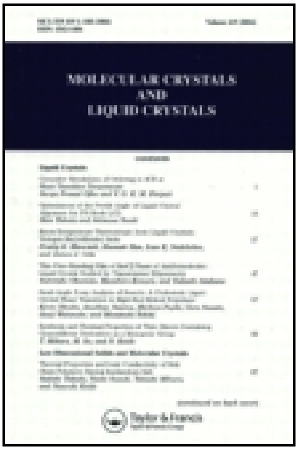

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Inter- and Intramolecular Reorientations in Liquid Crystals

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Inter- and Intramolecular Reorientations in Liquid Crystals

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Data of dielectric relaxation measurements so far obtained for isotropic, nematic and solid phases of seven members of di-*n*-alkoxyazoxybenzene (*n*-OAOB) homologous series have been reanalysed in order to discuss the influence of the end chains on the molecular reorientations. The relaxation times characterizing the intermolecular reorientations show odd-even alternation in the temperature range both below and above the clearing points. Below the melting temperatures dielectric relaxation processes have been observed for high-temperature solid phases of two substances with $n = 4$ and 5.

The specific behaviour of reorientational dynamics at both clearing and melting points may be related to the corresponding behaviour of thermodynamic quantities.

1. INTRODUCTION

The reorientational dynamics of molecules in liquid crystals is a great variety and complexity. The motions can be classified into two types: collective and single-molecular ones. Among the single-molecular motions one can deal with reorientations of molecules as a whole (intermolecular reorientations) or reorientations of molecule segments (intramolecular reorientations).

The problem has been the subject of intensive investigations for about three decades with involving several spectroscopic techniques.[1,2] Results obtained by different methods frequently happened not to be in agreement with each other, so that it requires a long time of systematic studies to elucidate the disagreement. Only recently collective reorientations in nematic phase have been confirmed to appear in kilohertz range.[3] The disagreement concerning the time scales of the fast dielectric relaxation (DR) process and the process observed by quasi-elastic neutron scattering (QNS) method could be explained by assuming different mechanisms of reorientations: The first process originates from the reorientation of molecule around the long axis, while the other one is related to the reorientation of molecule segments around the para-axes.[1,4,8]

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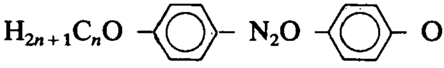
It seems obvious that the mutual relation between intermolecular and intramolecular reorientations can be verified with greater certainty by carrying out the research for the substances of a given homologous series. This is the case of di-*n*-alkoxyazoxybenzenes (*n*.OAOB) which have been systematically studied by the DR and QNS methods.[1,4-8] For substances with *n* from 1 to 7 Janik *et al.*[9] have recently managed to discover an odd-even effect of so called 'excess elasticity' parameter introduced in a new analysis of QNS results.

In this paper we present and discuss some results of analysis of dielectric relaxation data so far obtained for *n*.OAOB substances. The attention has been focused on the influence of the end chains on the reorientation properties. In the clearing temperature region the odd-even alternation of relaxation times has been shown to exist. For substances with $n = 4$ and 5 the reorientational disorder has been found below the melting points.

2. SUBSTANCES AND EXPERIMENTAL TECHNIQUE

Di-*n*-alkoxyazoxybenzenes are well known liquid-crystalline substances, whose general chemical formula is:



The substances possess three dipole moments situated at azoxy and at alkoxy groups. The clearing temperatures, T_c, show alternation effect. The smectic structures were found for substances with $n \geqslant 6$.

Gruger et al.[10] have shown the existence of more than one solid phase for all the first seven members of the homologous series. For future discussion the solid state polimorphism of 4.OAOB and 5.OAOB are of special importance. The phase sequence of these two substances is the following:

4.OAOB: CrIV-42.3°C-CrIII-50.2°C-CrII-87.5°C-CrI-102°C-N [11]
5.OAOB: CrII-69.0°C-CrI-78.5°C-N.

For the liquid crystals, the complex dielectric permittivities $\varepsilon^*_\lambda = \varepsilon'_\lambda - i\varepsilon''_\lambda$ are measured as a function of frequency for two orientations of sample, i.e. $\perp$ and $\|$. In order to describe a dielectric relaxation process, one uses the Cole-Cole equation

$$\frac{\varepsilon^*_\lambda - \varepsilon_{\infty,\lambda}}{\varepsilon_{0,\lambda} - \varepsilon_{\infty,\lambda}} = \frac{1}{1 + (i\omega\tau_\lambda)^{1-\alpha_\lambda}}, \qquad (1)$$

where: λ denotes the isotropic (is) or two orientations of the nematic phases ($\perp$ or $\|$), $0 \leqslant \alpha_\lambda < 1$, α_λ is a parameter describing the distribution of relaxation times, τ_λ.

The temperature dependence of the relaxation times observed for liquid crystals can be fitted by Arrhenius equation

$$\tau_\lambda = \tau_{0,\lambda} \exp(\Delta E_\lambda / RT), \qquad (2)$$

where ΔE_λ is the activation energy of the reorientation process.

3. RESULTS OF DIELECTRIC RELAXATION INVESTIGATIONS FOR *n*.OAOB

The results of the first period of studying dielectric relaxation properties of di-*n*-alkoxyazoxybenzenes were presented in the work of Axmann.[12] In this work the results obtained for four members of the homologous series with $n = 1, 4, 6$ and 7 were presented. During the last few years the Cracow Liquid Crystal Group carried out systematic investigations of dielectric properties of substances with $n = 2 \div 5$ in both the megahertz and gigahertz frequency ranges and for all the liquid and solid phases.[4–8] The results obtained on the same apparatus for subsequent members of *n*.OAOB series enable us to discuss the influence of the end chains on the DR properties with more confidence.

3.1. DR properties in the vicinity of the clearing point

The main results for the liquid phases of *n*.OAOB obtained by these two groups can be summarized as follows. In isotropic phases of the substances with $n = 1 \div 7$ only one relaxation process has been observed at high frequency range. This is a complex process characterized by a distribution parameter $\alpha_{is} \approx 0.25$, a relaxation time $\tau_{is} \approx 10^{-11} \div 10^{-10}$ sec and an activation energy $\Delta E_{is} \approx 25 \div 20$ kJ/mol. On passing to the nematic phase the relaxation pictures for the two orientations become quite different. In the perpendicular orientation one observes the Cole-Cole diagram similar to that seen in the isotropic phase, i.e. with $\alpha_{\perp} \approx 0.20$, $\tau_{\perp} \approx 10^{-11} \div 10^{-10}$ sec, and activation energy of the order of 20 kJ/mol. In the parallel orientation, apart from a high-frequency relaxation process a second process appears in megahertz frequency range. This process is characterized by a single relaxation time, $\tau_{\parallel} \approx 10^{-9} \div 10^{-7}$ sec and activation energy $\Delta E_{\parallel} \approx 80 \div 100$ kJ/mol. The process undoubtedly comes from reorientation of molecules around the short axis.

The high-frequency relaxation process observed in the perpendicular orientation has been found to be mainly related with reorientation of molecule as a whole about the long axis.[7,8]

The temperature dependences of the relaxation times obtained for the isotropic (τ_{is}) and the nematic ($\tau_{\perp}$ and $\tau_{\parallel}$) phases of 2.OAOB, 3.OAOB, 4.OAOB and 5.OAOB are shown in Figure 1. The obtained values of relaxation times at the clearing temperatures T_C and at $T = T_C - 10°$ (corresponding to $1/T - 1/T_C = 0.0625$) are listed in Table I. The second and the last two columns of the Table are presented in Figure 2. From the Table and Figure 2 one can see odd-even effects for all three relaxation times which are far behind the experimental errors. (The total errors are estimated to be not larger than 40%. The difference between the times measured by the two groups—see data for 4.OAOB—are of ca. 10%).

The phenomenon observed can be formulated as follows. For *n*.OAOB homologous series the relaxation times characterizing both reorientations of molecules around the long and short axes show alternations such that the τ_{λ} values are larger for the odd members. Additionally, general tendency of increasing of τ_{λ} with the length of the end chains is observed for even n as well as for odd n.

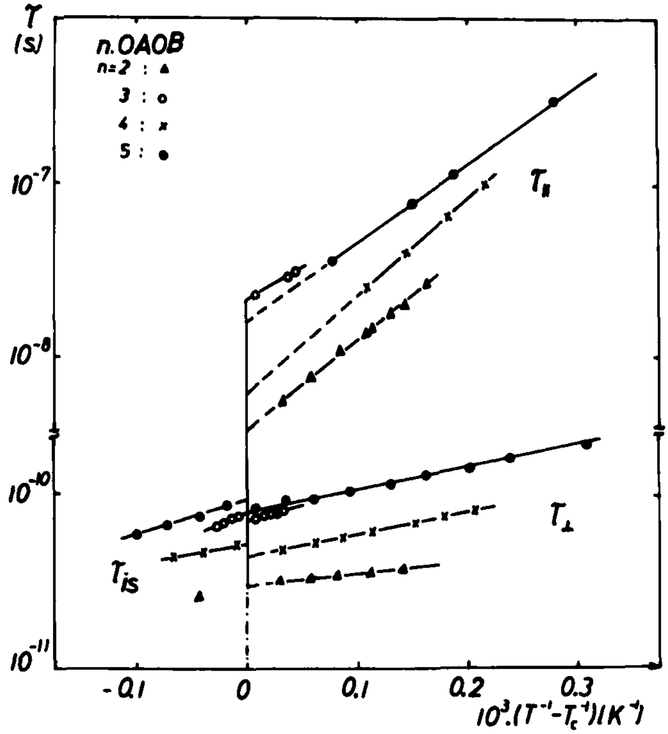


FIGURE 1 Temperature dependence of the dielectric relaxation times observed for the isotropic (τ_{is}) and two orientations of nematic phases ($\tau_{\perp}$, $\tau_{\parallel}$) of *n*.OAOB. The relaxation times are presented in log scale, the temperature in ($1/T - 1/T_c$) scale.

3.2. Dielectric relaxation properties below the melting point

Among the seven substances under study the dielectric relaxation effects in the solid state have been observed for two members with $n = 4$ and 5.[4,7,8] The dielectric properties of the solid phases of 4.OAOB and 5.OAOB are shown in Figures 3

TABLE I

Dielectric relaxation times obtained at the clearing temperatures T_c and 10° below T_c for seven substances of n.OAOB homologous series. The values in brackets are the data of Axmann [12].

	$T = T_c$			$T = T_c - 10°$	
n	τ_{is} (ps)	$\tau_{\perp}$ (ps)	$\tau_{\parallel}$ (ps)	$\tau_{\perp}$ (ps)	$\tau_{\parallel}$ (ns)
1	(32)	—	—	(32.9)	(4.3)
2	—	30	4	32	7.5
3	75	68	20	85	34
4	50 (46.8)	44	6	52 (56.7)	15 (15.8)
5	90	75	15	100	42
6	(81)	—	—	(81.1)	(24.7)
7	(94)	—	—	(92.2)	(36.7)

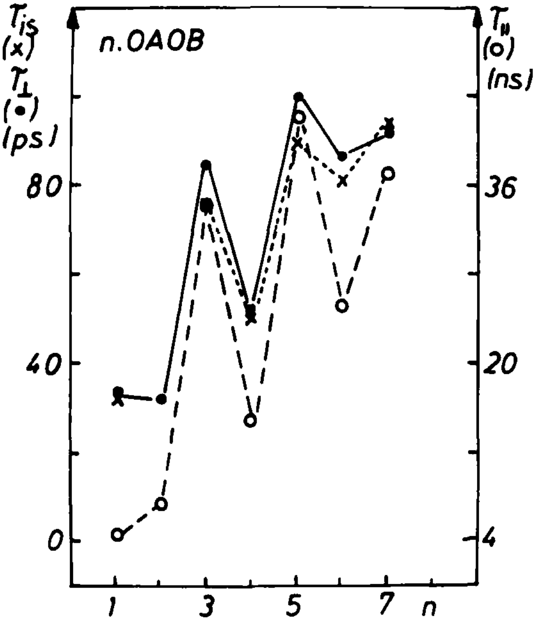


FIGURE 2 *n*.OAOB. Odd-even effect of the dielectric relaxation times at clearing temperatures (*x*) and at 10° below clearing points (● and ○).

and 4. As can be seen from Figure 3 at both radio and microwave frequencies the dielectric permittivities do not decrease to the n^2-values at the transition from nematic to CrI phases. Such values are only obtained on further cooling of the samples till the lowest-temperature phases, i.e. to CrII phase of 5.OAOB and CrIV phase of 4.OAOB. In the middle phases of the substances the remaining dielectric increments, $\delta\varepsilon = \varepsilon' - n^2$, are equal to ca. 0.5, which is largely reduced in comparison with the ones observed in the nematic phases. This fact suggests that in these rotatory phases (ODIC) the possible reorientations of dipole moments are rather restricted.

Figure 4 presents the absorption curves for the rotatory phases of the two substances. For 5.OAOB a broad spectrum ranging from 10 MHz to 10 GHz was observed. For such a broad spectrum it seems more reasonable to suggest the existence of two processes with relaxation times of the order of 10^{-8} and 10^{-10} sec. Having taken into account both the dielectric and QNS results for the CrI phase of 5.OAOB we suggested the fast process to be ascribed to the relaxation of pentoxy groups together with the benzene ring around the para axis, while the slow process probably originates from reorientation of molecules around the long axis.[7]

In the case of 4.OAOB, dielectric absorption and dispersion in radio frequencies was observed for all the middle phases (Figure 4). The maxima of the absorption curves correspond to relaxation times of 10^{-7} and 10^{-8} sec for CrII and CrI phases, respectively. This process is probably related to the reorientations of butoxy groups

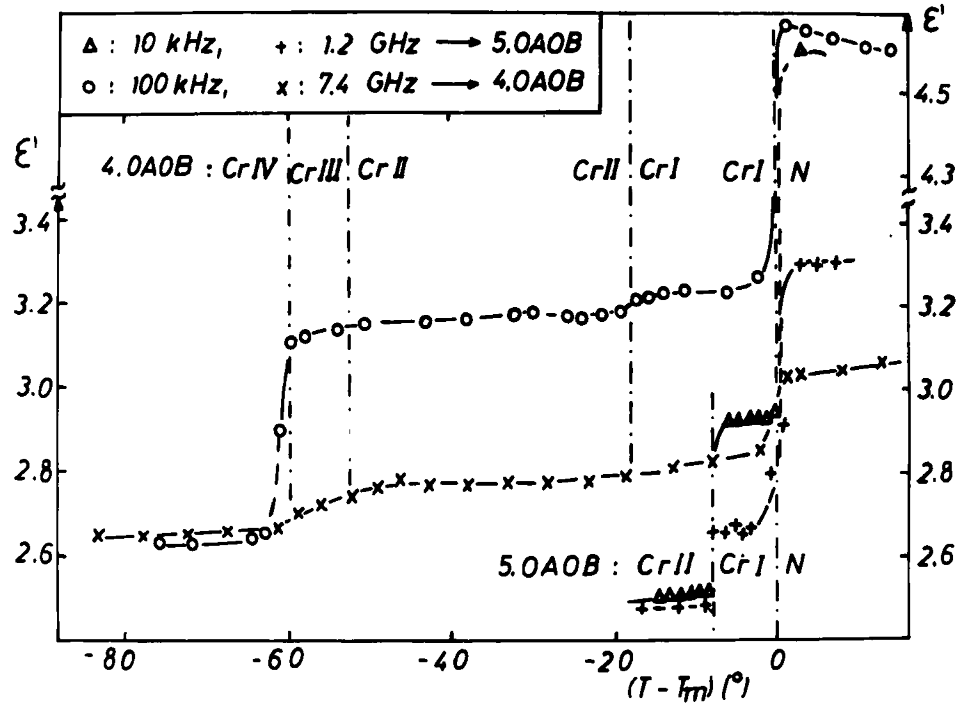


FIGURE 3 Dielectric permittivities ε' vs temperature for the ODIC phases of 4.OAOB and 5.OAOB.

(or of moieties) around the para axes. In microwave frequencies no absorption and dispersion effects could be observed for 4.OAOB. The deviation of ε' measured in GHz frequencies from n^2 detected for this substance could then be related to large-angle libration of molecule as a whole in the ODIC phases.

Summing up the restricted reorientations of dipole moments have been observed for high temperature solid phases of two members of n.OAOB homologous series, i.e. the ones with $n = 4$ and 5.

4. DISCUSSION AND CONCLUSIONS

The influence of molecular end chains in orientational ordering process was successfully considered theoretically by Marčelja.[13] By evaluation of end chain order the theory could explain the odd-even alternations of clearing temperatures T_C and of corresponding entropies ΔS_C. The coupling of the ordering of end chain and the aromatic core makes the order parameter of the latter, η_a, to vary from one member to another in a homologous series. Taking into account the different initial order for various molecular cores the explanation of the general trend of T_C to increase or to decrease with increasing of the chain length was given.

The effect of odd-even alternations of dielectric relaxation times is probably

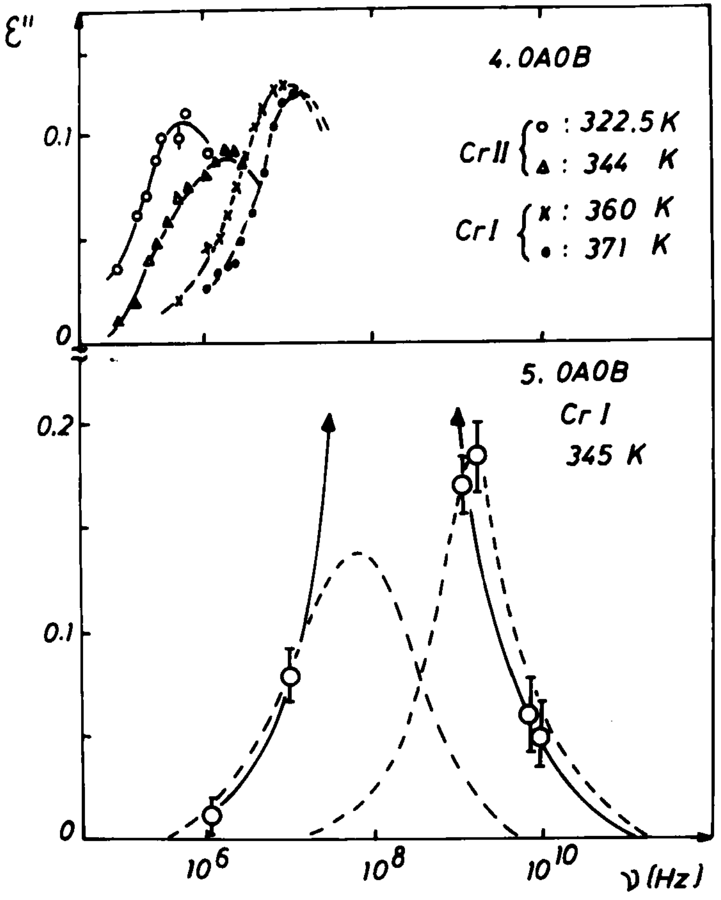


FIGURE 4 Dielectric absorptions ε'' as function of measuring frequency obtained at different temperature of ODIC phases of 4.OAOB and 5.OAOB.

related to the alternation of orientational parameter η_a. It is, however, very difficult to make a quantitative discussion of the observed effect in *n*.OAOB:

(i) For *n*.OAOB it is impossible to evaluate the so called Martin-Meier-Saupe retardation factor, $g_{\parallel}$, which, in turn, is related to the order parameter.

(ii) Since a realistic formula for dielectric relaxation time contains not only temperature dependence (like in Arrhenius equation) but also other factors such as: moment of inertia, entropy and energy of activation, which change from one member to another in a homologous series, it must be taken into account in such considerations.

In order to discuss the orientational ordering (or disordering) in the regions of the melting temperature let us consider the behaviour of the thermodynamic parameters. Figure 5 presents the dependences of the values of the melting temperatures, T_m, and entropies, ΔS_m, of the end chain length. One could distinguish two

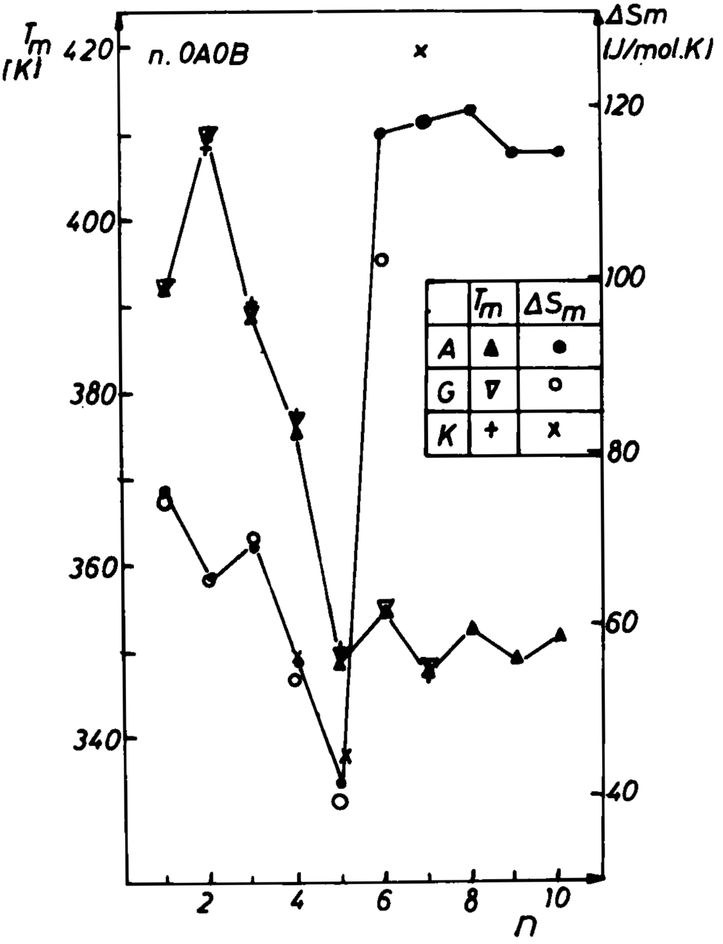


FIGURE 5 Entropy changes (ΔS_m) and transition temperatures (T_m) at melting points vs end chain length of *n*.OAOB. The results were obtained by three groups: A—Arnold,[14] G—Gruger *et al.*[10] and K—Cracow Liquid Crystal Group. The points by Arnold are connected to give a guide for the eyes.

ranges: In the first one, i.e. for $n = 1 \div 5$ general trend of changes for both T_m and ΔS_m to decrease with increasing n was observed. In the second one, i.e. for $n \geqslant 6$ general trend of changes doesn't show a further decrease of T_m and indicate abnormal increase of ΔS_m with increasing n.

In order to explain the behaviour of entropy change at melting points let us suppose the following three components of ΔS_m:

$$\Delta S_m = \Delta S_{\text{pos.}} + \Delta S_{\text{conf.}} + \Delta S_{\text{orient.}}$$

The large values of ΔS_m obtained for smectogens ($n \geqslant 6$) (see Figure 5) show that the positional contribution, $\Delta S_{\text{pos.}}$, is almost independent of n. The remaining conformational, $\Delta S_{\text{conf.}}$, and orientational, $\Delta S_{\text{orient.}}$, entropy changes are rather coupled. ODIC phases have been observed for substances with $n = 4$ and 5 for which ΔS_m values are extremely small. This fact could be explained as follows: For high temperature solid phases of those substances the orientational ordering of molecules is abnormally weak, which makes enough room for orientations of molecules or/and their segments.

It should be noted that the above discussed two-region behaviour of the melting temperatures and entropies can be noticed in several other homologous series of liquid crystals like di-*n*-alkylazoxybenzenes, alkylcyanobiphenyls, 1,4-di-4-*n*-alkylphenyl cyclohexanes.[15]

In summary the following two conclusions can be deduced:

1. Odd-even effects have been observed for dielectric relaxation times characterizing the intermolecular reorientations both below ($\tau_\perp$ and $\tau_\parallel$) and above the clearing points (τ_{is}). The fact is consistent with the results obtained by other experimental methods.
2. The observation of ODIC phases for two substances with very small melting entropy suggests a significant role of orientational disorder in the melting process of liquid crystals with rod-like molecules.

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