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MEASUREMENTS OF TRANSPORT PROPERTIES IN THE NEMATIC AND SMECTIC PHASES OF VARIOUS COMPOUNDS (*)

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Résumé. — On a mesuré les conductivités parallèle et perpendiculaire à l'axe long des molécules ($\sigma_{\parallel}$ et $\sigma_{\perp}$ respectivement) dans les phases nématiques et smectiques (A et B) de produits variés. Des effets prétransitionnels se manifestent dans la phase nématique de tous les corps étudiés. L'étude de la conductivité de la phase smectique A nous a conduits à distinguer deux groupes de corps : dans le premier $\sigma_{\parallel}$ devient égal à $\sigma_{\perp}$ quelques degrés au-dessus de la transition smectique A-nématique et est environ cinq fois plus petit que $\sigma_{\perp}$ dans la phase smectique ; de plus, dans ce rouge, $\sigma_{\perp}$ se comporte d'étrange façon, comportement qui se retrouve pour le coefficient de diffusion $D_{\perp}$ du rouge de méthyle perpendiculairement à l'axe long des molécules. Dans le second groupe $\sigma_{\parallel}$ est peu différent de $\sigma_{\perp}$. Cette différence des propriétés de conductivité entre les deux groupes pourrait s'expliquer par des structures différentes de la phase smectique A.

Abstract. — Electrical conductivities parallel and perpendicular to the long axis of the molecules (respectively $\sigma_{\parallel}$ and $\sigma_{\perp}$) are presented for the nematic and smectic (A and B) phases of various compounds having a low latent heat of transition smectic A $\leftrightarrow$ nematic. All the materials show pretransitional effects in their nematic phase. The study of conductivity in smectics A has led us to distinguish two groups of materials. In the first one $\sigma_{\parallel}$ becomes equal to $\sigma_{\perp}$ a few degrees above the smectic A-nematic transition, while $\sigma_{\parallel}$ is at least five times smaller than $\sigma_{\perp}$ in the smectic A phase. Furthermore $\sigma_{\perp}$ increases anomalously with decreasing temperature, which is observed also for the dye diffusion coefficient normal to the molecular axis. In the second group $\sigma_{\parallel}$ differs only slightly from $\sigma_{\perp}$. The different behaviour of the conductivity in this group is probably related to the fact that the smectic A layers comprise two molecules.

Introduction. — Data of Carr [1] on ethyl-p-(p'-methoxybenzilidene)-aminocinnamate have suggested that in the smectic A phase the conductivity along the long molecular axis, $\sigma_{\parallel}$, is lower than the conductivity $\sigma_{\perp}$ normal to this axis, contrary to what happens in nematics such as MBBA and PAA [2]. This fact has been indirectly confirmed by Rondelez [3], who has found an unusual decrease of the ratio $R = \sigma_{\parallel}/\sigma_{\perp}$ with decreasing temperature in some nematic compounds exhibiting short-range smectic order.

In this paper we report on measurements of $\sigma_{\parallel}$, $\sigma_{\perp}$ and R in the whole mesomorphic range of compounds presenting a nematic, a smectic A, and for some of them a smectic B phase. For one compound we have also determined the diffusion coefficients of dyes parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the long axis of the molecules, and the ratio $R' = D_{\parallel}/D_{\perp}$.

Experimental conditions. — 1. ELECTRICAL CONDUCTIVITIES. — We have studies several compounds :

a) *some Schiff bases* :

N-(p-butyloxybenzylidene)-p'-octylaniline (40.8).
N-(p-hexyloxybenzylidene)-p'-octylaniline (60.8).
N-(p-pentyloxybenzylidene)-p'-pentylaniline (50.5).
N-(p-pentyloxybenzylidene)-p'-heptylaniline (50.7).
N-(p-cyanobenzylidene)-p'-octyloxyaniline (CBOOA).

b) *some biphenyls* :

p-cyano-p'-octylbiphenyl (COBP).
p-cyano-p'-octyloxybiphenyl (COOBP)

and

c) p,p'-di-heptylazoxybenzene (HEPTAB) [4].

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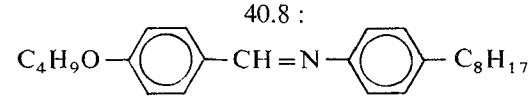
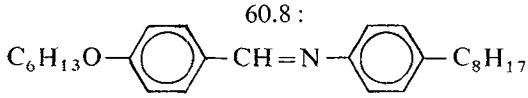
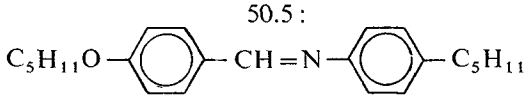
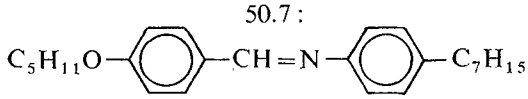
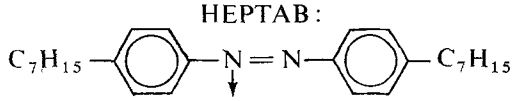
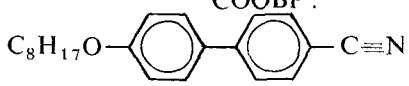
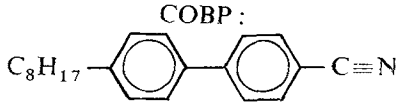
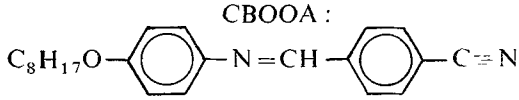
TABLE I

Phase diagrams and temperature and latent heat of transition for the smectic A ↔ nematic transition in the studied compounds. K means crystal, S_A smectic A, S_B smectic B, S_C smectic C, S_4 is an unidentified smectic phase and I the isotropic phase. The temperatures are in degree Celsius ; the latent heat in calories per mole is given in brackets.

Compound	Phase diagram
40.8 : 	K 33 S_B 49.5 S_A 63.7 N 79 I (83)
60.8 : 	K 29 S_B 66.3 S_A 81.7 N 82.5 I (98)
50.5 : 	K 29 S_4 46 S_B 48 S_C 52 S_A 53.6 N 77.5 I (50)
50.7 : 	K 29.5 S_4 37.3 S_B 52.1 S_C 55.5 S_A 64 N 78 I (100)
HEPTAB : 	K 34 S_A 54.5 N 70.5 I (38)
COOBP : 	K 54.5 S_A 67 N 79 I
COBP : 	K 21 S_A 32.5 N 40 I
CBOOA : 	K 73 S_A 82.6 N 108.4 I (< 12)

Their formulae, phase diagrams and heats of transition are summarized in table I. They all have a low heat of transition at the nematic to smectic A phase transition.

The determination of the components of the tensor of conductivity is made by measuring the capacity and the losses of a nematic slab placed between two parallel SnO_2 coated glass electrodes spaced by two 75 μm-thick teflon spacers. Measurements are performed at 1 kHz, using a Gereal Radio 1609 A bridge. The measurements on HEPTAB are at 1 592 Hz, using a Wayne-Kerr B 642 autobalance bridge.

The sample is set inside an electronically regulated oven whose overall stability is better than 0.01 °C. A magnetic field of 20 kOe is used to align the molecules parallel or perpendicular to the glass plates in the nematic phase. When slowly cooling down the sample with the field on, the alignment is maintained in the smectic A phase. This could be verified optically.

2. DYE DIFFUSION COEFFICIENTS. — We have used a method developed by Rondelez [5] for MBBA and made it suitable for 40.8. A drop of a 1 % solution of methyl red (MR) in 40.8 is injected in a 200 μm diameter hole drilled in the upper glass plate limiting the sample. Planar anchoring of the molecules is achieved by evaporating silicon monoxide on the glass plates at oblique incidence [6], and is checked by conoscopy.

The sample is inserted in a similar oven. The lateral gradient over the whole sample (25 × 25 mm) is smaller than 10^{-2} °C. The coloured spot is photographed as a function of time. From the optical density parallel and perpendicular to the molecular axis we can deduce $D_{\parallel}$ and $D_{\perp}$.

Results. — Figure 1 shows $\sigma_{\parallel}$, $\sigma_{\perp}$, and the ratio $R = \sigma_{\parallel}/\sigma_{\perp}$ for undoped 40.8 as a function of temperature. R, which is larger than unity close to the nematic-isotropic phase transition T_{NI}, decreases with

decreasing temperature down to unity a few degrees above the nematic to smectic A phase transition T_{SN}. R decreases further in the smectic A phase, and finally reaches a very small value, 0.1, in the smectic B phase. In the nematic phase, depending on the temperature, values of R larger than 1, equal to 1 or smaller than 1 are observed. The latter case gives rise to interesting electrohydrodynamic properties [7].

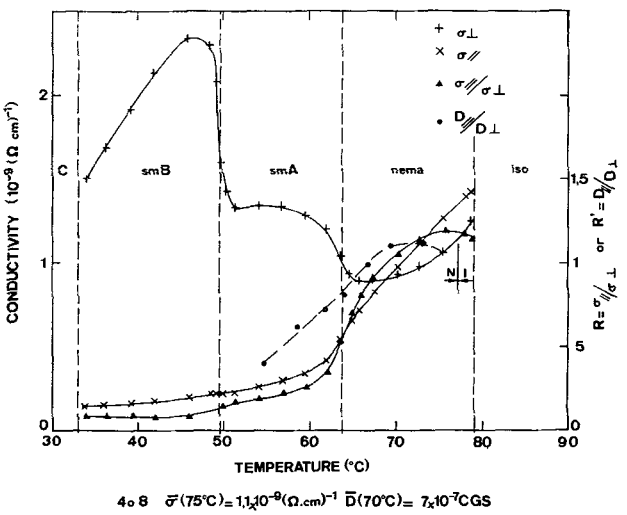


FIG. 1. — $\sigma_{\parallel}$, $\sigma_{\perp}$ and $R = \sigma_{\parallel}/\sigma_{\perp}$ versus temperature for 40.8. The dotted line represents $R' = D_{\parallel}/D_{\perp}$ for methyl red in 40.8 ; in this case the temperature of transition have slightly shifted and are : $T_{NI} = 77.2$ °C, $T_{SAN} = 63.5$ °C.

In the smectic phases $\sigma_{\parallel}$ decreases continuously with decreasing temperature and then saturates. The saturation value depends on the quality of the molecular alignment. This can be explained by the fact that defects, if present, correspond to small disoriented volumes in the sample for which we measure the conductivity $\sigma_{\perp}$ which is much larger than $\sigma_{\parallel}$.

The behaviour of $\sigma_{\perp}$ is more surprising : $\sigma_{\perp}$ decreases with decreasing temperature in the nematic phase, then increases around T_{SAN}, becomes stationary in the smectic A phase, then sharply increases at the smectic A-smectic B transition. Clearly the smectic B ordering strongly favours the motion of the charged particles inside the smectic layers.

The electric conductivities of 60.8, 50.7, 50.5 (Fig. 2 and 3) and HEPTAB (Fig. 4) have the same characteristics. In figure 4 the dotted curves represent $\sigma_{\perp}$ and R for a 3 °/oo TMAB (tetramethyl-ammonium bromide) doped sample of HEPTAB. The increase of $\sigma_{\perp}$ has disappeared, and R has somewhat higher values than in a pure sample [8].

These conductivity data are hard to interpret as long as we are not able to know the exact nature of the charge carriers. For that reason we have also the measured the dye diffusion coefficients of MR in 40.8.

The ratio $R' = D_{\parallel}/D_{\perp}$ is plotted in figure 1. R' behaves in a way similar to R, with an overall translation towards lower temperatures. We have not been able

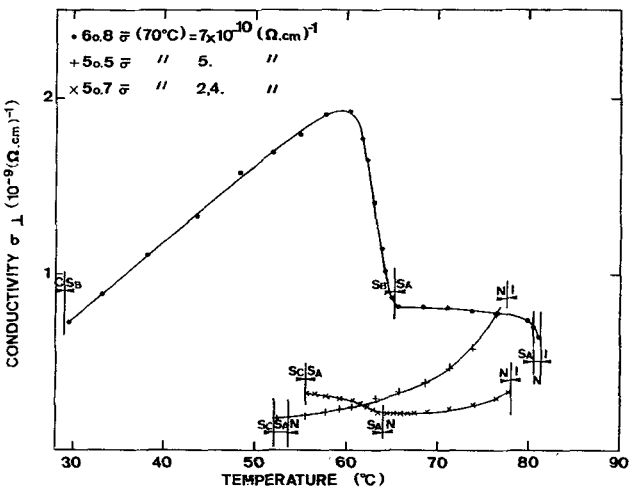


FIG. 2. — $\sigma_{\perp}$ versus temperature in 50.5, 50.7, 60.8.

to measure R' for temperatures lower than 54 °C : only $D_{\perp}$ can be measured, $D_{\parallel}$ becomes too small to be determined with some accuracy by the method we use. But $D_{\perp}$ behaves in a way completely similar to $\sigma_{\perp}$: leveling off in the smectic A phase and an increase at the smectic A-smectic B transition.

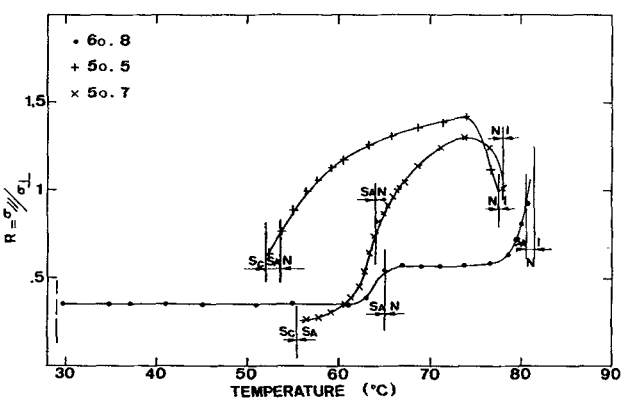


FIG. 3. — $R = \sigma_{\parallel}/\sigma_{\perp}$ versus temperature in 50.5, 50.7, 60.8.

For the three other compounds studied the behaviour of the electrical conductivities is completely different. Figures 5 and 6 display $\sigma_{\parallel}$, $\sigma_{\perp}$ and R for COOBP and CBOOA, respectively. In that case $\sigma_{\parallel}$ and $\sigma_{\perp}$ decrease with decreasing temperature. After an increase near T_{NI}, R decreases continuously and saturates in the smectic A phase at the value 1 for COOBP (no anisotropy of the electrical conductivities) and at a value close to 1 (0.85) in CBOOA. COBP behaves like COOBP.

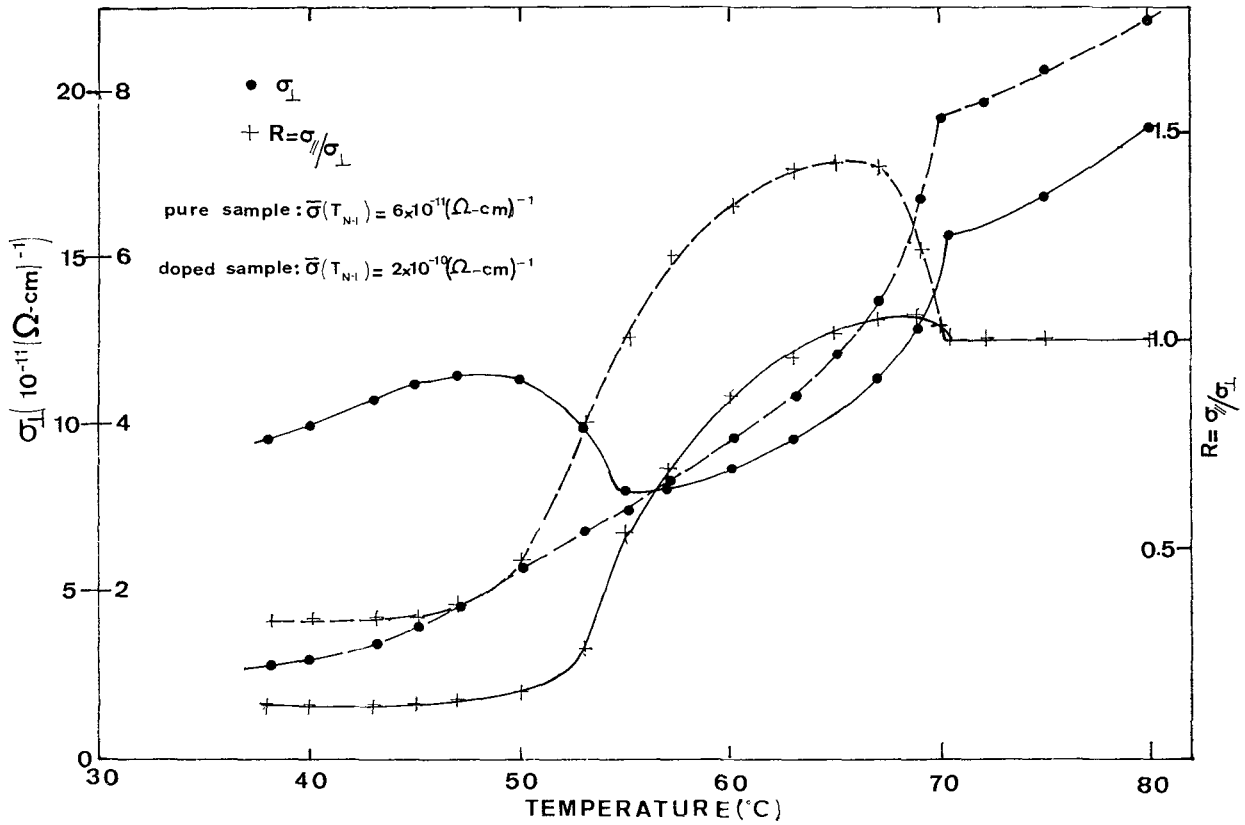


FIG. 4. — $\sigma_\perp$, $R = \sigma_{\parallel}/\sigma_\perp$ versus temperature in HEPTAB. The broken lines represent $\sigma_\perp$ and R in a sample of HEPTAB doped with 0.3 °/₀₀ TMAB : the temperatures of transition are now $T_{SAN} = 53.6$ °C, $T_{NI} = 70$ °C.

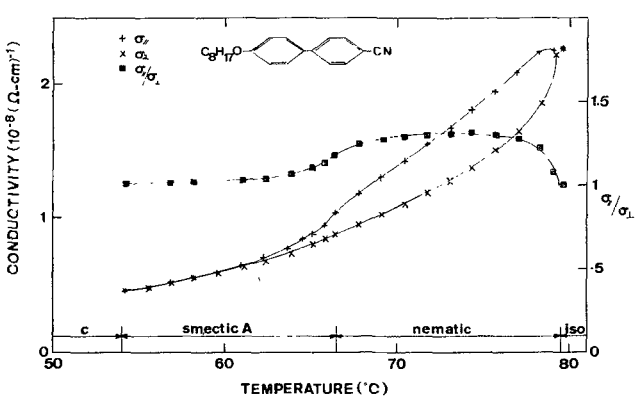


FIG. 5. — $\sigma_{\parallel}$, $\sigma_\perp$ and $R = \sigma_{\parallel}/\sigma_\perp$ versus temperature in COOBP.

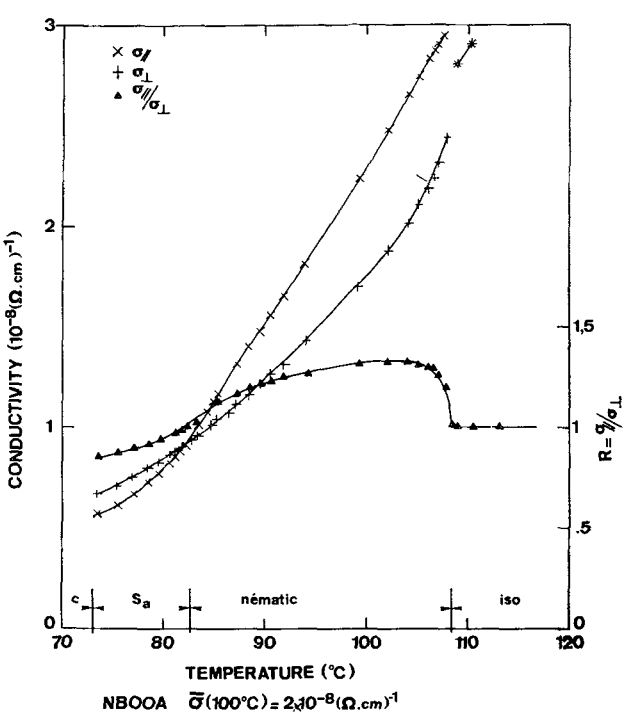


FIG. 6. — $\sigma_{\parallel}$, $\sigma_\perp$ and $R = \sigma_{\parallel}/\sigma_\perp$ versus temperature in CBOOA.

Discussion. — The shape of the curve for R in the nematic phase is a feature common to all the compounds studied and can be explained as follows. Near T_{NI}, R behaves in the same way as the nematic order parameter. Then, when the temperature decreases, the ions begin to experience a short-range smectic order superimposed to the nematic order [9], leading to a gradual decrease of R until the characteristic situation of smectic A is reached. For HEPTAB this short-range smectic order was found to have a profound effect on the dielectric properties too [10].

With regard to the transport properties in the smectic A phase we can distinguish two groups of compounds :

— The first group includes 40.8, 60.8, 50.5, 50.7 and HEPTAB. It is characterized by a very low ratio $\sigma_{\parallel}/\sigma_\perp$

in the smectic phases : the flow of charge carriers or dyes is much easier in the smectic layers than normal to them. $\sigma_{\parallel}$ is about five times smaller than $\sigma_{\perp}$. Qualitatively this can be understood from the anisotropic forces between the molecules leading to a smectic potential that is periodic in the direction of the layer normal. Consequently anisotropic ions or dyes will tend to stay in the centre of the smectic layer like the mesomorphic molecules themselves. In addition, both spherical and anisotropic ions may form weak charge-transfer complexes with the aromatic parts of the mesomorphic molecules. Some preliminary results on dye diffusion coefficients indeed indicate that the shape of the $D_{\perp}$ versus T curve strongly depends on the size of the dye. It seems that small dyes can travel very quickly inside the smectic layers, while for dyes of the size of the molecules or larger we no longer observe the increase of $D_{\perp}$ in the smectic B phase. Further investigations and a comparison with self diffusion measurement, for example by neutrons scattering, are necessary to ascertain this last point. Recently some conductivity measurements in smectic phases were reported by Heppke *et al.* [11], that also fit into this group.

— The second group consists of CBOOA, COOBP, COBP. For those compounds $\sigma_{\parallel}$ and $\sigma_{\perp}$ are monotonous decreasing functions of temperature, but there is apparently no preferential direction for the flow of charges (R takes values close to 1). For these compounds X rays data have shown that the interlayer spacing is larger than the molecular length, and that two molecules are associated within a layer [12]. This is to be contrasted with the first groups where the layer thickness equals the molecular length. Probably this difference in structure of the smectic phase between the two groups could explain the observed differences in transport properties.

Conclusion. — We have measured the electrical conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$ (respectively parallel and perpendicular to the long axis of the molecules) in the whole mesomorphic range of various compounds. In the smectic A phases usually a strong anisotropy is observed : the conductivity is much larger in the smectic layers than normal to them. This last kind of behaviour was also observed for the dye diffusion coefficients. However, for some smectic A compounds with two molecules per smectic layer the electrical conductivities are no longer anisotropic.

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