.9753	1.5780	1.4500	33.352	74.730	0.495
7.5	0.9723	1.5720	1.4502	33.391	74.665	0.471
5	0.9693	1.5660	1.4510	33.437	74.655	0.445
2.5	0.9657	1.5560	1.4520	33.461	74.502	0.402
1.75	0.9633	1.5510	1.4540	33.511	74.609	0.375
1	0.9620	1.5450	1.4550	33.500	74.489	0.348
-1	0.9530		1.4820	33.411	74.455	
-3	0.9512		1.4808	33.447	74.422	
-5	0.9482		1.4798	33.530	74.513	
-7	0.9464		1.4788	33.571	74.509	
-10	0.9422		1.4770	33.680	74.579	

Table 4. Refractive indices, density, polarizability anisotropy $(\alpha_\parallel - \alpha_\perp)$, polarizability tensor component $\alpha_\parallel$ and order parameter S of $C_nH_{2n+1}OC_6H_4C(O)OH$ liquid crystal for n=9 Transition temperatureto the isotropic liquid crystal $T_o=140.5$ C°.

| ΔT	d g/cm^3	n_e	n_o	$(\alpha_\parallel - \alpha_\perp)$ 10^{-23}cm^3	$\alpha_\parallel$ 10^{-23} cm^3	S
25	0.9837	1.5938	1.4513	29.925	75.771	0.647
22.5	0.9817	1.5910	1.4511	29.956	75.755	0.635
20	0.9783	1.5880	1.4510	30.030	75.847	0.622
17.5	0.9759	1.5851	1.4510	30.075	75.876	0.609
15	0.9745	1.5815	1.4510	30.083	75.790	0.593
12.5	0.9711	1.5777	1.4510	30.150	75.849	0.575
10	0.9675	1.5740	1.4510	30.225	75.930	0.559
7.5	0.9651	1.5680	1.4510	30.240	75.794	0.531
5	0.9614	1.562	1.4520	30.306	75.84	0.499
2.5	0.9578	1.5520	1.4540	30.340	75.788	0.445
1.75	0.9564	1.5474	1.4550	30.348	75.745	0.419
1	0.9542	1.5400	1.4560	30.353	75.615	0.381
-1	0.9470		1.4800	30.216	75.323	
-3	0.9446		1.4788	30.268	75.333	
-5	0.9419		1.4777	30.332	75.382	
-7	0.9398		1.4765	30.375	75.368	
-10	0.9361		1.4750	30.465	75.438	
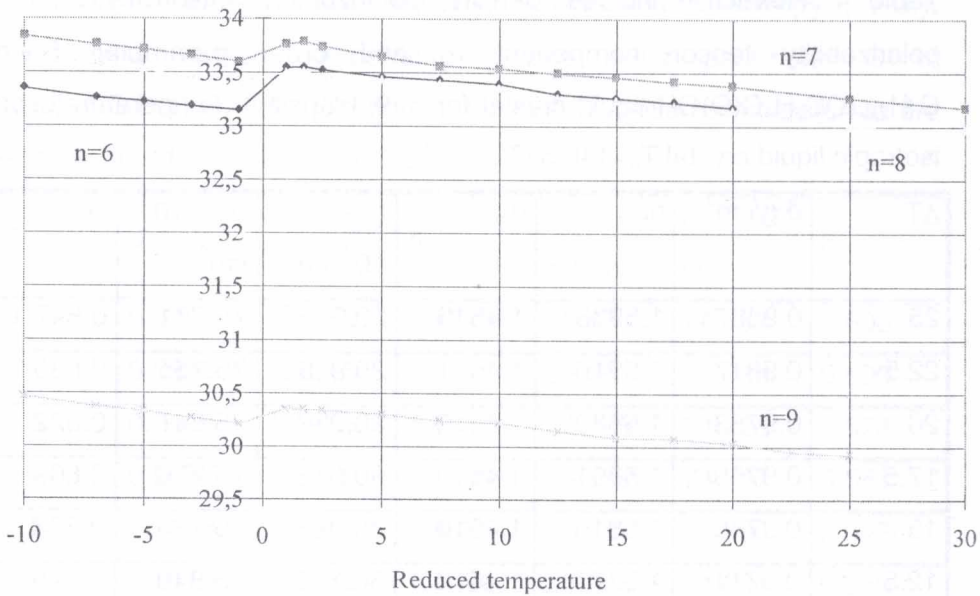
Figure 1. Polarizability anisotropy ($\alpha_{\parallel}-\alpha_{\perp}$) of all four investigated liquid crystals as a function of reduced temperature
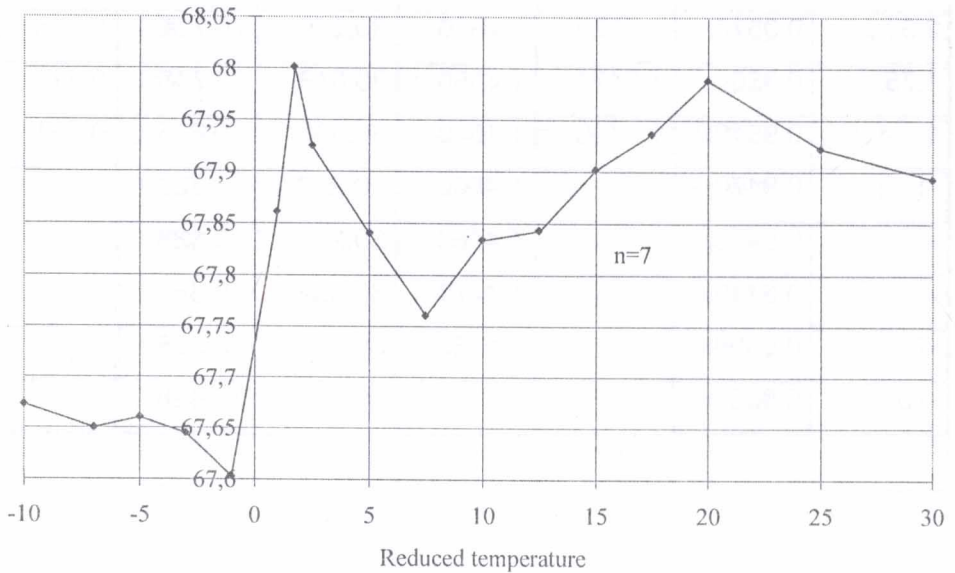

Figure 2. Polarizability tensor component of $\alpha_{\parallel}$ 10^{-23} cm^3 of $C_7H_{15}OC_6H_4C(O)OH$, as a function of reduced temperature.

In order to calculate the parameters interesting us we can use the values of k_A coefficient for each liquid crystal molecule. In our recent work [4] we described a method of such calculations using experimental data (refractive indices). For our four liquid crystals we obtained the following values of k_A coefficients: for n=6 k_A is equal 3.368; for n=7 k_A is equal 3.595; for n=8 k_A is equal 3.867; for n=9 k_A is equal 4.539. Basing on the data from Tables 1-4, we calculated the polarizability anisotropy ($\alpha_{\parallel}-\alpha_{\perp}$) and polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$ of our liquid crystals. The results of these calculations are collected in Tables 1-4 too. Moreover, the order parameter S of the investigated liquid crystal was calculated in this case. We plotted three figures in order to present our results more clearly. In Figure 1. the polarizability anisotropy ($\alpha_{\parallel}-\alpha_{\perp}$) of all four liquid crystals is shown as a function of reduced temperature. The Figure 2. represents the same dependency of $\alpha_{\parallel}$ of liquid crystals with n=7 (7 CH_2 groups in the alkyl chain). Now we see the conformation change of liquid crystal molecule proved by the change of $\alpha_{\parallel}$ values with the change of temperature. Therefore we see that this relation is not linear function of temperature. In Figure 3. one can see the relationship between the order parameter S and reduced temperature. These relationships have the same characters, but the values of S increase when the number of CH_2 group in alkyl chain increases. The different conformations of each liquid crystal molecule for n=6, 7, 8, 9 influence on the values of order parameter S of any sample of liquid crystals.
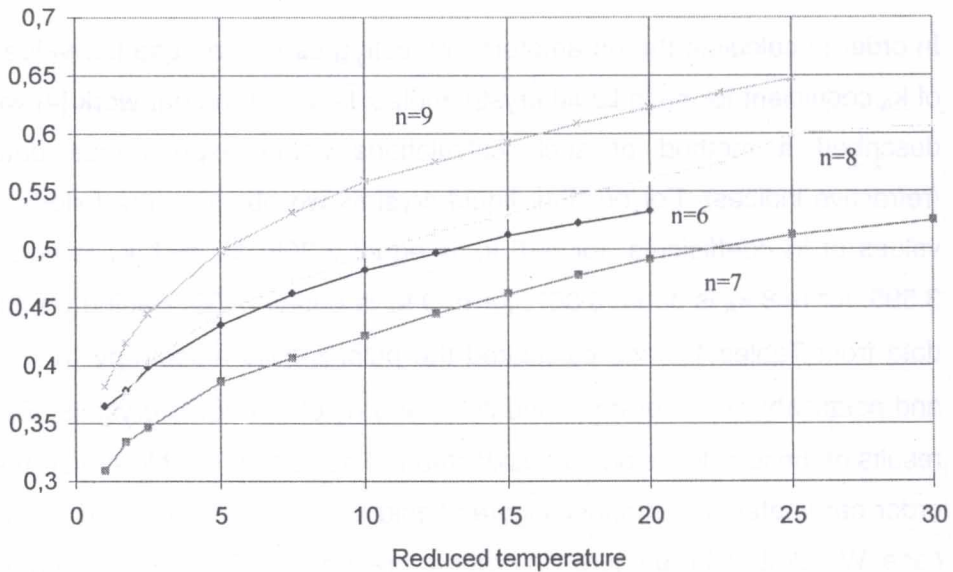
Figure 3. Order parameter S of $C_nH_{2n+1}OC_6H_4C(O)OH$ for n=6, 7, 8, 9 as a function of reduced temperature.

DISCUSSION

In Figure 1. we can see the relation of polarizability anisotropy $(\alpha_{\parallel}-\alpha_{\perp})$ of all four liquid crystals investigated as a function of reduced temperature. The values of $(\alpha_{\parallel}-\alpha_{\perp})$ increase slightly with the increase in temperature. In this Figure one can see a small change of $(\alpha_{\parallel}-\alpha_{\perp})$, about 0.09×10^{-23} cm³, at the transition temperature to the isotropic liquid. It can be ascertained that the two parts of $(\alpha_{\parallel}-\alpha_{\perp})$ relation are linear functions of temperature. The inclination of this function is very small, so one can say that the value of $(\alpha_{\parallel}-\alpha_{\perp})$ characterises the liquid crystal molecule very well. An increase in number of CH_2 groups in the molecule of the investigated liquid crystal almost doesn't change the values of $(\alpha_{\parallel}-\alpha_{\perp})$ for n=6, 7, 8. The biggest change is observed for n=9. The difference of $(\alpha_{\parallel}-\alpha_{\perp})$ equals 3×10^{-23} cm³ in this case, and 0.11×10^{-23} cm³ for n=6, 7, 8. We don't know what is a reason of this fact. Perhaps the alkyl chain of molecule with n=9

is so long that the polarizability anisotropy differs so much. In Figure 2. we can see the relation between $\alpha_\parallel$ and reduced temperature. It is known that the conformation type influences on the $\alpha_\parallel$ temperature relation. Therefore the $\alpha_\parallel$ is not a linear function of the temperature in the mesophase region. Moreover we can assume that the $\alpha_\parallel$ dependency is almost linear for an isotropic liquid state of liquid crystal. There is a second factor which influences on the values of $\alpha_\parallel$ and $\alpha_\perp$. As we know, the $\alpha_\parallel$ and $\alpha_\perp$ are functions of sum of mean square electron-proton distance in the molecule. The temperature change of liquid crystal sample has not only influenced on the conformation of molecule but also changed the interactions between molecules and electron-proton in a molecule. The separation of these two phenomena is a very big problem for a physicist. In our opinion, the polarizability anisotropy ($\alpha_\parallel-\alpha_\perp$) may be a measure of mean square distant sum in this case. We do not have a good theory which could give us a good solution of this problem, but we know that the interactions between molecules of liquid crystal decrease when the temperature of liquid crystal sample increases. In this case, the interactions of electron and proton are increased in all atoms of the molecule, what results in a decrease in the sum of mean square distance. It may be the reason of the fact that the ($\alpha_\parallel-\alpha_\perp$) value is a linear function of temperature in mesophase, as well as in isotropic liquid state of liquid crystal sample. Now we can assume that this problem is only suggested, but not solved.

In Figure 3. one can see the temperature dependence of order parameter S of the investigated liquid crystals. Character of all these dependencies is similar. The order parameter S is a decreasing function of temperature, which cannot overcome of one. Each liquid crystal sample has its specific function of order parameter S at a different range of temperature. It proves that an addition of another CH_2 group to the

molecule is a cause of conformation change in the molecule; the changes are different for each molecule of various liquid crystals. The addition of new CH_2 group to the molecule changes the physical properties of the molecule in different manner.

CONCLUSIONS

The liquid crystal molecules change conformation with the temperature by the free or hindered rotation of one molecule part around the other part.

Addition of new CH_2 group to the liquid crystal molecule creates a new molecule, which main coordinate system is different than the one of the initial molecule.

Addition of new CH_2 group to the molecule changes the value of polarizability anisotropy $(\alpha_{\parallel}-\alpha_{\perp})$, polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$, and order parameter S in various manners.

There are two reasons of the change of $(\alpha_{\parallel}-\alpha_{\perp})$ and $\alpha_{\parallel}$ values for liquid crystal molecule with the temperature: a conformation change and electron-proton distance change at the molecules' atoms.

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