Nematic Phenyl Benzoates in Electric Fields: I. Static and Dynamic Properties of the Dielectric Permittivity

W. H. De Jeu [a] & Th. W. Lathouwers [a]

[a] Philips Research Laboratories, Eindhoven, Netherlands
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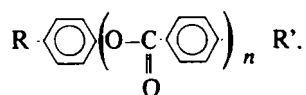# Nematic Phenyl Benzoates in Electric Fields
I. Static and Dynamic Properties of the Dielectric Permittivity[†]

W. H. de JEU and Th. W. LATHOUWERS

Philips Research Laboratories
Eindhoven
Netherlands

A discussion is given of the dielectric properties of some nematic phenyl benzoates with the structure

$$R \cdot \hexagon \left(O - \underset{\underset{O}{\|}}{C} \cdot \hexagon \right)_n R'.$$

For $n = 2$ the dielectric anisotropy $\Delta\epsilon = \epsilon_{//} - \epsilon_{\perp}$ is found to be positive. For $n = 1$, however, the sign depends on the *para* substituents. In particular, replacement of an alkyl group by an alkoxy group shifts $\Delta\epsilon$ towards negative values. The frequency dependence of $\epsilon_{//}$ shows a relaxation at relatively low frequencies (kHz range), while $\epsilon_{\perp}$ remains constant. The activation energy for this relaxation is 0.4 till 0.5 eV for all the compounds studied. In case of a positive static $\Delta\epsilon$ the relaxation leads to a change of sign of $\Delta\epsilon$ which is of interest for the study of electrohydrodynamic instabilities.

INTRODUCTION

Since the pioneering work by Meier and Maier[1] it is well known that the dielectric permittivities $\epsilon_{//}$ and $\epsilon_{\perp}$, respectively parallel and perpendicular to the preferred axis of a nematic liquid crystal, can have a different frequency dependence. $\epsilon_{\perp}$ exhibits the normal Debije dipole relaxation of a fluid which usually
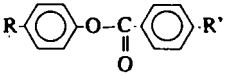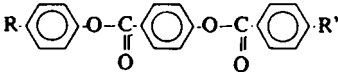

[†] Presented at the Fourth International Liquid Crystal Conference, Kent, Ohio, USA, August 21–25, 1972.

occurs in the GHz region. $\epsilon_{//}$ may show an additional dispersion in the MHz region[1,2] or even in the kHz region.[3-5] In one of these cases this relaxation lead to a change of sign of the dielectric anisotropy $\Delta\epsilon = \epsilon_{//} - \epsilon_{\perp}$.[4]

A change of sign of $\Delta\epsilon$ as a function of the frequency is interesting because it gives the opportunity to study the behaviour of a nematic under the influence of electric fields for $\Delta\epsilon > 0$ and $\Delta\epsilon < 0$ in the same sample. For practical reasons the frequency f_0 where $\epsilon_{//} = \epsilon_{\perp}$ must not be too high. Consequently, the relaxation of $\epsilon_{//}$ should take place at frequencies as low as possible, while $\epsilon_{\perp}$ should be somewhat smaller than $\epsilon_{//}$. This favourable combination has been found[4] in WI, a mixture of four nematic phenyl benzoates[6] (B1, B2, A with n-butyl and methoxy as p-substituents, and the same with the end groups interchanged; see Table 1). At room temperature $\Delta\epsilon$ was found to be positive for frequencies below 10 kHz and negative above this frequency. However, as this is a non-eutectic mixture of rather different compounds it is not very suitable for more detailed investigations.

In this paper we shall first give the static dielectric permittivities of five nematic phenyl benzoates (Table 1). Then the frequency dependence will be considered at a reduced temperature of $0.93T_c$. Finally the relaxation of $\epsilon_{//}$ will be discussed as a function of temperature. The different types of electrohydrodynamic instabilities above and below f_0 will be discussed in detail in Part II.

TABLE 1

The Compounds Investigated

No. compound	Formula		Nematic range (°C)
A	R $\langle\bigcirc\rangle$-O-C $\langle\bigcirc\rangle$·R' (with C=O below)		
A1	n-C$_7$H$_{15}$	n-C$_4$H$_9$	9 – 15
A2	n-C$_6$H$_{13}$O	n-C$_4$H$_9$	31 – 49
A3	C$_2$H$_5$O	O-CO-OC$_4$H$_9$	58 – 84
B	R·$\langle\bigcirc\rangle$-O-C·$\langle\bigcirc\rangle$-O-C $\langle\bigcirc\rangle$·R' (with C=O below both)		
B1	n-C$_4$H$_9$	n-C$_4$H$_9$	90 – 177
B2	n-C$_4$H$_9$	OCH$_3$	108 – 227

EXPERIMENTAL

Compounds A1, A2, B1 and B2 were synthetized by R. Steissträsser (E. Merck)[6,7] and used without further purification. Compound A3 was obtained commercially (Eastman Kodak) and recrystallized several times from methanol.

The dielectric permittivities were measured using cells consisting of two glass plates with evaporated copper electrodes. The distance was fixed using 80 μm mylar spacers and epoxy resin. Each cell was used only once, and its cell constant was determined at room temperature with chlorobenzene. The calibrated cell with the liquid crystal was placed in a heating stage (similar to the Mettler FP 52) built in this laboratory. Alignment was assured by a magnetic field of about 13 kOe. The temperature was stabilized within $0.5°C$ by a Eurotherm type 017 temperature controller. The set-up was checked by measuring the temperature dependence of the dielectric constant of n-decane. Over the range $20-100°C$ $d\epsilon/dt$ could be reproduced within 1%. The overall error is estimated to be about 3%, and somewhat larger at the highest temperatures.

The static values of the dielectric permittivity were measured at a frequency of 1592 Hz using a Wayne-Kerr B642 bridge. For other frequencies in the audio region the same bridge was used with an external source and detector. In the rf region a Wayne Kerr B201 bridge was used in combination with an SR 268 source and detector of the same make. In the higher frequency range errors can arise due to the small resistance and inductance in series with the dielectric cell. In our experiments with copper electrodes the series resistance R_s was $< 0.5\ \Omega$ so that for typical C-values of 100 pF $(R_sC)^{-1} >> 5$ MHz, the highest frequency used. The series inductance L, however, tends to a small increase in the measured capacitance above 2 MHz. This could not be circumvented because of the relatively long leads between the sample in the magnet and the bridge. The measured capacitance is given by

$$C_p = C \frac{1 - x^2 - 1/Q^2}{(1-x^2)^2 + x^2/Q^2},$$ (1)

where C is the capacitance of the cell, $x = \omega/\omega_0$ with $\omega_0 = 1/\sqrt{LC}$, and $Q = R\sqrt{L/C}$. As $x << 1$ and $Q >> 1$ this leads in a first approximation to

$$C_p = C(1 + x^2 - 1/Q^2).$$ (2)

Using this formula a correction was applied to $\epsilon_{//}$ assuming that $\epsilon_{\perp}$ still remains constant between 1 and 5 MHz. The dielectric losses above 2 MHz were also corrected for the series inductance by subtracting the apparent conductance of an air-spaced capacitance of the same value using the same leads.

THE STATIC DIELECTRIC PERMITTIVITIES

The results for the dielectric permittivities as a function of the temperature at 1592 Hz are given in Figures 1 and 2. Compound B2 was found to decompose slightly at about 200°C. Therefore no reliable dielectric measurements could be carried out in this region.

In A1 the dipole moment is almost completely due to the linkage group. As the dielectric anisotropy is about equal to that of the dipole-less di-alkyl-azo-benzenes,[8] the angle of the bridge dipole with the preferred axis must be close to 55°. At this angle the dipole moment would contribute equally to $\epsilon_{//}$ and $\epsilon_\perp$.[9] Replacing an alkyl group by an alkoxy group (compound A2) leads to a change of sign of $\Delta\epsilon$. The same effect is found in some azoxybenzenes[10] and can be understood from the fact that the alkoxy dipole moment makes an angle of 72° with the p,p'-axis of the adjacent ring.[11] The angle between this axis and the long molecular axis will be small, and therefore the alkoxy dipole moment contributes more to $\epsilon_\perp$ than to $\epsilon_{//}$.

In compound A3 the dipole moment of the carbonate group clearly contributes mainly to $\epsilon_{//}$, leading again to a positive $\Delta\epsilon$. A peculiar phenomenon here is that $\bar{\epsilon} = \frac{1}{3}(\epsilon_{//} + 2\epsilon_\perp)$ changes discontinuously at T_c. At present we cannot offer an adequate explanation, but similar effects have been found in p-alkoxy benzoic acids.[12] This suggests that the effect could be related to
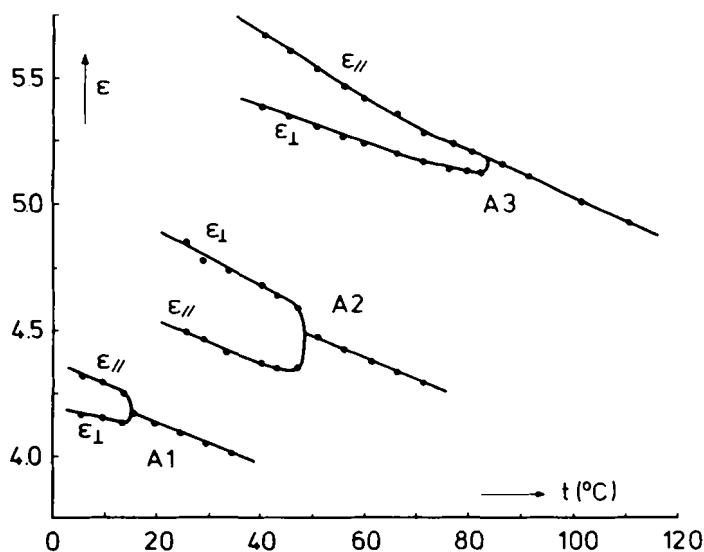

FIGURE 1   Static dielectric permittivities of the phenyl benzoates with two aromatic rings (see also Table 1).
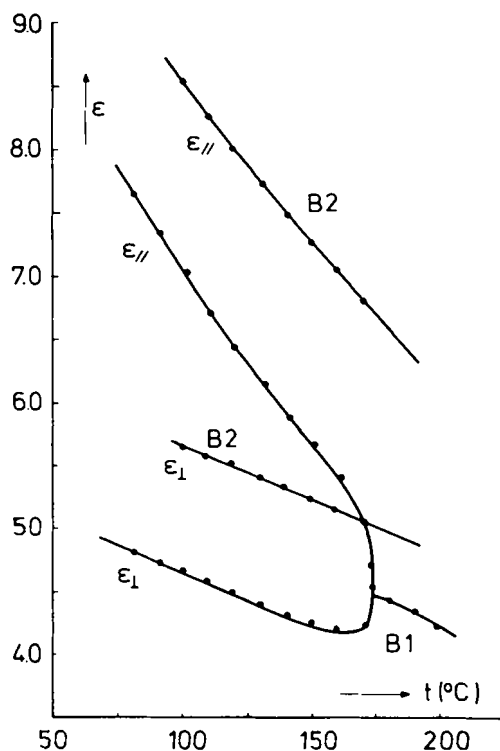
FIGURE 2   Static dielectric permittivities of the phenyl benzoates with three aromatic rings.

changes in intermolecular association at T_c. Going from A1 via A2 to A3 each additional dipole moment leads to an increase in $\bar{\epsilon}$, as expected.

The compounds with three rings show higher values for both $\bar{\epsilon}$ and $\Delta\epsilon$. This is mainly due to the increase in the absolute value as well as in the anisotropy of the electronic polarizability (as is also reflected in the higher clearing points). Replacing an alkyl group by an alkoxy group again increases $\bar{\epsilon}$, but now $\Delta\epsilon$ is not much affected. This means that in this case the angle between the p,p'-axis of an outer benzene ring and the long molecular axis is much larger.

THE RELAXATION OF $\epsilon_{//}$

The dielectric permittivities of compounds A2, A3 and B1 were measured as a function of the frequency at the same reduced temperature of 0.93 T_c. This corresponds theoretically to a value of the order parameter $S = 0.65$.[13] Taking

$\epsilon_{//} = \epsilon'_{//} - i\,\epsilon''_{//}$ the results for $\epsilon'_{//}$ are given in Figure 3. In Figure 4 the values for $\epsilon'_{//}$ and $\epsilon''_{//}$ are combined to Cole-Cole plots.[14] As the data can be fitted by a semi-circle we can describe the relaxation with a single relaxation time τ_R, determined by the maximum of $\epsilon''_{//}$.

Theoretically the relaxation time τ_R is given by[15,16]

$$\tau_R = g\,\tau_D \cdot \tag{3}$$

The effect of the nematic order is described by a retardation factor g related to the height of a potential barrier W by

$$g = (kT/W_1)\exp(W/k_2) - 1_3. \tag{4}$$

The ordinary Debeije-relaxation is defined by

$$\tau_D = 4\pi\,\eta\,a^3/kT \tag{5}$$

where η is the viscosity and a a molecular dimension.

In order to determine g it would be necessary to measure τ_D too. A rough impression of the variation of τ_D can be obtained from the change in viscosity. The viscosities were determined by measuring the flow through a capillary tube that was calibrated with glycerol-water mixtures of known viscosities. In the nematic phase the viscosity is, of course, anisotropic and the measured value is approximately η_1 because of the alignment of the molecules parallel to the flow. Nevertheless these values can serve as an indication of the relative difference between the compounds. The results are summarized in Table 2. From the fact that $f_R\eta$ varies appreciably less than either f_R or η we conclude that the differences in the relaxation of A2, A3 and B1 are mainly due to differences in τ_D because of variations in η. Comparison with MBBA and hexyloxy-azoxybenzene
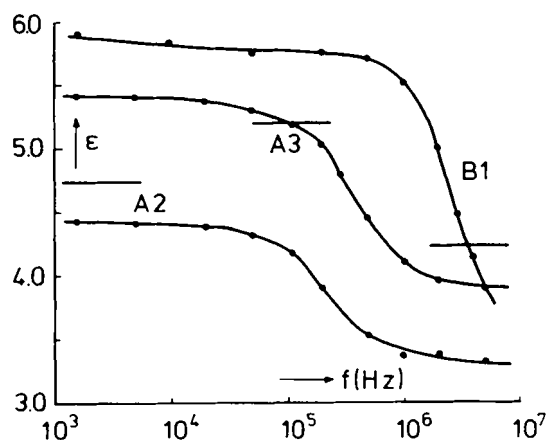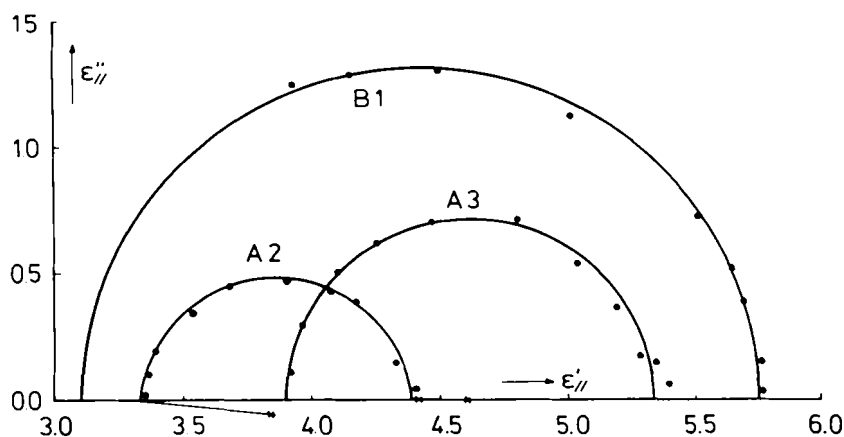

FIGURE 3   Relaxation of $\epsilon_{//}$ at $0.93T_c$. The horizontal bars indicate the value of $\epsilon_\perp$.

FIGURE 4   Cole-Cole plot of $\epsilon_{//}$ at 0.93 T_C.

shows that the same is approximately true for the latter compound, but MBBA seems to be an exception.

More information about the relaxation of $\epsilon_{//}$ can be obtained by varying the temperature. The temperature dependence of the viscosity could be fitted by

$$\eta \sim \exp{(W_{\mathrm{visc}}/kT)}. \qquad (6)$$

In the nematic and in the isotropic phase the same value was found for W_{visc}. Now the temperature dependence of the relaxation frequency $f_R = 1/(2\pi\tau_R)$ is approximately given by

$$f_R \sim_1 \exp_2 -(W+W_{\mathrm{visc}})/kT_3. \qquad (7)$$

Consequently low relaxation frequencies can be expected when using low temperatures and cooling down far below T_c. This requires nematics with a low

TABLE 2

Relaxation Frequency f_R of $\epsilon_{//}$ and Viscosity of some Nematic Compounds at $T = 0.93 T_c$

Compound	f_R (MHz)	η (cP)	$f_R \eta$
A2	0.2	40	8
A3	0.4	24[c]	10
B1	3.3	4	13
MBBA	1.2[a]	32[c]	38
hexyloxy-azoxybenzene	1.2[b]	8	9

[a] Calculated from data of Ref. 2
[b] Ref. 1
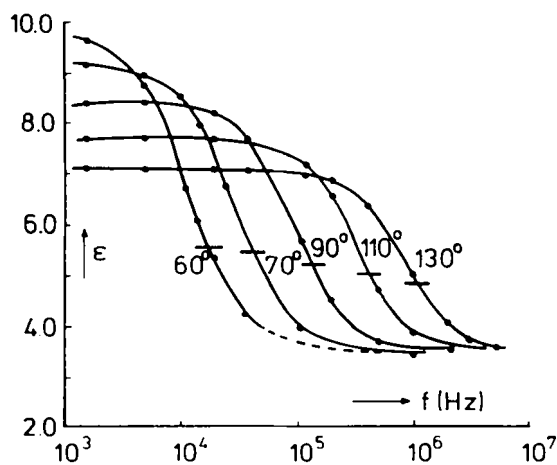[c] Calculated from data of Ref. 17.

FIGURE 5   Relaxation of $\epsilon_{//}$ of the eutectic B1/B2 mixture at various temperatures. The horizontal bars indicate the value of $\epsilon_{\perp}$.

melting point. In Figure 5 we give the dielectric constants as a function of frequency for various temperatures using the eutectic mixture of B1 and B2 (nematic range 68–191°C). In this way relaxation frequencies of the order of 10 kHz can easily be obtained. In Figure 6 f_R and the frequency of dielectric isotropy f_0 are displayed logarithmically against $1/T$. Within the experimental accuracy we find a straight line, the slope of which gives $-(W + W_{visc})$. As the lines for f_0 and f_R are approximately parallel we can also determine the activation energy from f_0 instead of f_R.

The frequency f_0 can easily be determined from the type of instability above the threshold in an electric field[4] (reorientation for $\Delta\epsilon>0$, turbulence and dy-
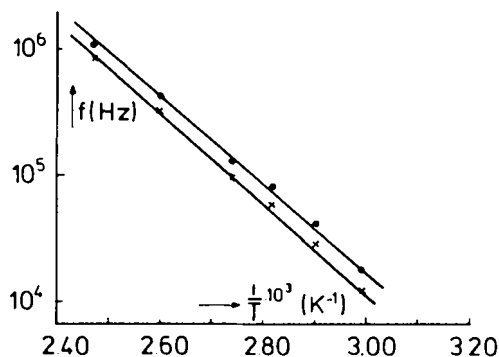

FIGURE 6 f_R and f_0 of the B1/B2 mixture as a function of $1/T$, respectively plotted as x and ●.

namic scattering for $\Delta\epsilon<0$), as will be discussed in some more detail in Part II. The variation of f_0 with temperature for all the above-mentioned nematic compounds and mixtures with $\Delta\epsilon>0$ is shown in Figure 7. From the slopes of the lines we obtain activation energies for the various phenyl benzoates that are rather similar (see Table 3). The same is true for hexyloxy-azoxybenzene and MBBA. On the other hand somewhat lower values for W have been reported for p-azoxyanisole ($g = 135$ at $125°C$,[18] leading to $W = 0.27$ eV)[16] and for a mixture of Schiff bases ($W = 0.21$ eV).[3] Hexyloxy-azoxybenzene, however, is more typical for the series of di-alkoxy-azoxybenzenes than p-azoxyanisole.[18]

The physical interpretation of the energy barrier W leading to the retardation factor g is not very clear. Usually it is thought to describe an individual molecule that is hindered in its rotation around a transverse axis because of the nematic order. However, then W would be expected to have a similar temperature dependence as the order parameter, while experimentally W is found to be rather independent of temperature. Therefore, it seems plausible that a rotation around a transverse axis is more determined by the short range order than by the nematic (long range) order.[19] Moreover, such a rotation will always be associated with local disorder, which in turn could lead to rotation of other molecules. Therefore it seems more correct to assume groups of molecules rotating together. This could also lead to a low frequency dispersion for $\epsilon_{//}$, while the relaxation of $\epsilon_{\perp}$ is still determined by the easy rotation of individual molecules around the long axis.
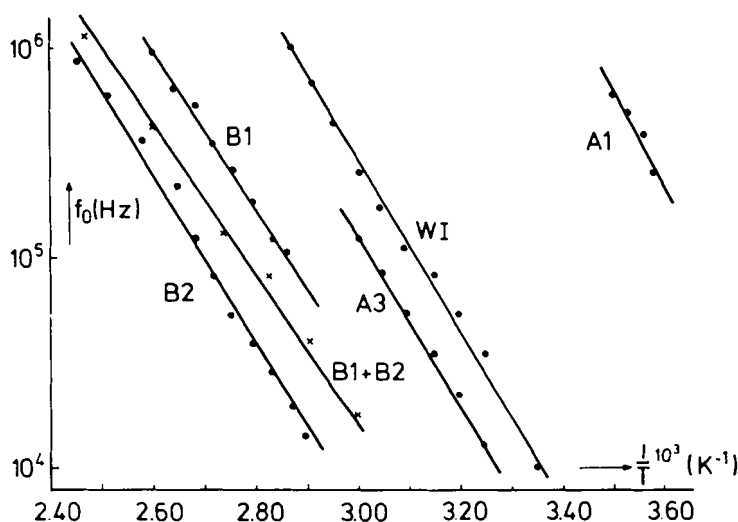

FIGURE 7 f_0 as a function of $1/T$ for various phenyl benzoates.

TABLE 3

Activation Energies for some Nematic Compounds (see text)

Compound	$W + W_{visc}$ (eV)	W_{visc} (eV)	W (eV)
A1	0.90	–	–
A3	0.81	0.38[2]	0.43
B1	0.75	0.22	0.53
B2	0.79	–	–
MBBA	0.65[a]	0.30[b]	0.35[c]
hexyloxy-azoxybenzene	0.81	0.30	0.5

(a) Calculated from data of Ref. 2.
(b) Calculated from data of Ref. 17.

For further improvement in this field not only τ_R but also τ_D should be measured in order to obtain values of g for various compounds. In fact Eq. (5) for τ_D gives rather poor agreement with experimental results in the isotropic phase, the theoretical values for τ being much higher than the experimental ones.

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