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Influence of Core Change of Liquid Crystal Molecules on the Trace of Its Polarizability Tensor

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The temperature dependence of the trace of the polarizability tensor was investigated for three liquid crystals, CB7, PCH 7, CCH7 whose molecule differ by the change of the molecule core. The results show that rotations of fragments of a molecule exist in the nematic phase of liquid crystals as well as in the solid state of CB7 and PCH7 liquid crystals. A linear temperature dependence of α_s exists in the isotropic liquid state of liquid crystals as well as for low molecular weight liquids.

INTRODUCTION

The relationship between a trace of the polarizability tensor of α_s of liquid crystal molecules and temperature was investigated in recent works.[1,2] If we want to investigate the conformation change of liquid crystal molecule we must find the physical quantity connected with the molecule. According to our suggestion two quantities may be used for this aim. One of them is the moment of innertia of molecule. The second one is the trace of polarizability tensor of molecule. The tensor trace is a quantity which values does not depend on the coordinate system and is a measure of change in the molecule conformation. A change in the conformation of a liquid crystal molecule may be caused by rotations of certain fragments of the molecule around its single bonds. Besides the other cause of conformation change there are at the liquid crystal molecule. It may be the change of length of chemical bonds and change of angle between these bonds.[3] Investigations of the dependence of α_s of low molecular weight liquid revealed them to be linear in nature. The hindered rotations do not take place in the low molecular weight liquid molecule.

In this work we use a undirectly manner of determination of polarizability tensor component. Namely we only need to use the results of Saupe and Maier theory[4] which describe the relationship between molecular order parameter S and polarizability tensor components. According to the Saupe-Maier theory, the polarizability tensor components α_1 and α_2 of liquid crystal sample depend on the polar-

izability tensor components $\alpha_{\parallel}$ and $\alpha_{\perp}$ of liquid crystal molecule and on the arrangement order parameter S by the relations:

$$\alpha_1 = \bar{\alpha} + (\alpha_{\parallel} - \alpha_{\perp}) \frac{2}{3} S \tag{1}$$

$$\alpha_2 = \bar{\alpha} - (\alpha_{\parallel} - \alpha_{\perp}) \frac{1}{3} S \tag{2}$$

where $\bar{\alpha} = (\alpha_{\parallel} + 2\,\alpha_{\perp})/3$. The quantity $\alpha_1 + 2\,\alpha_2 = \alpha_s$ is the trace of the polarizability tensor of a liquid crystal sample and is equal to the same quantity α_s of a liquid crystal molecule.

The equality $\alpha_1 + 2\,\alpha_2 = \alpha_{\parallel} + 2\,\alpha_{\perp} = \alpha_s$ does not mean that α_1 is equal to $\alpha_{\parallel}$ and α_2 equal to $\alpha_{\perp}$. This results from the fact that an additional condition connected with the arrangement order parameter S must be satisfied between the quantities α_1, α_2 and $\alpha_{\parallel}$, $\alpha_{\perp}$. This condition may be obtained by substracting from equation (1) a equation (2). In this case the equation for the molecular order parameter S is obtained in the form:

$$S = \frac{\alpha_1 - \alpha_2}{\alpha_{\parallel} - \alpha_{\perp}} = 1/2\,(3\,\overline{\cos^2\theta} - 1) \tag{3}$$

where θ is the angle between the main axis of a molecule and the direction of the optical axis of a liquid crystal sample. Equation (3) has been many times used in the investigations of molecular order parameter S of cholesteric and nematic liquid crystals.[5–8]

The aim of this work is to investigate the temperature dependence of the trace of the polarizability tensor of three liquid crystals which have a changed number of benzene rings in the core of their molecules. These studies are carried out for two state of liquid crystals—isotropic liquid and nematic phase.

EXPERIMENTAL

In order to calculate of α_s for a liquid crystal molecule the data of density and refractive index of liquid crystals were taken from a literature.[9] The values of polarizability tensor components of the liquid crystals samples were obtained by using the Lorenz-Lorentz equation in this work. In the literature there are also equations due to Vuks and Neugebauer. Neugebauer's equation is rarely used because of difficulties in the calculations. Vuks equation is equivalent to Lorenz-Lorentz equation in the case of the isotropic liquid state. The problem of local field at investigations of liquid crystal polarizability is not closed up to now. So that we have decided to calculate of α_1 and α_2 values by the use the Lorenz-Lorentz equation.

The calculated values of the trace of the polarizability tensor of a liquid crystal molecule are collected in Tables I–III. Moreover the temperature dependence of

TABLE I

Density (d), refractive indices (n_e and n_o) for sodium light and trace of polarizability tensor α_s for CB7[8]

t°C	d g/cm^3	n_e	n_o	α_s 10^{24} cm^3
30	1.0012	1.702	1.521	109.43
31.5	0.9998	1.698	1.521	109.39
33	0.9985	1.695	1.521	109.39
34.5	0.9970	1.692	1.521	109.42
36	0.9956	1.688	1.522	109.49
37	0.9946	1.683	1.523	109.47
38	0.9935	1.680	1.523	109.45
40	0.9912	1.672	1.525	109.53
42	0.9886	1.660	1.527	109.45
42.5	0.9878	1.655	1.531	109.73
43.4	0.9840	—	1.573	110.47
46	0.9815	—	1.571	110.43
49	0.9787	—	1.570	110.58
54	0.9746	—	1.567	110.58

TABLE II

Density (d), refractive indices (n_e and n_o) for sodium light and trace of polarizability tensor α_s for PCH7[8]

t°C	d g/cm^3	n_e	n_o	α_s 10^{24} cm^3
31	0.9520	1.593	1.484	107.53
34	0.9497	1.589	1.484	107.57
37	0.9472	1.586	1.483	107.56
40	0.9445	1.581	1.483	107.60
43	0.9419	1.578	1.482	107.60
46	0.9391	1.575	1.482	107.75
49	0.9362	1.569	1.482	107.75
52	0.9333	1.563	1.483	107.86
54	0.9312	1.559	1.483	107.88
56	0.9289	1.551	1.484	107.80
57	0.9275	1.547	1.485	107.85
58	0.9230	—	1.506	108.50
60	0.9212	—	1.505	108.53
63	0.9188	—	1.503	108.45
68	0.9150	—	1.501	108.53

α_s is plotted in Figures 1–3. These figures show that dependence of α_s of the investigated liquid crystals on temperature in their isotropic liquid state is linear. In our opinion this linear dependence is caused by a change of length of chemical bonds and angles between these bonds at molecule.

The appropriate structural formulae of the three liquid crystals are shown in Figure 4 in which axes of rotations suitable fragments of molecule are illustrated. The end chain C_7H_{15} is stretched and deviated from the position of the first axis. This chain belongs to a sufficiently rigid segment of the molecule because of the strong hindered rotations of its side groups. The minimum potential energy of the hindered rotation of side groups is reached in a transpositions. At higher temperatures the end chain may be swirled such that the rotation of the swirling end chain

TABLE III

Density (d), refractive indices (n_e and n_o) for sodium light and trace of polarizability tensor α_s for CCH7.[8]

t°C	d g/cm³	n_e	n_o	α_s 10^{24} cm³
71	0.8932	1.502	1.456	107.76
73.6	0.8908	1.498	1.455	107.66
75.6	0.8889	1.494	1.455	107.64
77.7	0.8870	1.491	1.454	107.56
79.7	0.8851	1.486	1.454	107.44
81.6	0.8831	1.484	1.454	107.56
82.5	0.8815	1.481	1.454	107.55
83.5	0.8803	1.477	1.454	107.44
84.5	0.8760	—	1.462	108.04
87	0.8741	—	1.461	108.07
90	0.8718	—	1.460	108.15
95	0.8681	—	1.457	108.21

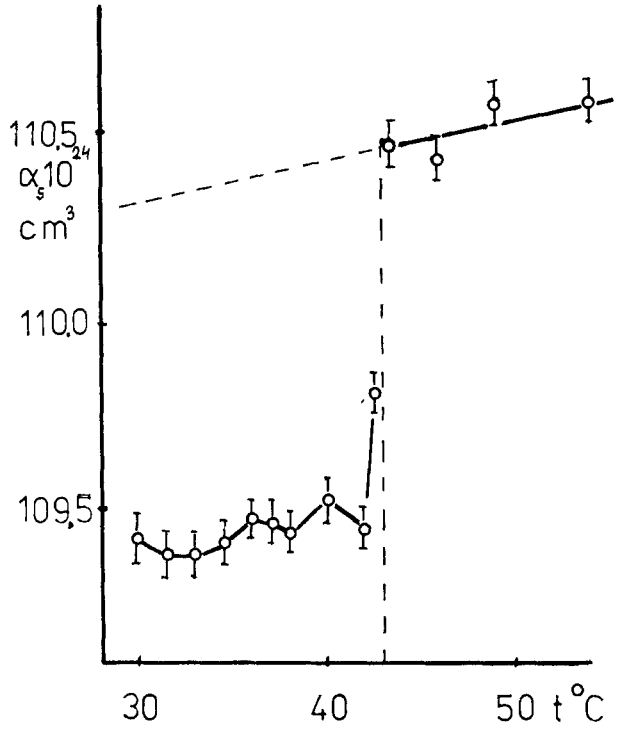

FIGURE 1 Temperature dependence of the trace of polarizability tensor of CB7.

around the first axis does not change clearly values of the polarizability tensor of trace of α_s. Therefore all the investigated liquid crystals are characterized by a linear temperature dependence of α_s in their isotropic liquid state.

The temperature dependence of α_s in Figures 1–3 are clearly different in the nematic phase of all investigated liquid crystals. Since the number of benzene rings is different in the molecule of our liquid crystals it is expected that the shape of

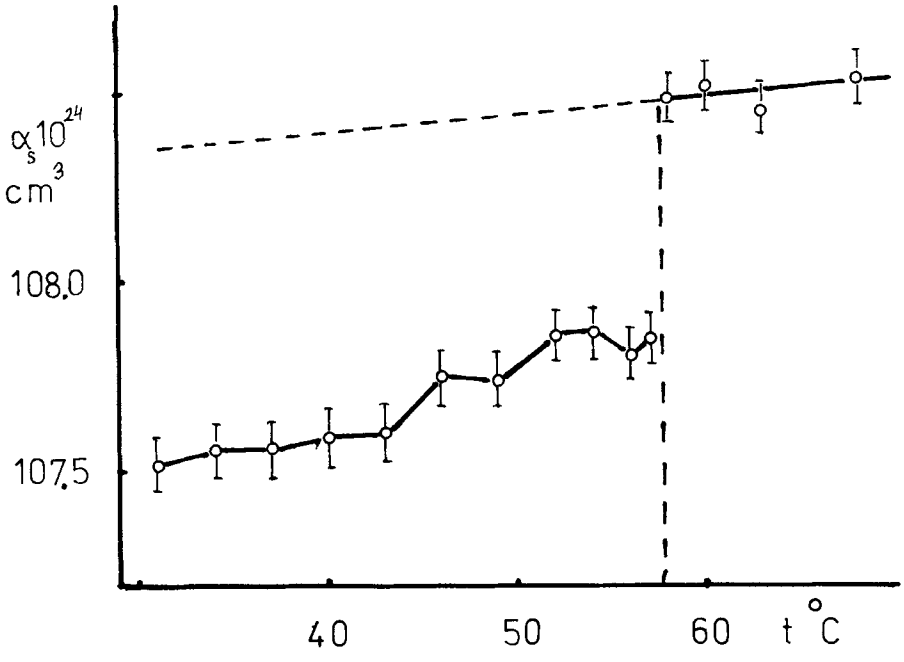

FIGURE 2 Temperature dependence of the trace of polarizability tensor of PCH7.

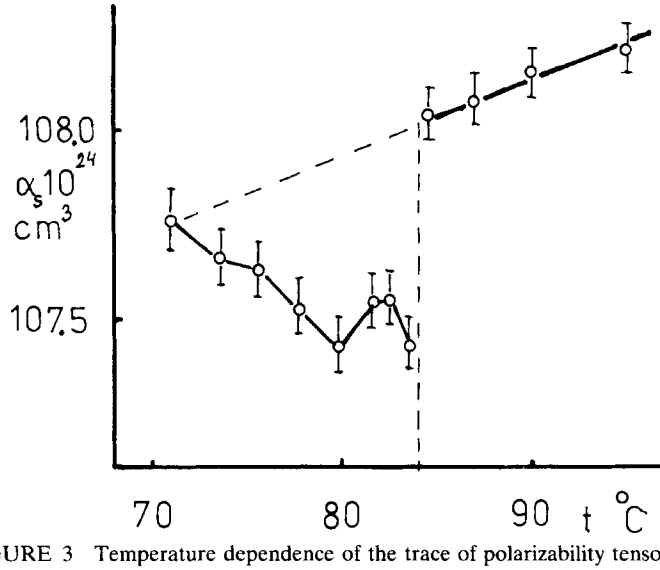

FIGURE 3 Temperature dependence of the trace of polarizability tensor of CCH7.

the molecule as well as the number of possible internal rotations is also different. Figure 4. The plane benzene ring in CB7 molecule is changed to the cyclohexyl ring in the molecule of PCH 7. This cyclohexyl ring have a chair shape and, therefore, two fragments of a PCH7 molecule may be rotated around the first axis.

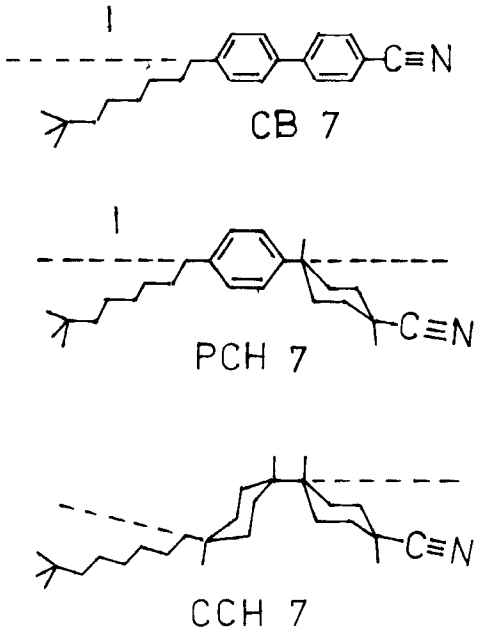

FIGURE 4 Chemical and space structure of CB7, PCH7, and CCH7 molecule and rotation axes of molecule fragments.

These rotations and the change in the position of centre of mass of the molecule affect on value of its trace of the polarizability tensor.

In the CB7 molecule the benzene rings can also rotate around the first axis but it does not give any change of trace of polarizability tensor. Therefore the temperature dependence of α_s is nearly a straight line parallel to the temperature axis for the CB7 molecule, while it increases with temperature for the PCH7 molecule.

In the CCH7 molecule there are two cyclohexyl rings in a molecule core. Therefore it has a new rotation axis. A change in the molecule core in this case cause a noticeable difference in the temperature dependence of α_s. The additional rotation leads to the wirling of molecule as it is seen from the plot of Figure 3. The above results show that a change in the molecule core of our liquid crystals has a evident influence on the character of the temperature dependence of α_s in the nematic state. In contrast with this influence, an increase in the number of CH_2 groups in the end chain of a liquid crystal molecule does not influence on the character of the temperature dependence of α_s.

In order to verify that the rotation does not exist in the molecule of liquid crystal at their isotropic state we calculated the trace of polarizability tensor of low molecular weight liquid. In this case the measurements of density and refractive index for bromocyclohexane was made with the accurency 10^{-4}.

Density measurements were made by method described elsewhere[10] and an Abbe refractometer was employed to determine refractive indices. The values of the trace of polarizability tensor of bromocyclohexane were calculated by the use of Lorenz-Lorentz equation. These results are shown in Figure 5 and in Table IV. Figure 5

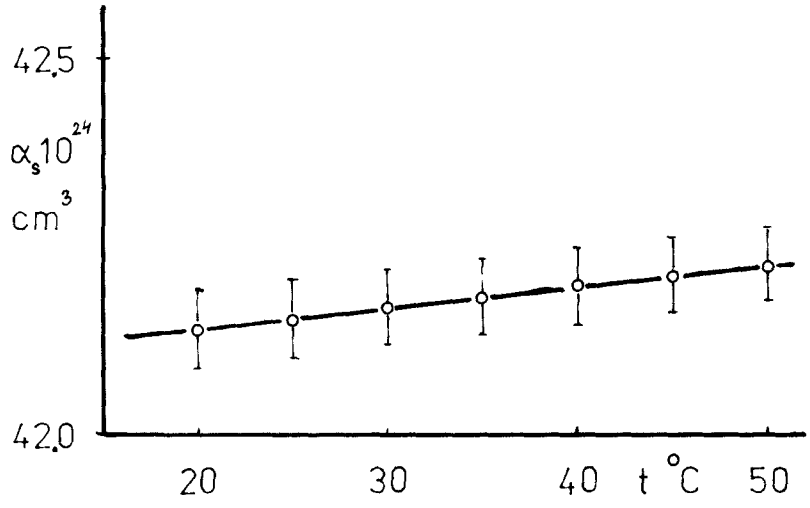

FIGURE 5 Temperature dependence of trace of polarizability tensor of bromocyclohexane.

TABLE IV

Density (d), refractive indices (n) and trace of polarizability tensor of α_s for Bromocyclohexane.

t°C	d g/cm^3	n	α_s 10^{24} cm^3
15	1.3402	1.4941	42.13
20	1.3344	1.4917	42.14
25	1.3284	1.4893	42.15
30	1.3225	1.4870	42.17
35	1.3166	1.4846	42.18
40	1.3107	1.4823	42.199
45	1.3049	1.4799	42.21
50	1.2991	1.4776	42.22

reveals that the temperature dependence of the trace of the polarizability tensor of bromocyclohexane is linear. We assume that the linear temperature dependence of α_s of low molecular weight liquid is not connected with the possibility of rotation of parts of the molecule. The liquid crystals in isotropic liquid state give the linear temperature dependence of α_s too. Therefore the molecules of liquid crystals in this state are not deprived of possibility of rotation of their parts.

Conclusions

1. Change in core of a molecule of liquid crystals has a clear influence on the character of the temperature dependence of the trace of polarizability tensor.
2. The hindered or free rotations of fragments of a liquid crystal molecule can occur only in the nematic state of liquid crystals.
3. The change of length of chemical bonds and of angle between these bonds may be taken as the other cause of conformation change of liquid crystals molecules.

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