POLARIZABILITY TENSOR OF CCH 7 MOLECULE

P. Adamski

Institute of Physics, Technical University of Łódź, str. Wólczańska 219, 93-005 Łódź Poland

ABSTRACT

Two phenomenon influence on the temperature dependence of component of polarizability tensor. First one is the change of distance between electrons and protons with temperature. The second is the conformation change of molecule. From the two reasons mentioned above the electron proton distance change is only the linear function of temperature. It gives the possibility of separation of two part of $\alpha_{\parallel}$ and $\alpha_{\perp}$ changes in polarizability tensor of liquid crystal molecule. In this work the polarizability tensor component changes was separated for CCH 7 liquid crystal and the implications of the results are discussed

INTRODUCTION

Liquid crystals are characterised by the anisotropy of several physical properties like dielectric permittivity, birefringence and viscosity. The anisotropy is associated with the specific arrangement of molecules. The birefringence properties of the liquid crystal are characterised by two polarizability tensors. One of them is the polarizability tensor of the liquid crystal sample, described by the components α_1 and α_2. These components can be calculated from the refractive indices by the use of the equations proposed by the author [1] or Lorenz-Lorentz, Vuks [2] and Neugebauer [3]. The second polarizability tensor, having the components $\alpha_{\parallel}$ and $\alpha_{\perp}$, is connected with the liquid crystal molecule. Both polarizability tensors are symmetrical but the tensor of the molecule has three different components $\alpha_{\parallel} = \alpha_z$, α_x and α_y in the co-ordinate system of the principal axes.. The components α_x and α_y have similar values, therefore ,one can introduce a new component $\alpha_{\perp} =(\alpha_x + \alpha_y)/2$ for these axes. Saupe and Maier [4] used them in the theory of the arrangement of liquid crystal molecules. The results of this theory are equations combining α_1 and α_2 with $\alpha_{\parallel}$, $\alpha_{\perp}$ and order parameter S of the molecules. The physical properties of liquid crystals have found great number of applications in technique and in every day life. They are connected with the shape and properties of liquid crystal molecule, so the information about these features of liquid crystal molecules is very important for a study of liquid crystal properties. The trace of polarizability tensor, polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$, moment of inertia, polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ characterise the

liquid crystal molecule. In this work we introduce such quantities as electron proton distance and conformation changes which exist in the polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$. Recently, [5-8] we proved the relations between the polarizability tensor components $\alpha_{\parallel}$, $\alpha_{\perp}$ and the refractive indices n_e, n_o, the density d and the coefficient k_A.

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

These equations are very useful for the calculation of the polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$ and for evaluation of polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ of the liquid crystal molecule. As we know $\alpha_{\parallel}$ and $\alpha_{\perp}$ are usually non-linear functions of temperature in the mesophase state of the liquid crystal. It is so, because two phenomenon influence the values of the polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$. First the electron proton distance as a linear phenomenon connected with temperature and second the conformation change as a non-linear one. The main problem of this work is the separation of these changes.

THEORETICAL

The subject of our investigation was the well known liquid crystal which chemical structural formula is CCH 7. Both quantities $\alpha_{\parallel}$ and $\alpha_{\perp}$ of this liquid crystal molecule are non-linear function of temperature, but the quotient of $\alpha_{\perp}/\alpha_{\parallel}$ is linear one. This result may be described by the function $\alpha_{\perp}/\alpha_{\parallel} = a_3 \ \Delta T + b_3$. It is easy to prove that the quotient of two linear functions is also a linear function if the inclination coefficients of these functions are very small. In this case we can write the relation.

$$\alpha_{\perp}/\alpha_{\parallel} = a_3 \ \Delta T + b_3 = (\ a_1 \ \Delta T + b_1 \ ) / (\ a_2 \ \Delta T + b_2 \ ) =$$
$$= (\ \alpha_{\perp 1})/(\ \alpha_{\parallel 1}). \qquad\qquad 2)$$

We believe the $\alpha_{\perp 1}$ and $\alpha_{\parallel 1}$ are connected with the electron proton distance change of $\alpha_{\perp}$ and $\alpha_{\parallel}$. Taking the middle part of the mentioned relation (2) we can write the expression ($a_1 \ \Delta T + b_1$) in the new form as: ($a_1 \ \Delta T + b_1$) $= a_3 a_2 \ \Delta T^2 + (\ a_2 \ b_3 + a_3 \ b_2 \ ) \ \Delta T + b_3 \ b_2$.

Table I. Refractive indices, density, polarizability anisotropy $(\alpha_\| - \alpha_\perp)$, polarizability tensor component $\alpha_\|$ and order parameter S of CCH 7 liquid crystal Transition temperature to the isotropic liquid crystal $T_o = 84\ C^o$

ΔT	d g/cm^3	n_e	n_o	$(\alpha_\| - \alpha_\perp)$ 10^{-23} cm^3	$\alpha_\|$ 10^{-23} cm^3	S
13	0.8932	1.502	1.456	9.673	69.164	0.757
10.4	0.8908	1.498	1.455	9.683	69.019	0.708
8.4	0.8889	1.494	1.455	9.691	68.942	0.642
6.3	0.887	1.491	1.454	9.698	68.814	0.609
4.3	0.8851	1.486	1.454	9.703	68.681	0.527
2.4	0.8831	1.484	1.454	9.718	68.724	0.494
1.5	0.8815	1.481	1.454	9.726	68.681	0.444
0.5	0.8803	1.477	1.454	9.726	68.55	0.379
-0.5	0.876		1.462	9.75	68.918	
-2.5	0.8741		1.461	9.765	68.902	
-5.5	0.8718		1.46	9.784	68.919	
-10.5	0.8681		1.457	9.805	68.715	

From the experimental data we know that coefficient a_3 is very small (about $10^{-4}\ C^{-1}$) so a_3, a_2 must be small too. In this way we obtained the new linear relation:.

$$(a_1\ \Delta T + b_1) = (a_2\ b_3 + a_3\ b_2)\ \Delta T + b_3\ b_2. \qquad (3)$$

We see that in this case, $a_1 = (a_2\ b_3 + a_3\ b_2)$ or $a_1 = (a_3\ b_2)/ (1 - b_3)$ if the a_1 is equal to a_2. In the same way we obtain $b_1 = b_3\ b_2$. In the end we have $a_1 = (a_3\ b_2^2)/ (b_2 - b_1)$. We must remember the quantities b_1, b_2 are the values of $\alpha_\perp$ and $\alpha_\|$ for the ΔT equal to zero. Similarly, b_3 is the value of $\alpha_\perp / \alpha_\|$ when the ΔT equals zero. Besides the coefficient a_1 must be equal of a_2, because the same phenomenon influences the values of $\alpha_{\perp 1}$ and $\alpha_{\| 1}$, namely the change of electron proton distance with temperature. Now having the values a_3, b_2 and b_1 from experimental data we can calculate the functions of $\alpha_{\perp 1}$ and $\alpha_{\| 1}$. In order to find the conformational part of the change of $\alpha_\perp$ and $\alpha_\|$ we must perform subtractions $\alpha_{\perp 1} - \alpha_\perp$ and $\alpha_{\| 1} - \alpha_\|$.

EXPERIMENTAL

The aim of this work is the separation of conformational and electron proton distance changes existing in the polarizability tensor components $\alpha_\|$ and $\alpha_\perp$. The investigated liquid crystal has a chemical structure of molecule CCH 7. The data referring to a refractive indices

n_e and n_o , density d, polarizability tensor component $\alpha_\parallel$, $\alpha_\perp$, and polarizability anisotropy ($\alpha_\parallel$ - $\alpha_\perp$) are collected at the table 1. The temperature dependence the new quantity $A=\alpha_\perp /\alpha_\parallel$ is illustrated in Figure 1, where $\alpha_\parallel$ and $\alpha_\perp$ are a polarizability tensor components of molecule. As we know $\alpha_\parallel$ and $\alpha_\perp$ are non-linear functions of temperature what one can see in the Figure 2, where the temperature dependence of $\alpha_\parallel$ is illustrated. In our calculations the knowledge of b_1 and b_2 with good accuracy is very important.

Table II. Temperature dependence of the polarizability tensor components of CCH 7 molecule for conformational and electron proton distance changes

ΔT	$\alpha_{\parallel 1}$ 10^{-23} cm^3	$\alpha_{\perp 1}$ 10^{-23} cm^3	$\alpha_{\parallel c}$ 10^{-23} cm^3	$\alpha_{\perp c}$ 10^{-23} cm^3
13	69.705	59.996	-0.5415	-0.5053
10.4	69.506	59.796	-0.4876	-0.4611
8.4	69.353	59.643	-0.4114	-0.3924
6.3	69.192	69.482	-0.3786	-0.3672
4.3	69.039	59.329	-0.3582	-0.3511
2.4	68.894	59.184	-0.1694	-0.1776
1.5	68.825	59.115	-0.1440	-0.1599
0.5	68.748	59.038	-0.1981	-0.2139
-0.5	68.672	58.962	0.2465	0.2062
-2.5	68.519	58.809	0.3842	0.3294
-5.5	68.289	58.579	0.6302	0.5563
-10.5	67.906	58.196	0.8088	0.7134

Having the value of $\alpha_\parallel$ for ΔT equal zero we can find b_2 from Figure 2. We can do the same with the value of b_1 from the function of $\alpha_\perp$. In order to obtain a_3 we must calculate the inclination of the function A = $\alpha_\perp /\alpha_\parallel$ for mesophase from Figure 1. Having b_1, b_1 and a_3 one can calculate a_1, which will be used for calculation of the $\alpha_{\parallel 1}$ and $\alpha_{\perp 1}$. The temperature functions $\alpha_{\parallel 1}$ and $\alpha_{\perp 1}$ are connected with the electron proton distance change. If we want to obtain the change of $\alpha_\parallel$ or $\alpha_\perp$, connected with the conformation change of molecule , we must subtract $\alpha_{\parallel 1}$ or $\alpha_{\perp 1}$ from $\alpha_\parallel$ and $\alpha_\perp$. All results of our calculation for the molecule of CCH 7 liquid crystal are gathered in the Table II. In our calculations the knowledge of b_1 and b_2 with good accuracy is very important. We can find b_1 and b_2 from the relevant curves by reading the values of $\alpha_\parallel$ or $\alpha_\perp$ for ΔT equals zero. In Figure 3 the temperature dependencies of $\alpha_\parallel$ and $\alpha_{\parallel 1}$ are introduced. The results of subtractions $\alpha_\parallel$ - $\alpha_{\parallel 1}$ are plotted in Figure 4. This quantity is non-linear function of temperature

and is connected with the conformational part of the polarizability tensor component $\alpha_{\parallel}$. One can say that the separation of two parts of the polarizability tensor components, connected with the conformational and electron proton distance changes is possible for all liquid crystal molecules.
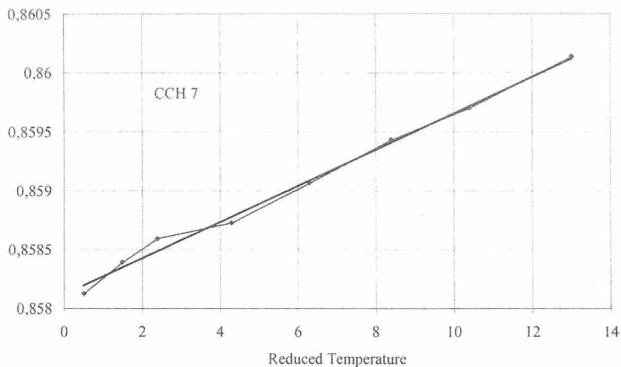

Fig.1. Temperature dependence of the quotient $A = \alpha_{\perp} / \alpha_{\parallel}$ of CCH 7 molecule

DISCUSSION

We can see from the results obtained in this article that the possibility of separation of conformational and electron proton distance changes exist for the polarizability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$ of the liquid crystal molecule. We can test our theory by the calculation of inclination sign of temperature dependence of $\alpha_{\parallel 1}$ and $\alpha_{\perp 1}$. In this work the temperature dependence of $\alpha_{\parallel 1}$ and $\alpha_{\perp 1}$ has the negative inclination sign. It means that the electron proton distance decreases when the temperature of the liquid crystal sample increases. We know that the intermolecular actions decrease in the liquid crystal sample when its temperature go up. Then the electron is strongly pulled by the protons in the core of each atom of liquid crystal molecule. So the electron proton distance must be shorter in higher temperature. It is seen from our investigation. We can assume, after these examinations, that the smallest electron proton distance exists in the isolated atom. These changes cause the increase of the polarizability tensor component of the liquid crystal molecule, when the temperature of sample decrease.
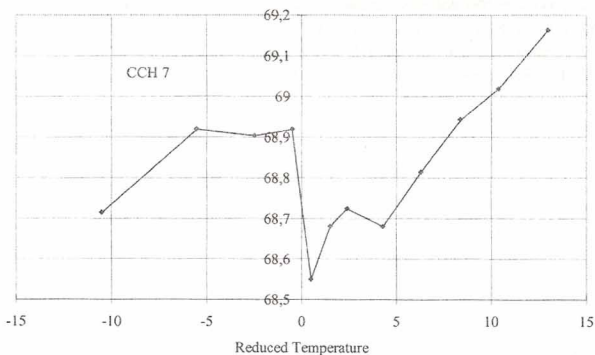
Fig. 2. Temperature dependence of the polarizability tensor component $\alpha_{\parallel}$ 10^{-23} cm^3 of CCH 7 molecule
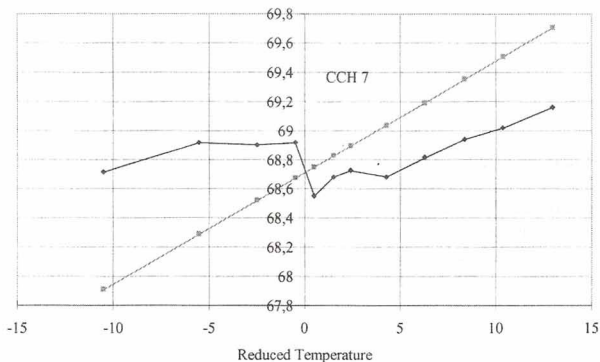

Fig. 3. Temperature dependence of polarizability tensor component $\alpha_{\parallel}$ 10^{-23} cm^3 and $\alpha_{\parallel 1}$ 10^{-23} cm^3 (straight line) of electron proton distance change of CCH 7 molecule

We remember that the inclination sign a_1 of the electron proton distance change is constant at all temperature ranges of the mesophase. Having the electron proton distance change of $\alpha_{\parallel}$ as $\alpha_{\parallel 1}$ one can calculate the conformational change of $\alpha_{\parallel}$ subtracting $\alpha_{\parallel 1}$ from $\alpha_{\parallel}$. The results of

these calculations are shown in the Figure 4. We see the $\alpha_{\|c} = \alpha_{\|} - \alpha_{\|1}$ has a very small value when compared with the value of $\alpha_{\|}$. In Figure 4 one can see that $\alpha_{\|c}$ is a non-linear function of temperature, having a positive and negative sign of inclination. The conformational changes of liquid crystal molecule can influence the polarizability tensor components in two directions. These conformational changes are connected with the hindered or free rotation of one part of the molecule around the other part. The rotations can have positive or negative direction and therefore the $\alpha_{\|c}$ can have both signs.
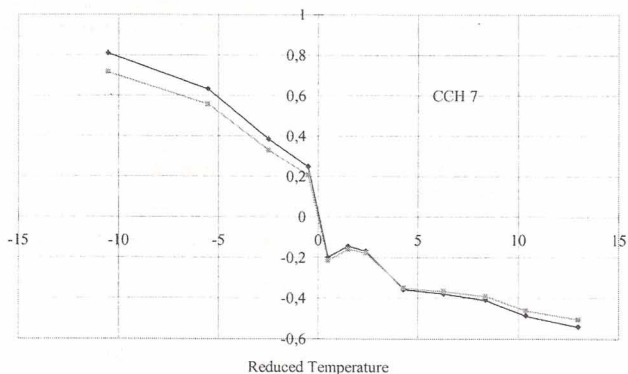

Reduced Temperature

Fig. 4. Temperature dependence of conformational part of $\alpha_{\|c}$ 10^{-23} cm^3 = $\alpha_{\|}$ - $\alpha_{\|1}$ and $\alpha_{\perp c}$ of CCH 7 molecule

As we know the polarizability tensor components $\alpha_{\|}$ and $\alpha_{\perp}$ can be written as the functions of electron proton distance by the mathematical formula [9].

$$\alpha_{\|} = 4[(\sum r_i\, e_{\|i}\,)^2]^2 \, / \, N\, r_o \; . \qquad \alpha_{\perp} = 4[(\sum r_i\, e_{\perp i}\,)^2]^2 \, / \, N\, r_o$$

where N - is number of electrons in the liquid crystal molecule. r_o - is the radius of electron Bohr's orbital in hydrogen atom. $[(\sum r_i\, e_{\|i}\,)^2$ - is the square of electron proton distance sum in molecule parallel to its main axes. The authors of article do not know how to divide the square sum like $[(\sum r_i\, e_{\|i}\,)^2$ into the two parts connected with the conformational and electron proton distance changes in this case. This problem will be solved in the future.

CONCLUSIONS

1). Both quantities $\alpha_{\parallel}$ and $\alpha_{\perp}$ of liquid crystal molecules are non-linear functions of temperature, but the quotient $(\alpha_{\perp}/\alpha_{\parallel})$ is a linear function.

2). The quotient $(\alpha_{\perp}/\alpha_{\parallel})$ may be described by the function $a_3\Delta T + b_3$.

3). The quotient $(\alpha_{\perp}/\alpha_{\parallel})$ is the linear function of temperature because the two phenomena influence the values of $\alpha_{\parallel}$ and $\alpha_{\perp}$. First the electron proton distance as a linear phenomenon and second the conformational change of molecule.

4). The separation of two parts of polarizability tensor components connected with a conformational and electron proton distance changes is possible for all liquid crystal molecules.

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