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Polarizability Anisotropy of CB6, CB7, CB8 and OCB8 Liquid Crystal Molecules

The temperature dependence of the polarizability anisotropy ($\alpha_{\parallel}-\alpha_{\perp}$), relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ and polarizability tensor components α_{\parallel} and α_{\perp} were investigated for four liquid crystals, CB6, CB7, CB8, and OCB8, whose molecules differ by the number of CH_2 group in the alkyl chain. It was found that: (1) a change in the number of CH_2 group in the alkyl chain does not lead to the same change in the values of ($\alpha_{\parallel}-\alpha_{\perp}$) and $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$, (2) the values of α_{\parallel} and α_{\perp} increase with the addition of a CH_2 group, and that (3) abrupt changes in the values of ($\alpha_{\parallel}-\alpha_{\perp}$) and $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ occur at the temperature of nematic-isotropic phase transition. The implications of the results are discussed.

Keywords: liquid crystals; polarizability anisotropy of molecules; phase transition

1. Introduction

It is well known that liquid crystals are characterised by the anisotropy of some of their physical properties like dielectric permittivity, birefringence and viscosity. The anisotropy is associated with the arrangement of molecules. This arrangement of molecules restricts the thermal motion of liquid crystal molecules. Axially symmetrical arrangement of molecules exists in liquid crystal samples in the mesophase state.

The birefringence properties of liquid crystals 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 using the equations proposed recently by the author (ADAMSKI 1989,1994), or by using Lorenz-Lorentz', Vuks' and Neugebauer's equations (VUKS 1966; NEUGEBAUER 1954) relating α_1 and α_2 with the refractive indices. The second polarizability tensor, with components α_{\parallel} and α_{\perp} , is connected with the liquid crystal molecule. The liquid crystal molecules are anisotropic. Both polarizability tensors are symmetrical, but the tensors of molecules have three different components: $\alpha_{\parallel} = \alpha_z$, α_x and α_y in the main coordinate system. 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 (1961) used them in the theory of arrangement of liquid crystal molecules. The results of this theory are equations combining α_1 and α_2 with α_{\parallel} , α_{\perp} and an order parameter S of the molecules (SAUPE, MAIER 1961):

$$\alpha_1 = \alpha_s / 3 + (2/3)(\alpha_{\parallel} - \alpha_{\perp}) S, \alpha_2 = \alpha_s / 3 - (1/3)(\alpha_{\parallel} - \alpha_{\perp}) S. \quad (1)$$

The quantities α_{\parallel} , α_{\perp} and $(\alpha_{\parallel} - \alpha_{\perp})$, which are physical properties of liquid crystal

molecules, depend on the temperature of liquid crystal sample. Their values can change when the conformation of molecule undergo a change. Therefore, measurements of the values of these quantities enable one to obtain information about the change in the conformation of molecules.

Our recent investigations of the dependence of α_{\parallel} and α_{\perp} on temperature revealed that, when a liquid crystal is in the nematic or smectic phase, the change in the conformation of molecules may be connected with the free or hindered rotations of some part of molecule around the other (ADAMSKI 1989). The component α_{\parallel} or α_{\perp} is a linear function of temperature for the isotropic liquid state of liquid crystal. This means that the length of the chemical bond and the angle between them are changed in this case. The polarizability anisotropy ($\alpha_{\parallel} - \alpha_{\perp}$) does not depend on temperature, implying thereby that it also does not depend on the change in the conformation of molecules. From ($\alpha_{\parallel} - \alpha_{\perp}$) one can infer how the physical properties of molecules are changed when their core or the alkyl chain is changed. Recently, the author reported (ADAMSKI 1995, 1996, 1997) the influence of a change in the benzene ring in a hexyl ring in the three liquid crystals: CB7, PCH7 and CCH7. It was found that the values of ($\alpha_{\parallel} - \alpha_{\perp}$) for the above liquid crystal molecule are different.

In this paper the results of a study of the influence of CH_2 group in the alkyl chain of liquid crystal molecules on the values of polarizability anisotropy ($\alpha_{\parallel} - \alpha_{\perp}$), relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{\parallel} - \alpha_{\perp})$ and polarizability tensor components α_{\parallel} and α_{\perp} are presented and discussed.

2. Compounds and the method of calculations

Four liquid crystals CB6, CB7, CB8 and OCB8 characterised by difference in the constitution of their molecules were selected for the study. The molecules of these liquid crystals are composed of two benzene rings, CN group and alkyl chain. The benzene rings and CN group are a rigid part of molecule. The alkyl chain can change the number of CH_2 group, which gives the next member of the homologue. Therefore, the difference lies in the additional CH_2 group in the alkyl chain, which enables us to investigate the influence on the polarizability anisotropy of the molecules.

The method of calculation of polarizability anisotropy ($\alpha_{\parallel} - \alpha_{\perp}$), and polarizability tensor components α_{\parallel} and α_{\perp} of liquid crystal molecules from the refractive data has been described earlier (ADAMSKI 1996). The basic equations for the calculations are:

$$(\alpha_{\parallel} - \alpha_{\perp}) = (M/N)[(n_e + n_o)/k_A d], \quad (2)$$

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

$$\alpha_{\perp} = (M/N)[(n^2 - 1)/d - (n_e + n_o)/3 k_A d], \quad (4)$$

where M is the molecular weight of liquid crystal, N is the Avogadro number, d is the density of liquid crystal, n_e and n_o are the refractive indices of extraordinary and ordinary light, respectively, $n^2 = (n_e^2 + 2n_o^2)/3$ and k_A is a coefficient in the Valentova equation: $S = k_A (n_e - n_o)$ (VALENTOVA et al. 1985; POGGI et al. 1973).

The quantities α_{\parallel} , α_{\perp} and ($\alpha_{\parallel} - \alpha_{\perp}$) for the liquid crystals were calculated from the values of their refractive indices, the density d and the coefficient k_A . The experimental data of refractive indices and densities of the liquid crystals were taken from a previous study (ADAMSKI 1997). The accuracy in the measurements of Δn_e and Δn_o was $\pm 10^{-3}$ while that of Δd was $\pm 10^{-3} \text{ g/cm}^3$. The relative error in the estimation of the polarizability anisotropy ($\alpha_{\parallel} -$

α_{\perp}) calculated from these data is 0.002. Taking a typical value of $40 \cdot 10^{-23} \text{ cm}^3$ for $(\alpha_{\parallel} - \alpha_{\perp})$, one obtains $\Delta(\alpha_{\parallel} - \alpha_{\perp}) = 0.08 \cdot 10^{-23} \text{ cm}^3$.

3. Results

The calculated values of the polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ and the polarizability tensor component α_{\parallel} for the four liquid crystal molecules are presented in Figures 1a and 1b, respectively, as a function of reduced temperature $\Delta T = T_0 - T$ where T_0 is the transition temperature of a liquid crystal from mesophase to the isotropic liquid state. The values of α_{\perp} can be obtained by subtracting $(\alpha_{\parallel} - \alpha_{\perp})$ from α_{\parallel} .

4. Discussion

Figures 1a and 1b show that the value of the polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ and polarization tensor component α_{\parallel} are different for different liquid crystals. A careful examination of the figure reveals that the value of $(\alpha_{\parallel} - \alpha_{\perp})$ is practically a constant for a liquid crystal molecule in the entire range of temperature of measurements (Figure 1a) but the value of α_{\parallel} for most of the compounds shows a general increasing tendency with an increase in temperature (Figure 1b). However, as seen from Figure 1b, a CH_2 group does not change the values of α_{\parallel} (and hence of α_{\perp}) of different liquid crystal molecules by the same amount. This results in different values of $(\alpha_{\parallel} - \alpha_{\perp})$ for different molecules (Figure 1a).

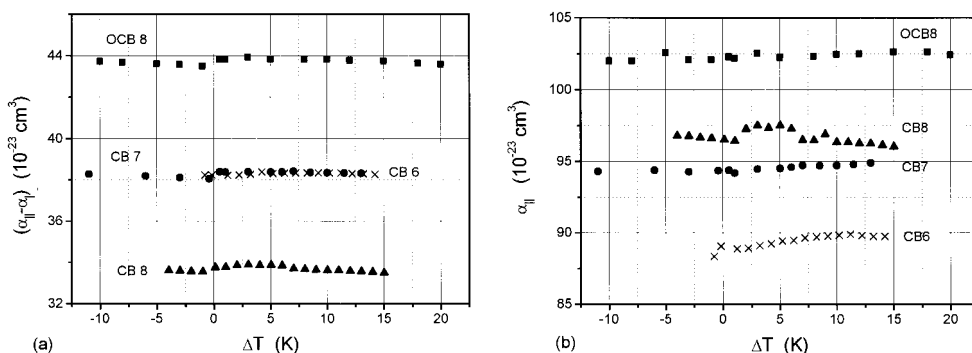


Fig. 1: Plots of (a) polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ and (b) polarization tensor component α_{\parallel} for different liquid crystal molecules against reduced temperature ΔT .

The above general increasing trend of α_{\parallel} for different liquid crystal molecules with temperature may be attributed to a decrease in the density d of liquid crystals with increasing temperature (see Eq. (3)). However, a roughly constant value of $(\alpha_{\parallel} - \alpha_{\perp})$ in the entire range of temperature used for measurements suggests that the quantity $(n_e + n_o)/d$ is practically temperature independent. In other words, $(n_e + n_o)$ also increases with temperature (see Eq. (2)).

In contrast to above roughly constant values of polarizability anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ for different liquid crystal molecules in the entire range of temperature, a careful examination of the dependence of $(\alpha_{\parallel} - \alpha_{\perp})$ on reduced temperature ΔT at the temperature of nematic-

isotropic phase transition reveals a sudden 1 - 1.5% change from the the average $(\alpha_{\parallel}-\alpha_{\perp})$. This behaviour is illustrated in Figure 2 for CB7 and OCB8. The figure reveals that $(\alpha_{\parallel}-\alpha_{\perp})$ exhibits linear dependence on reduced temperature ΔT in the nematic and isotropic liquid states. The slopes of the linear plots are different in the mesophase and isotropic liquid states, and breaks in the linear plots occur at the transition temperature. The appearance of sudden breaks in the plots of $(\alpha_{\parallel}-\alpha_{\perp})$ against ΔT implies that the changes in (n_e+n_o) and d for the molecules of a liquid crystal with temperature do not compensate each other (see Eq. (2)).

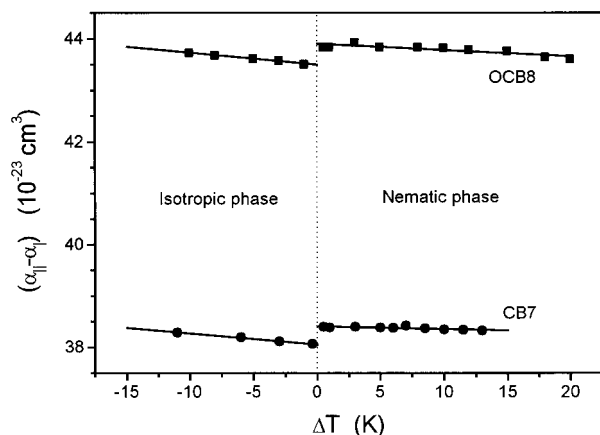


Fig. 2: Plots of the dependence of polarizability anisotropy $(\alpha_{\parallel}-\alpha_{\perp})$ of CB7 and OCB8 on reduced temperature ΔT .

In order to exclude the effect of density d on the temperature dependence of polarizability anisotropy $(\alpha_{\parallel}-\alpha_{\perp})$ and assess the influence of the term (n_e+n_o) alone, the temperature dependence of ratios like $(\alpha_{\parallel}-\alpha_{\perp})/\alpha_{\perp}$ and $(\alpha_{\parallel}-\alpha_{\perp})/\alpha_{\parallel}$ or their inverse quantities $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ and $\alpha_{\parallel}/(\alpha_{\parallel}-\alpha_{\perp})$, which do not contain the density d , should be analysed. The latter quantities have the advantage that they predict a linear dependence (cf Eqs (2) and (4)):

$$\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp}) = k_A(n^2 - 1)/(n_e+n_o) - 1/3. \quad (5)$$

According to Eq. (5) $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ is also a measure of the polarizability anisotropy of liquid crystal molecules, and all changes in its value are associated with the nature of molecules.

The plots of the relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ against ΔT are illustrated in Figure 3. It may be seen from the figure that the average value of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ is 1.33, 1.46 and 1.87 for CB6, CB7 and CB8 liquid crystals, respectively. This means that the relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ increases with the addition of a CH_2 group, but the increase is not the same for a CH_2 group. It should be noted that the average value of 1.34 of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ for OCB8 is comparable with that for CB6 but is much lower than that for CB8. Obviously, the number of CH_2 group in the alkyl chain alone does not determine the average value of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$.

Figure 3 also shows that, as in Figure 2, the dependence of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ on ΔT is practically linear both in the nematic and isotropic phases. The slopes and the intercepts of the plots are listed in Table 1. The difference in the values of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ at the transition temperature is up to 1.7% (for CB7).

Examination of the slopes of plots for CB6, CB7 and CB8 reveals that their values decrease with the addition of a CH_2 group. In fact the slope for CB8 is negligibly low that

$\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ is practically temperature independent and a break is not discerned at the transition temperature. The value of the slope for OCB8 is much higher than that for CB8 but is close to those for CB6 and CB7. This observation suggests that the slopes and intercepts of plots of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ against ΔT are inversely related. The value of the intercept reflects the average value of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ for a liquid crystal. The fact that $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ increases with temperature means that the quantity $k_A(n^2-1)/(n_e+n_o)$ is temperature dependent.

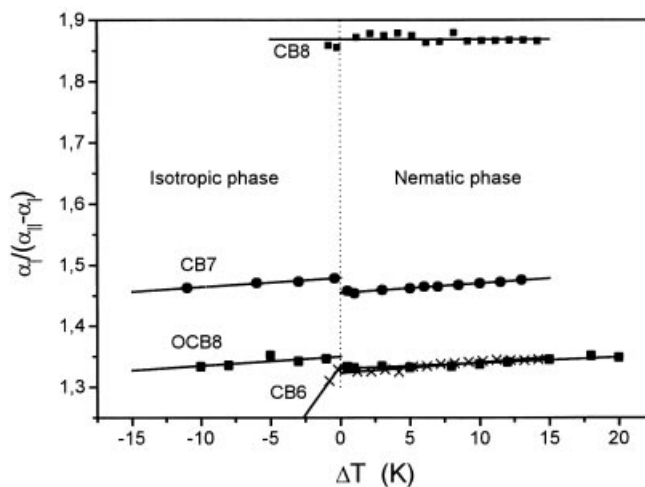


Fig. 3: Plots of relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ for CB7 and OCB8 on reduced temperature ΔT .

The practically constant values of $(\alpha_{\parallel}-\alpha_{\perp})$ and $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$, which are characteristic for a liquid crystal, mean that they contain information about its chemical constitution. Since the values of $(\alpha_{\parallel}-\alpha_{\perp})$ and $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ poorly depend on temperature, they may be considered as a visiting card of the liquid crystal molecule.

Compound ¹⁾	Slope (K ⁻¹)	Intercept
CB6 N	$1.74 \cdot 10^{-3}$	1.3232
I	$3.18 \cdot 10^{-2}$	1.3355
CB7 N	$1.58 \cdot 10^{-3}$	1.4546
I	$1.48 \cdot 10^{-3}$	1.4789
CB8 N	$-5.81 \cdot 10^{-6}$	1.8687
I	$6.0 \cdot 10^{-6}$	1.8795
OCB8 N	$9.76 \cdot 10^{-4}$	1.3301
I	$1.53 \cdot 10^{-3}$	1.3503

¹⁾ N and I denote nematic and isotropic phases, respectively.

Table 1: Values of slope and intercepts of plots of $\alpha_{\perp}/(\alpha_{\parallel}-\alpha_{\perp})$ against ΔT

In the literature (CHELKOWSKI 1979) in low molecular weight liquids, one finds the description of a phenomenon, called Kerr effect, which assumes that the polarizability anisotropy of low molecular weight liquid molecule is a constant, independent of temperature. In the light of our results it can be concluded that to a good approximation this assumption is also valid in the case of liquid crystal molecules. However, since a CH₂ group does not change the values of α_{\parallel} and α_{\perp} of different liquid crystal molecules by the same

amount, it is obvious that the method of calculation of dipole moments used in the literature (MINKIN et al. 1970) from $\alpha_{||}$ or α_{\perp} by the addition of polarizability components connected with the chemical bonds of groups like CH_2 is wrong. The same argument also applies to the polarizability anisotropy ($\alpha_{||}-\alpha_{\perp}$) and relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{||}-\alpha_{\perp})$.

5. Conclusions

- (1) The quantities ($\alpha_{||}-\alpha_{\perp}$), $\alpha_{\perp}/(\alpha_{||}-\alpha_{\perp})$, $\alpha_{||}$ and α_{\perp} are typical characteristics of liquid crystal molecules.
- (2) Change in the number of CH_2 group in an alkyl chain does not cause the same change in the values of polarizability anisotropy ($\alpha_{||}-\alpha_{\perp}$) and relative polarizability anisotropy $\alpha_{\perp}/(\alpha_{||}-\alpha_{\perp})$ of different liquid crystal molecules.
- (3) All liquid crystal investigated here show a weak linear dependence of ($\alpha_{||}-\alpha_{\perp}$) and $\alpha_{\perp}/(\alpha_{||}-\alpha_{\perp})$ on temperature. At the transition temperature to isotropic liquid state, ($\alpha_{||}-\alpha_{\perp}$) and $\alpha_{\perp}/(\alpha_{||}-\alpha_{\perp})$ show a sudden change in their values up to 1.7 % of the average values.

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