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REORIENTATION OF THE LONG MOLECULAR AXIS
IN SMECTIC PHASES

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REORIENTATION OF THE LONG MOLECULAR AXIS
IN SMECTIC PHASES

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ABSTRACT

The low frequency dielectric dispersion was measured of 6OB6A in nematic, smectic A and B phases and that of 5OB6A in nematic, smectic A,C,B,F and G phases.

АННОТАЦИЯ

Низкочастотная диэлектрическая дисперсия была изучена для 6OB6A в нематической, смектической A и B фазах и для 5OB6A в нематической, в смектической A,C,B,F и G фазах.

KIVONAT

Alacsony frekvenciás dielektromos diszperziót vizsgáltunk 6OB6A anyagon nematikus, szmektikus A és B fázisokban és 5OB6A anyagon nematikus, szmektikus A,C,B,F és G fázisokban.

INTRODUCTION

In liquid crystalline phases the long axes of molecules are macroscopically ordered, i.e. they are parallel to a preferred direction. In nematics only the long molecular axes are ordered, the centres of gravity of the molecules have random distribution. In smectics the centres of gravity of the molecules are settled in layers and the ordering direction of the long molecular axes is perpendicular to the layer in the smectic A (Sm A) phase and has a non zero angle with the layer normal in the smectic C (Sm C) phase. In the highly ordered (or low temperature) smectic phases the centres of gravity are not only positioned in layers, but they are ordered in two dimensions, in a hexagonal or quasi hexagonal structure. When centres of gravity are ordered within the layers the direction of the long molecular axes may either be perpendicular to the layer - this phase is called the smectic B (Sm B) phase; or it may be tilted from the layer normal in which case it is known as the smectic F (Sm F) phase. In cases when not only the centres of gravity are ordered inside the layer but the short molecular axes have definite directions we speak about smectic G (Sm G) and other smectic phases.

The parallel ordering of the long molecular axes compared with the isotropic liquid results in a new dielectric dispersion, a "low frequency" one in the nematic phase. This effect has been extensively studied [1-3] and interpreted by the reorientation of the long molecular axes or by the rotational jump around the short axes of molecules. This investigations has been extended to the SmA and SmC phases [4-7], and a small jump or break was found at

the phase transition in the relaxation time. In the SmB and SmG phases there appear new orderings so the question arises as to how the process of the reorientation of the long molecular axes alters in well ordered smectic phases. It was supposed that reorientation of the long axes is frozen out in phases which appear at temperatures lower than the SmB phase. The purpose of this article is to throw some light on this question. So far as the authors are aware this will be the first such publication.

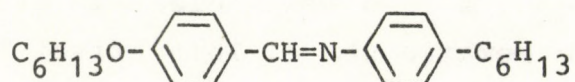
EXPERIMENTAL

The rotation of the long molecular axes around the short axes in liquid crystalline phases can be studied by low frequency dielectric dispersion. Measurements in the 50 Hz - 100 kHz frequency range were carried out on a General Radio 1615A capacitance bridge, and those in the 100 kHz - 10 MHz range using a Wayne Kerr B 602 bridge. The compounds were studied in a two-terminal tantalum-plated parallel plate capacitor.

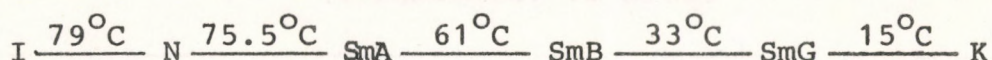
The ordering of the long molecular axes was achieved by means of an external static magnetic field of 1.5 T. The thermostat maintained the temperature to within 0.2°C. The sample was cooled slowly in the aligning field from the nematic to the smectic phases.

COMPOUNDS

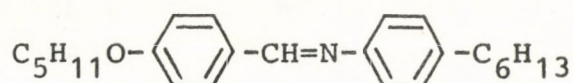
Compound 4-n-hexyloxybenzylidene-4'-n-hexylaniline (I) i.e. 6OB6A



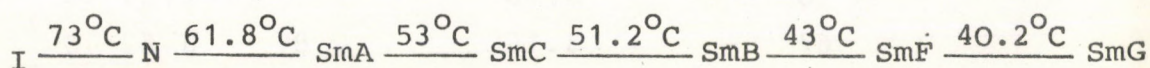
was chosen to study the SmA - SmB phase transition; it exhibits the following phases:



In order to extend the studies to other well ordered smectic phases the compound 4-n-heptyloxybenzylidene-4'-n-hexylaniline (II) i.e. 5OB6A



was investigated which possesses the phases:



The compounds were synthesized at Halle University (GDR). The calorimetric and polarizing microscope studies were carried out for both substances in order to determine the phase transition temperatures and the structures.

RESULTS

The low frequency dielectric dispersion of the parallel permittivity component was investigated for compound I and for compound II. Characteristic parameters of the measured Debye-type processes are given in Tables I and II.

The temperature dependence of the relaxation time for compound I is shown in Fig. 1 and that for compound II in Fig. 2.

DISCUSSION

In accordance with our earlier results for other compounds [5,7] there appears a change for substances I and II as well in the Arrhenius plot (Figs 1 and 2) at the N-SmA phase transition. In some cases there is a discontinuity (compound II) suggesting the phase transition to be of first order, but a decrease occurs

Table I. (compound I)

Phase	T /°C/	$\epsilon(0)$	$\epsilon(\infty)$	$\tau/s/$
N	79	3.35	2.83	$3.42 \cdot 10^{-8}$
	78	3.32	2.83	$4.42 \cdot 10^{-8}$
	77	3.28	2.83	$5.79 \cdot 10^{-8}$
	76	3.27	2.83	$9.1 \cdot 10^{-8}$
Sm A	72	3.17	2.81	$1.92 \cdot 10^{-7}$
	70	3.16	2.81	$2.57 \cdot 10^{-7}$
	67	3.16	2.81	$3.62 \cdot 10^{-7}$
	64	3.15	2.81	$5.68 \cdot 10^{-7}$
Sm B	61.5	3.01	2.68	$1.06 \cdot 10^{-5}$
	59	3.08	2.75	$1.33 \cdot 10^{-5}$
	57.5	3.08	2.75	$1.59 \cdot 10^{-5}$
	49	3.02	2.67	$4.55 \cdot 10^{-5}$
	42.5	3.05	2.76	$5.90 \cdot 10^{-5}$

$\epsilon(0)$, $\epsilon(\infty)$ - respective dielectric permittivities before and after the relaxation process

τ - relaxation time

of the activation energy for all investigated compounds. There is a further decrease at the SmA - SmC transition [7]. In the present case the short SmC temperature range of compound II did not allow us to investigate the SmA - SmC transition in detail.

The very new effect is detected at the transition from the low ordered phases (SmA and SmC for I and II respectively) towards the highly ordered SmB phase and similarly at the SmF-SmG transition for II. The molecular reorientation around the short axis detected earlier by the frequency dispersion of the parallel dielectric permittivity component in the N, SmA and SmC phases is preserved in the well ordered smectic phases as well. But the relaxation

Table II. (compound II)

Phase	T / °C /	ϵ (0)	ϵ (∞)	τ / s /
N	71.6	3.34	2.95	$3.46 \cdot 10^{-8}$
	70.5	3.34	2.95	$4.42 \cdot 10^{-8}$
	68.5	3.34	2.88	$5.13 \cdot 10^{-8}$
	66.5	3.33	2.89	$6.97 \cdot 10^{-8}$
	63.2	3.32	2.86	$1.1 \cdot 10^{-7}$
Sm A	61	3.28	2.80	$1.59 \cdot 10^{-7}$
	60	3.23	2.79	$1.73 \cdot 10^{-7}$
	59.5	3.22	2.78	$2.41 \cdot 10^{-7}$
	56.8	3.17	2.73	$3.18 \cdot 10^{-7}$
	56	3.16	2.72	$3.70 \cdot 10^{-7}$
	54	3.15	2.71	$4.42 \cdot 10^{-7}$
Sm C	52.2	3.14	2.72	$5.31 \cdot 10^{-7}$
Sm B	50	3.11	2.70	$7.76 \cdot 10^{-6}$
	48.5	3.11	2.70	$1.04 \cdot 10^{-5}$
	47.3	3.11	2.70	$1.10 \cdot 10^{-5}$
	45	3.12	2.70	$1.38 \cdot 10^{-5}$
	44	3.12	2.70	$1.59 \cdot 10^{-5}$
	43	3.12	2.70	$1.73 \cdot 10^{-5}$
Sm F	42.5	3.12	2.70	$2.02 \cdot 10^{-5}$
	41.1	3.12	2.70	$2.31 \cdot 10^{-5}$
	40.6	3.12	2.70	$2.65 \cdot 10^{-5}$
Sm G	39	3.17	2.68	$4.95 \cdot 10^{-5}$
	38.2	3.18	2.68	$6.92 \cdot 10^{-5}$
	32.2	3.20	2.68	$1.73 \cdot 10^{-4}$
	27.2	3.20	2.68	$2.84 \cdot 10^{-4}$

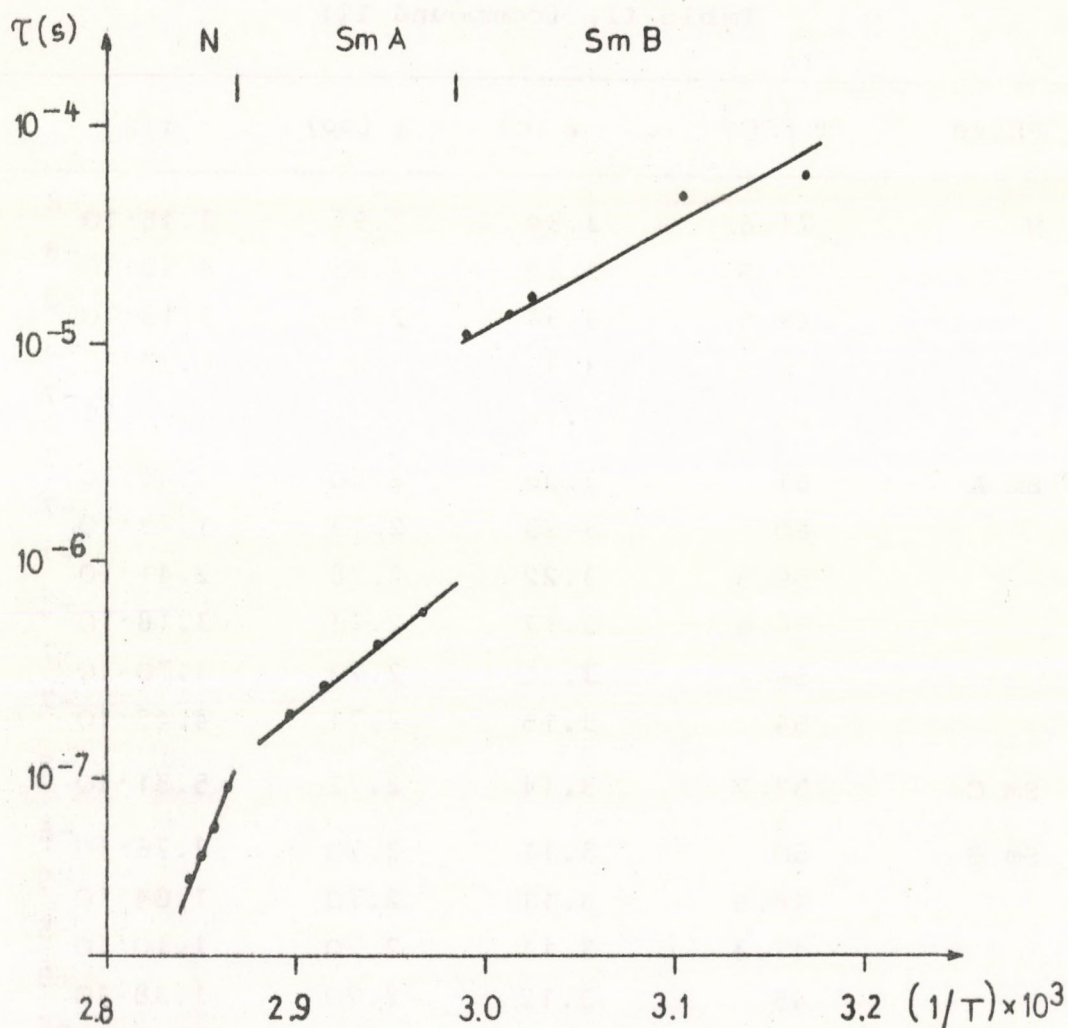


Fig. 1. Arrhenius plot of compound I

process is shifted so strongly to the lower frequencies that the relaxation time increases by about one decade.

This results show that the two dimensional ordering of the centres of gravity inside the smectic layer (SmB) hinder the re-orientation of the long molecular axis much stronger than the appearance of the layers does at the N-Sm transition. Other changes in the ordering inside the smectic layer (SmF and SmG) hinder the reorientation of the long molecular axis even further.

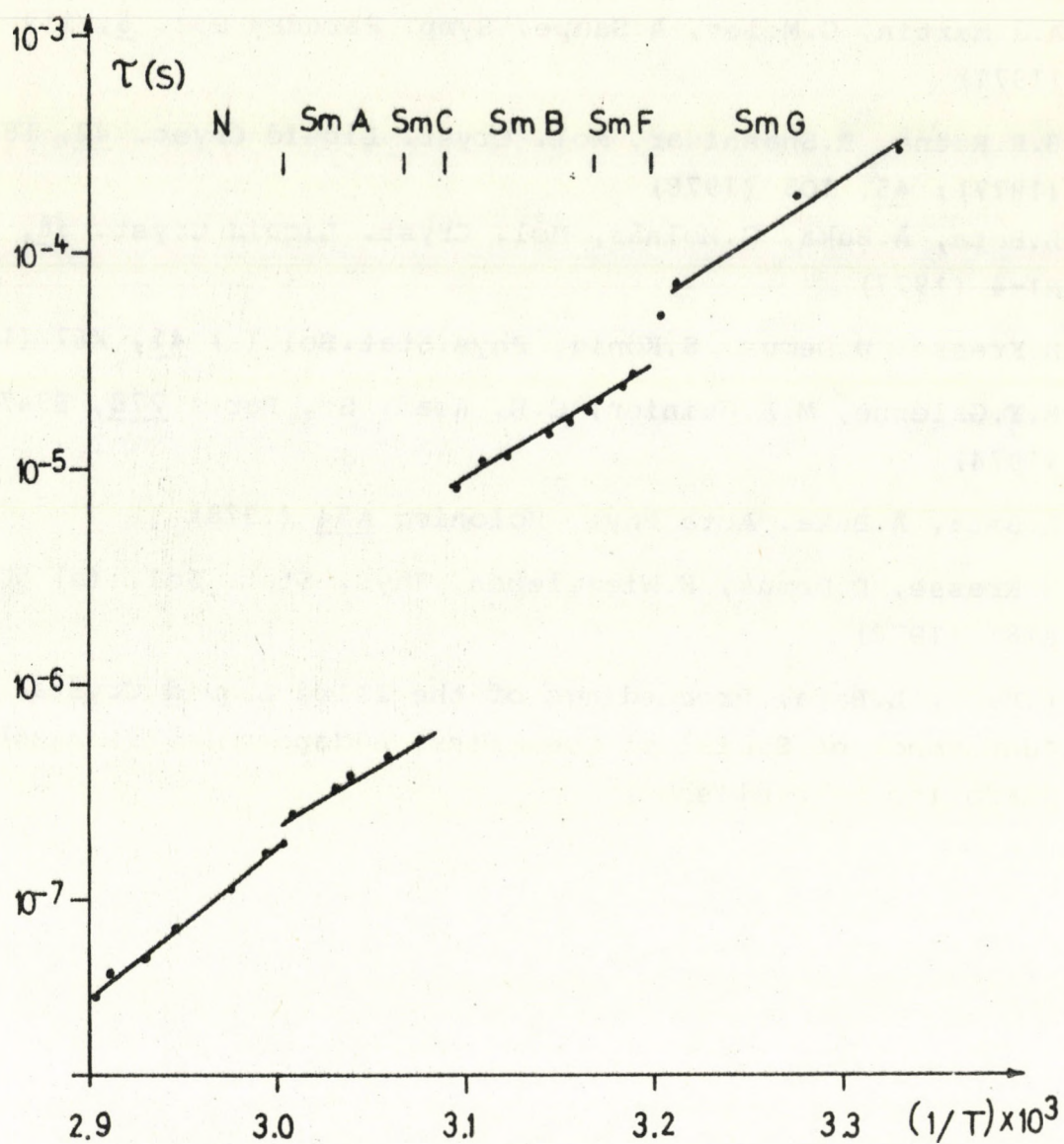


Fig. 2. Arrhenius plot of compound II

Activation energy decreases slightly towards the low temperature phases.

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