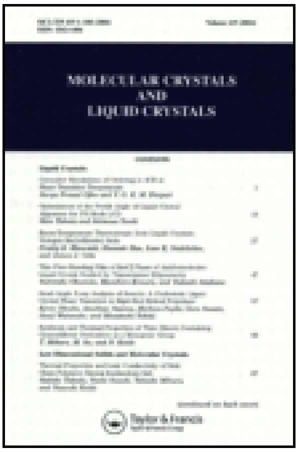

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Dielectric Relaxation in Liquid Crystals with the Nematic and Smectic A Polymorphism

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DIELECTRIC RELAXATION IN LIQUID CRYSTALS WITH THE NEMATIC AND SMECTIC A POLYMORPHISM

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Abstract Dielectric relaxation studies are reported of several substances exhibiting the nematic (N) and smectic A (Sm A) polymorphism. From the relaxation times $\tau_{\parallel}$ characterizing molecular reorientations around the short axes the activation enthalpies $\Delta H_{\parallel}$ for both phases were calculated. It was found that $\Delta H_{\parallel}(N)$ is markedly larger than $\Delta H_{\parallel}(SmA)$. The effect is interpreted on the basis of existing models of Sm A phase.

INTRODUCTION

The nematic (N) and smectic A (Sm A) phases are two of the more common intermediate phases between the crystal and the isotropic liquid. The nematic phase has a high degree of long-range orientational order of the molecules, but no long-range translational order. The Sm A phase has a layered structure with layer planes perpendicular to the preferred direction of molecular long axes; within the layers the centers of mass of the molecules are randomly distributed [1]. In both phases the degree of long-range orientational order is similar [2,3].

However, some variety of Sm A phases can be distinguished if the ordering of molecules in layers is considered [4,5]. Generally two factors play important role in forming different subtypes of Sm A phase: the dipolar effects and steric effects, and for rod-like molecules the first ones play a dominant role [6]. The main factor which allows one to distinguish the particular subtypes of the Sm A phases is the ratio of the smectic layer spacing d to the molecular length l in its most extended form - see fig. 1.

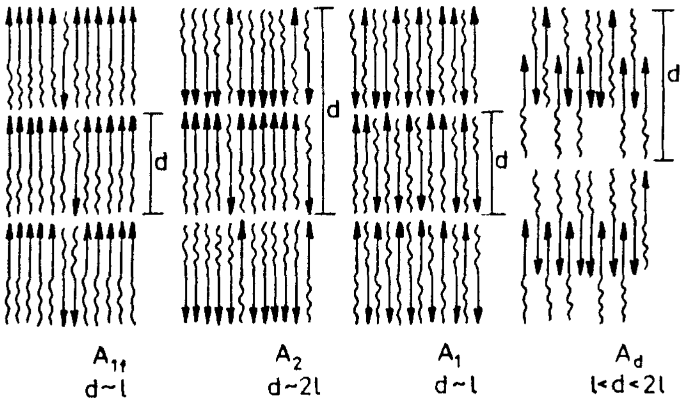


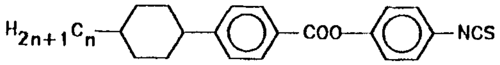
FIGURE 1 Molecular ordering in subtypes of the smectic A phase.

The dielectric method is a powerful tool for studying the properties of LC phases. Static field measurements give information about the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$ which strongly depends on the dipole-dipole interactions in a LC phase. However, a proper value of $\Delta\varepsilon$ can be directly measured for the nematic phase only; in the case of a smectic phase the monodomain sample cannot be obtained easily. A study of the dielectric dispersion and absorption enables us to analyze the different relaxation processes associated with the dipolar molecules of LCs. In the case of the phases under consideration the relaxation process measured for parallel oriented sample is especially interesting. This process is connected with the molecular rotations around the short axes and is characterized by a simple Debye model with the relaxation time $\tau_{\|}$ [7-10]. From the temperature dependence of $\tau_{\|}$ one can calculate the activation enthalpy $\Delta H_{\|}$ which reflects a strength of the molecular interactions at a given LC phase. It is commonly assumed [11,12] that for the nematic phase $\Delta H_{\|}$ consists of two main parts accounting for the viscosity effects (which also can be observed in the isotropic phase), W_{η}, and the 'nematic potential' q [13]: $\Delta H_{\|} = W_{\eta} + q$. In the case of the substances with strong dipole moments, like cyanobiphenyls, the dipole-dipole associations should be additionally taken into consideration [12]. The aim of this work is the analysis of the influence of the N - Sm A phase transition on the values of $\tau_{\|}$ and $\Delta H_{\|}$ in different subtypes of Sm A phase.

In the literature one can only find a small number of the dielectric studies of the low frequency relaxation process in LCs exhibiting both the nematic and smectic A polymorphism [7-10]. Additionally, some of the phases exist within a relatively narrow temperature ranges which causes that the relaxation times obtained are influenced by the pretransitional effects. Therefore the values of the activation enthalpies characterizing the molecular reorientations around the short axes were often misleading. In our studies we have chosen the substances with relatively broad temperature ranges of both phases.

EXPERIMENTAL

The substances under study belong to the homologous series of 4-isothiocyanatophenyl 4-(*trans*-4-alkylcyclohexyl)benzoates (*n*PCHB-NCS) [14]



Their transition temperatures are shown in Fig. 2. The substances with *n* = 4, 5, 6, 7 and 10 were studied. Additionally, the dielectric spectra for two other compounds have been obtained (5F and 8OCB - see Table I).

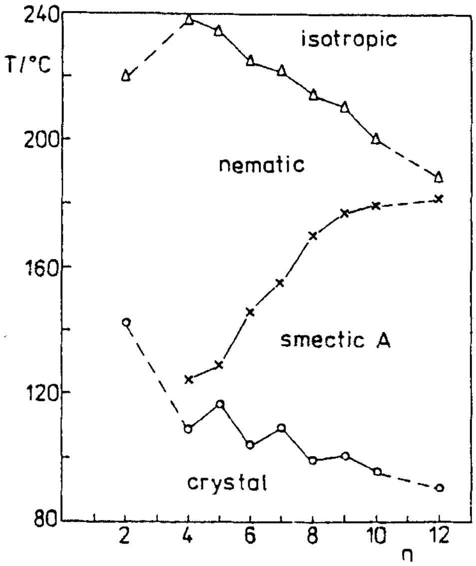


FIGURE 2 Transition temperatures for *n*PCHB-NCS homologous series as a function of *n*.

The measurements of the complex permittivity $\varepsilon^*_{\parallel}(\omega) = \varepsilon' - i\varepsilon''$ were performed in the frequency range 1 kHz - 10 MHz using a HP 4192A bridge. A parallel-plates capacitor (A ≈ 1 cm^2) was calibrated with the use of standard liquids. The distance between electrodes was 0.2 mm. The samples were oriented by both the electric DC ($\mathbf{E} \approx 1500$ V/cm) and magnetic ($\mathbf{B} \approx 0.7$ T) fields. However, at the phase transition from the nematic to smectic A phase a drop of the permittivity were observed. The temperature of a sample was stabilized with the accuracy of ±0.05 K with the use of Eurotherm temperature controller type 900.

RESULTS

As an example Fig. 3 presents the absorption $\varepsilon'(\nu)$ and dispersion $\varepsilon''(\nu)$ spectra obtained for 6PCHB-NCS in the nematic and smectic A phases. The values of permittivity obtained for the Sm A phase cannot be treated as a material property due to insufficient orientation of the sample. The relaxation times were calculated from the values of the frequencies ν_{max} corresponding to the maxima of losses ε''_{max}: $\tau_{\|} = 1/2\pi\nu_{max}$. The relaxation frequency ν_{max} was not influenced by the orientation of the sample. The obtained results are presented in Fig. 4 in the form of the Arrhenius plots. The values of the activation enthalpies calculated from the plots are gathered in Table I. To check the observed relationships the results obtained for some other substances are also included.

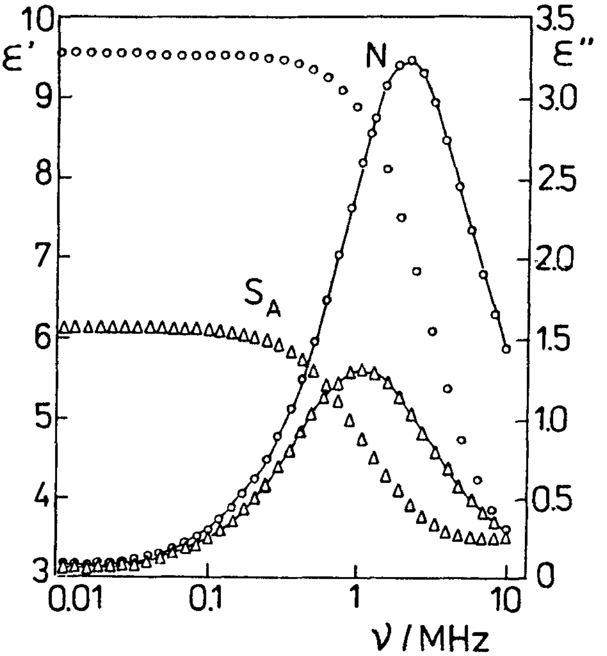


FIGURE 3 Dispersion and absorption spectra measured in the nematic (433 K) and smectic A (391 K) phases of 6PCHB-NCS. The sample was parallel oriented by both the DC electric and magnetic fields. The lines correspond to the Lorentz curves fitted to the experimental loss points.

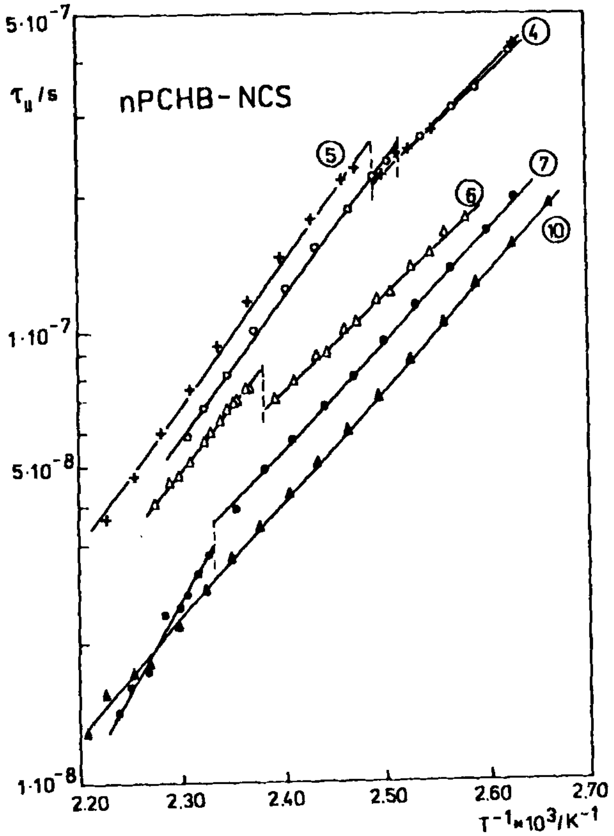


FIGURE 4 Arrhenius plots for particular substances of *n*PCHB-NCS homologous series in the nematic and smectic A phases.

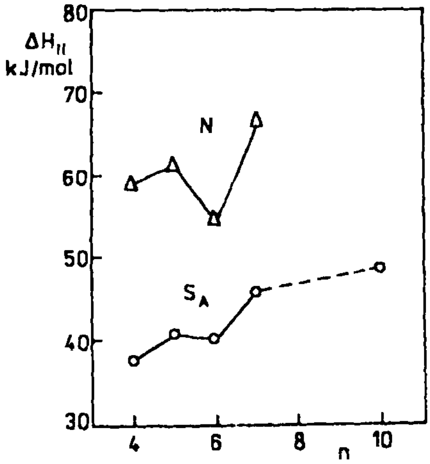


FIGURE 5 Variations of the activation enthalpy $\Delta H_{\parallel}$ with the number of carbon atoms in *n*PCHB-NCS series.

DISCUSSION

Fig. 5 and Table I show that the activation enthalpies characterizing the molecular reorientations around the short axes alternate with *n* stronger in the nematic than in the smectic A phase. However, the most important feature of the results is the fact that $\Delta H_{||}^{N}$ is considerably higher than $\Delta H_{||}^{SmA}$. It holds for A_1 and A_d smectic phases as well - see results gathered in Table I. Does layered smectic A structure minimize the interaction potential between the molecules or other factors independent of the details of the structure cause such effect?

Fig. 1 shows the molecular orderings in layers of different subtypes of Sm A phase [4]. Sm A_1 can be regarded as a classical smectic A phase and is characteristic of all non-polar and many weakly polar compounds like $\bar{9}$S5 (see table). Also substances with strong asymmetry of the geometrical shapes like 'swallow-tailed compounds' (S_n in the table) form Sm A_1 phase but the molecules exhibit considerable anti-parallel correlations in the layers [15,16]. Sm A_d is called 'partially bilayer smectic' and is formed by the compounds with the strongly polar terminal groups such as -CN, -CHO and $-NO_2$ [4] (three substances gathered in the table belong to this group: 8COO CB, 8CB and 8OCB). The substances belonging to *n*PCHB-NCS series exhibit behaviour which places them between A_1 and A_d smectic phases: they show a slow expansion of the smectic layer with increasing *n* and their intrinsic structure changes in a continuous way (see Table I); they were called 'the enhanced monolayer smectic' (A_{1e}) [4,14]. The bilayered Sm A_2 phase is observed usually as the lowest temperature smectic A phase (below A_d and A_1 phase [19-22]), whereas the ferroelectric A_{1f} phase has not been experimentally observed in strong polar systems [4].

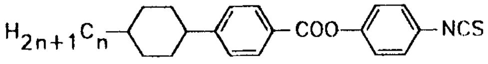
A relation between the flow viscosity of a substance and a 'rotational viscosity' experienced by a rotating molecule cannot be readily found. However, from the well known fact that the viscosity of smectic phases is distinctly higher than that of the nematic phase one can suppose a similar relation between the rotational viscosities of both phases. Thus, the observed effect, $\Delta H_{||}^{N} > \Delta H_{||}^{SmA}$, is in opposition to the change of viscosity. Moreover, it seems to be doubtful that the anisotropy of interactions between the rod-like molecules, which leads to the creation of the 'nematic potential', can be lower in Sm A than in

Table I The data for different substances forming the nematic and smectic A phases. (μ - dipole moment, β - angle between μ and the symmetry axis, ΔT - the range of N or Sm A phase, d/l - ratio of the layer spacing to the molecular length, $\Delta H_{\parallel}$ - activation enthalpy for molecular rotations around the short exes).

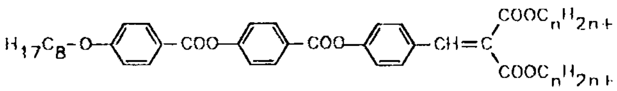
Name of substance	n	$\Delta T(N)/\Delta T(SmA)$ [K]	μ / β [D]/[°]	d/l	Sm phase	$\Delta H_{\parallel}^{N}$ [kJ/mol]	$\Delta H_{\parallel}^{SmA}$ [kJ/mol]
nPCHB-NCS	4	114.5 / 15.5	4.6/9 [14]	1.01	A_{1e}	59.2	37.6 1)
	5	106 / 12	4.5/10	1.00	A_{1e}	61.3	40.6
	6	78.5 / 42.5	4.6/8	1.03	A_{1e}	54.5	40.0
	7	66.5 / 46	4.6/7	1.02	A_{1e}	66.3	45.8
	10	20 / 84.5	4.6/6	1.06	A_{1e}		48.8
5F	5	35.3 / 26.9		1	A_1	117.4	74.7 1)
Sn	2	33 / 8		1	A_1	100±3	80±1 2)
	4	12.5 / 22		1	A_1	110±3	84±1
	10	7 / 22.5		1	A_1	?	90±1
8COO CB	8	13 / 20.5	3.8/25	1.4	A_d	73.3	48.2 3)
8CB	8	7.1 / 11.9	4.7/0	1.4	A_d	64.3	44.3 4)
8OCB	8	13.0 / 12.5	5.1/16	1.37	A_d	90.5	56.2 5)
$\bar{9}$S5	9	12 / 12	2.25/50	1	A_1	126.2	105.2 6)

1)Present studies, 2)Ref. [23], 3)Ref. [8], 4)Ref. [17], 5)Ref. [24], 6)Ref. [10]

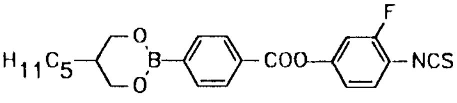
nPCHB-NCS



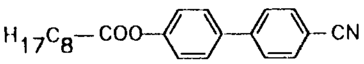
Sn



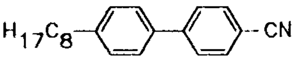
5F



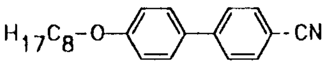
8COO CB



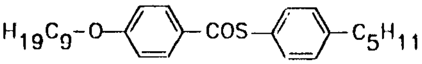
8CB



8OCB



$\bar{9}$S5



N phase. (It should be noted that $\delta H_{\parallel} = \Delta H_{\parallel}^{N} - \Delta H_{\parallel}^{SmA} \approx 20$ kJ/mol is more than twice as large as the values of the nematic potential estimated from the dielectric relaxation studies of cyanobiphenyls [12,17]).

A possible explanation of such change of the activation enthalpy at the N - Sm A phase transition has been proposed by Druon and Wacrenier [8] on the basis of the results of dielectric studies for 8COO CB. This compound forms nematic and partially bilayer Sm A_d phase (see table). They suggested that the order of molecules in layers involves the changes in the potential which partially can also give tendencies to an anti-parallel orientation of neighbouring molecules. In such a case the potential "seen" by a molecule has asymmetrical shape in Sm A whereas it becomes symmetrical in N phase on an average. According to the dielectric relaxation theory [18] in the case of large difference between two non-equivalent rotational positions, the relaxation time is connected with the lower potential barrier and the relaxation process is described by a simple Debye equation. If it is a suitable model one can suppose that $\delta H_{\parallel}$ roughly corresponds to the difference in the depths of the potential minima.

The above model seems to be consistent with the frustrated spin-gas model developed by Berker *et al.* [19-22]. However, in both models the molecules with strong dipole-dipole interactions are considered. The results of the dielectric relaxation studies presented in Table I indicate that the substances built with molecules of different chemical structures, various shapes and polarity show a very similar behaviour. More light could be shed on this problem if similar studies are performed for the compounds showing up the Sm C - N, Sm B - N or Sm E - N phase transitions.

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