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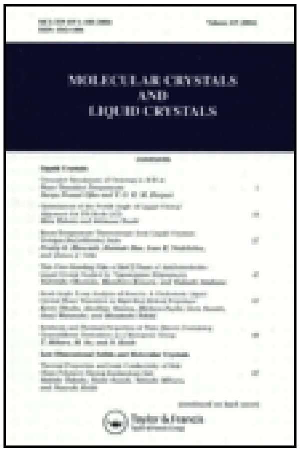

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Anisotropy of Static Electric Permittivity and Conductivity in Some Nematics and Smectics A

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Version of record first published: 19 Dec 2006.

To cite this article: J. Jadzyn & P. Kêdziora (1987): Anisotropy of Static Electric Permittivity and Conductivity in Some Nematics and Smectics A, Molecular Crystals and Liquid Crystals, 145:1, 17-23

To link to this article: http://dx.doi.org/10.1080/00268948708080210

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Mol. Cryst. Liq. Cryst., 1987, Vol. 145, pp. 17–23
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Anisotropy of Static Electric Permittivity and Conductivity in Some Nematics and Smectics A

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(*Received July 3, 1986; in final form September 6, 1986*)

Anisotropy of static electric permittivity and conductivity was measured for three groups of liquid crystals: (I) p-n-alkyl-p′-cyanobiphenyls ($C_nH_{2n+1}—\phi—\phi—CN$, $n = 5,6,7,8$), (II) p-p′-dialkylazoxybenzenes ($C_nH_{2n+1}—\phi—N(O)=N—\phi—C_nH_{2n+1}$, $n = 5,6,7,8$) and (III) p-alkyloxyphenyl-p′-alkoxybenzoates ($C_nH_{2n+1}—O—\phi—COO—\phi—O—C_mH_{2m+1}$, $n = 8$, $m = 5$; $n = 8$, $m = 7$; $n = 10$, $m = 5$; $n = 11$, $m = 5$). The nematic–smectic A phase transition for compounds of the I and II group manifests itself as a change of conductivity anisotropy sign due to a strong variation of the parallel component $\sigma_\parallel$ only; for compounds of the III group both components of electric conductivity and permittivity change considerably.

Keywords: permittivity, conductivity, anisotropy, nematics, smectics

INTRODUCTION

Anisotropy of physical properties of liquid crystals is caused by molecular long-range orientational ordering. In nematics the ordering concerns the direction of a long axis of molecules, whereas their centers of mass remain distributed at random. In smectics there is an additional ordering. The centers of the molecules are, on average, arranged in the equidistance planes. Direct evidence of the layered structure gives the X-ray diffraction pattern, in which a sharp reflexion at small Bragg angles corresponding to a layer thickness is observed. The smectogenic molecules with a strongly polar group, such as nitro- or cyano-group, form the bilayer structures of various types.

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In static dielectric measurements the anisotropy of liquid crystals manifests itself as a difference in the value of electric permittivity measured along $\epsilon_{\parallel}$ and perpendicular $\epsilon_{\perp}$ to the preferred axis. The value and sign of the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ depend on electronic structure of molecules, or more precisely, on a distribution of dipole moment of a polar group with respect to the long axis of molecule.[1,2] In the most liquid crystals the nematic-smectic A phase transition involves only a small change in electric permittivity.[2,3]

The studies of anisotropy of conductivity are important since the ions moving along a particular direction of the oriented sample may serve as a microscopic probe delivering some significant structural information. Contrary to electric permittivity, the conductivity always undergoes a severe change when the layered structures appear.[4-6]

In this paper we present the results of permittivity and conductivity measurements for three groups of polymorphous liquid crystals.

TABLE I

Phase transition temperatures (in °C).

$C_nH_{2n+1}—\phi—\phi—C\equiv N$

n	I—N	N—S_A
5	36.0	—
6	29.8	—
7	43.2	—
8	41.4	34.2

$C_nH_{2n+1}—\phi—N(O) = N—\phi—C_nH_{2n+1}$

n	I—N	N—S_A
5	69.0	—
6	48.5	23
7	72.5	55.5
8	69.5	67.5

$C_nH_{2n+1}—O—\phi—COO—\phi—O—C_mH_{2m+1}$

n	m	I—N	N—S_A	S_A—S_C	N—S_C
8	5	86.8	65.7	63.5	
8	7	89.5	—	—	71.5
10	5	86.0	81.3	69.0	
11	5	85.5	84.0	70.0	

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EXPERIMENTAL

Materials: p-n-alkyl-p'-cyanobiphenyls (BDH), p,p'-dialkyl-azoxybenzenes and p-alkyloxy-phenyl-*p*'-alkoxybenzoates (CHEMIPAN) were used without further purification. The phase transition temperatures of the studied materials are listed in Table I.

Apparatus: Static electric permittivity and conductivity were measured with a Wayne-Kerr B 330 bridge at 1.5 kHz. The samples were measured in a plane copper capacitor with gold-covered electrodes. The thickness of liquid crystal layer was 1 mm. To orientate the samples the 1 T magnetic field was used. The temperature was stabilized with an accuracy of ± 0.01°C. Electric permittivity and con-

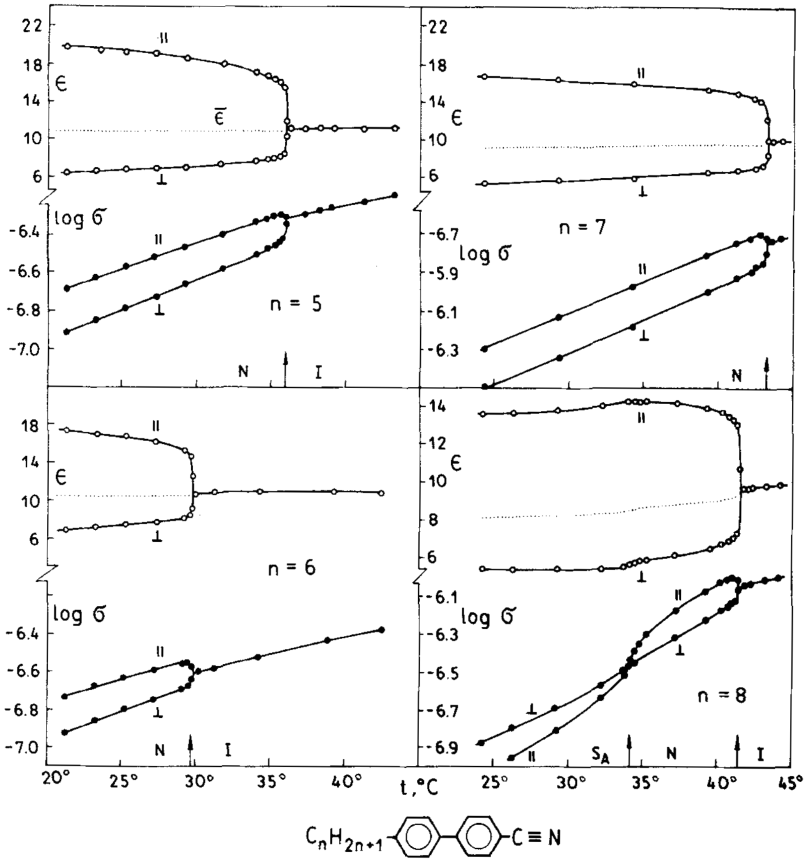

FIGURE 1 Static electric permittivity, (ε), and conductivity, (σ), of some p-n-alkyl-p'-cyanobiphenyls.

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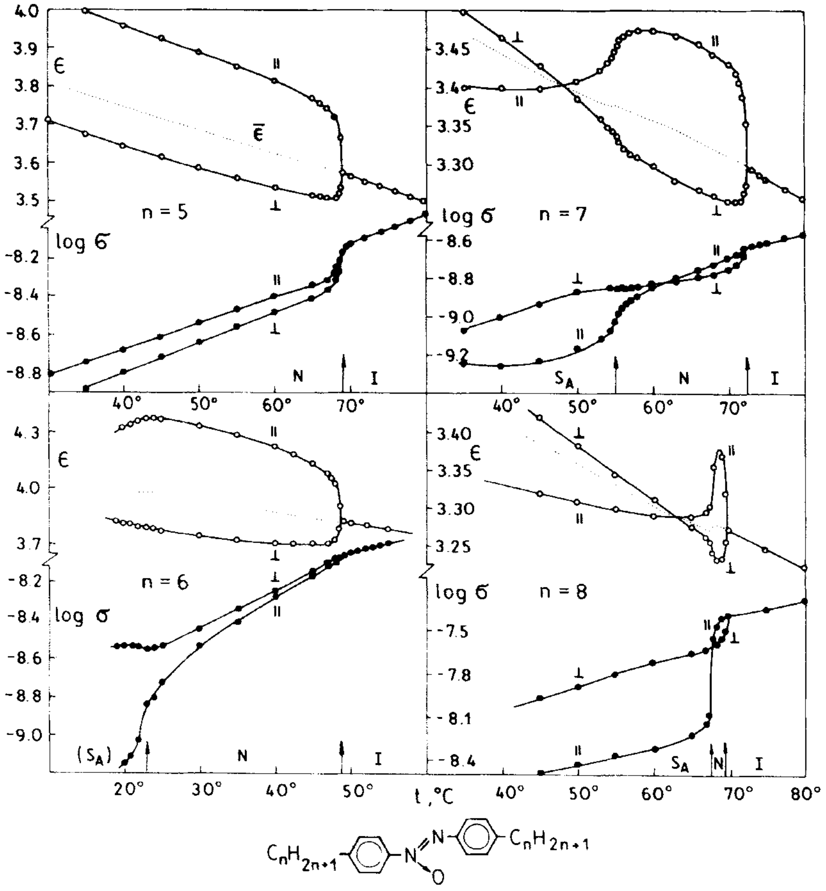

FIGURE 2 Static electric permittivity, (ε), and conductivity, (σ), of some p,p′-di-n-alkyl-azoxybenzenes.

ductivity were measured with an accuracy of 0.01 and 0.1%, respectively. The conductivity measurements were carried out for pure samples i.e. without special ionic admixtures.

RESULTS AND DISCUSSION

The temperature dependences of anisotropy of static electric permittivity and conductivity for the three groups of liquid crystals are shown in Figures 1–3. For the first two groups, i.e. (I) p-n-alkyl-p′-cyanobiphenyls (*n*-CB), and (II) p,p′-dialkyl-azoxybenzenes (*n*-AB)

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the experimental results concerning the anisotropy of permittivity are in good agreement with those published previously.[7–11]

For *n*-CB and *n*-AB, with the exception of 6-AB, in the nematic phase the conductivity along the ordering direction is higher than that in perpendicular direction, $\sigma_{\parallel}/\sigma_{\perp} > 1$. This agrees with the data on electric conductivity[4–6,12] and self-diffusion[13–15] which lead to the conclusion that in most nematics a mass transport is easier in the ordering direction than in the perpendicular direction.

The most interesting effects are observed at the nematic-smectic A transition point. For both, 8-CB (Figure 1) and *n*-AB (Figure 2), the parallel component of conductivity $\sigma_{\parallel}$ considerably decreases at

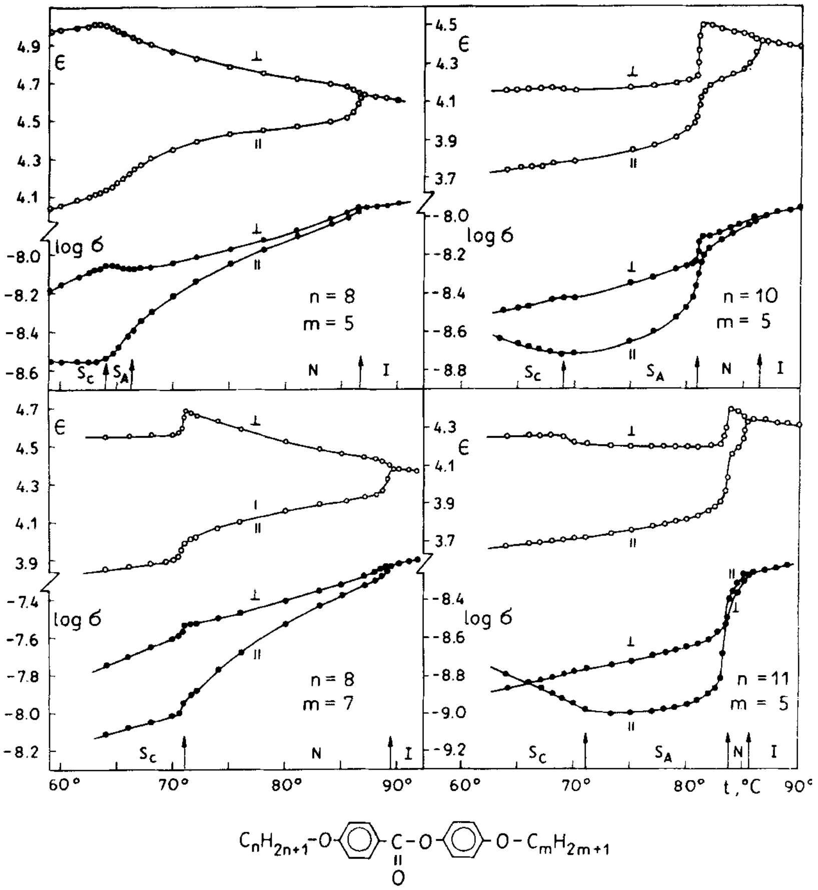
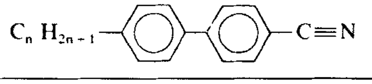
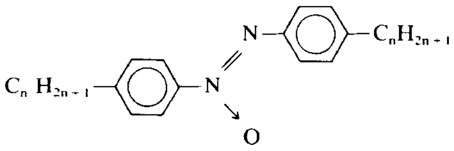
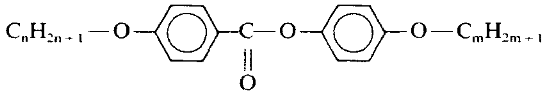


FIGURE 3 Static electric permittivity, (ε), and conductivity, (σ), of some p-alkyloxyphenyl-p′-alkoxybenzoates.

TABLE II

Activation energy of conductivity (in kcal/mol).

		Isotropic	Nematic		Smectic A	
		E_A	$E_{A\parallel}$	$E_{A\perp}$	$E_{A\parallel}$	$E_{A\perp}$
						
n = 5		7.0	11.3	12.7	—	—
6		7.8	10.1	11.6	—	—
7		6.3	13.6	14.2	—	—
8		6.5	20.1	19.9	19.6	15.7
						
n = 5		8.8	6.4	7.5	—	—
6		5.3	10.9	8.6		
7		5.6	7.4	3.7	6.9	6.1
8		6.3			5.9	7.4
						
n = 8	m = 5	4.4	14.0	9.5		
8	7	7.4	16.0	9.3	—	—
10	5	8.5	18.1	9.4	20.8	10.6
11	5	9.1				8.9

the transition point, while the perpendicular component $\sigma_\perp$ practically does not see the transition at all. This leads to a change of sign of electric conductivity anisotropy from $\sigma_\parallel/\sigma_\perp > 1$ in nematic phase to $\sigma_\parallel/\sigma_\perp < 1$ in smectic phase. Analogous effect was observed in studies of anisotropy of the diffusion coefficient.[16]

The formation of smectic layers in liquid crystals of *n*-CB and *n*-AB types strongly affects the movement of ions in the direction perpendicular to the smectic layers only. For ions moving along the direction parallel to the layers, smectics still seem to have the nematic structure.

The results obtained for p-alkyloxyphenyl-p′-alkoxybenzoates are

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shown in Figure 3. In these compounds the smectic A phase transforms to a smectic C phase on cooling. Of course, because of biaxiality of the latter phase the results of simple measurements of the perpendicular and parallel components cannot be interpreted as those for a uniaxial system. However, it is worth noticing, that for the studied homologs of this group the temperature dependences of both electric permittivities and conductivities are surprisingly similar in all mesophases (Figure 3). For the two compounds of this group (10,5 and 11,5) the nematic-smectic A phase transition manifests itself as a considerable jump of both components of permittivity and conductivity.

Activation energies of conductivity, calculated from the Arrhenius plot, are collected in Table II. In some cases the values of E_A are approximate because of strong pretransitional effects causing a nonlinearity of the Arrhenius plot.

Acknowledgment

This work was supported by the Polish Academy of Sciences within the framework of Project CPBP 01.12.

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