This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 20 February 2013, At: 11:58
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

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

Time Domain Spectroscopy of Liquid Crystals

M. El Kadiri [a], J. P. Parneix [a] & C. Legrand [a]
[a] Centre Hyperfréquences et Semi Conducterurs, Laboratorie Associé C. N.R.S. n[ddot] 287, P4 Université de Lille I, 59655 Villeneuve d'Ascq, France
Version of record first published: 17 Oct 2011.

To cite this article: M. El Kadiri , J. P. Parneix & C. Legrand (1985): Time Domain Spectroscopy of Liquid Crystals, Molecular Crystals and Liquid Crystals, 124:1, 259-267

To link to this article: http://dx.doi.org/10.1080/00268948508079481

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages

whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

Mol. Cryst. Liq. Cryst., 1985, Vol. 124, pp. 259–267
0026-8941/85/1244–259/$15.00/0
© 1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

Time Domain Spectroscopy of Liquid Crystals†

M. EL KADIRI, J. P. PARNEIX, C. LEGRAND

Centre Hyperfréquences et Semi conducteurs, Laboratoire Associé C.N.R.S. n° 287, P4 Université de Lille I, 59655 Villeneuve d'Ascq - France

(*Received July 19, 1984*)

A new method of dielectric investigation of liquid crystals using a transient excitation is presented. A two channel set-up rapidly gives the response of the sample (for times less than 1 second). A new real time approach gives the dielectric response function directly for the time range 1 μs – 30 ps. The method is applied to an original dielectric characterization of cyano-mesogenic series: cyanostilbene, cyanoester and cyanoterphenyl compounds are studied. The data are compared with those of the homologous cyanobiphenyl. The experimental results are discussed in terms of the molecular dynamics.

I INTRODUCTION

The dielectric characterization of materials using a transient method (time domain spectroscopy) was introduced by Fellner-Felldegg in 1969.[1] In most cases the time domain information was converted into frequency domain information using the Fourier Transform to deduce the complex permittivity $\epsilon^*(\omega)$ of the material. But to give a proper physical interpretation of the data one had to revert to the time domain form.[2,3]

Some authors[4,5] have used Real Time Analysis (R.T.A.) to characterize the dielectric behaviour while remaining in the time domain, but to obtain the dielectric response function some analytical approximation was necessary. To make the Real Time Analysis general, we have proposed a new method[6] which gives the dielectric response function without needing any assumptions concerning the incident waveform or the nature of the relaxation mechanism. Moreover, in most of the preceding papers T.D.S. was used to characterize the

†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

dielectric behaviour of isotropic materials and we have extended this treatment to the study of anisotropic materials such as liquid crystals. In the present paper we describe the dielectric characterization of a cyano-mesogenic series. The influence of the central group on the dielectric behavior is discussed for a number of cyanomesogenic compounds: cyanobiphenyl, cyanostilbenes, cyanotolanes and cyanoterphenyls. The data are compared to those obtained using the classical frequency method.

II EXPERIMENTAL SET-UP

A two channel T.D.S. system is used (Figure 1). The step pulse generated by a Tunnel Diode travels through a coaxial line to the sample where part of the signal is reflected by the dielectric. The reflected waveform is transmitted to the channel A of the sampling oscilloscope using a matched T. In the second channel B, an impulse is generated by the rising front of the incident step pulse via a low band directional coupler. This impulse is used to fix the time origin and to reduce the timing errors (particulary slow drift).

To make the data acquisition an automatic analysis of the displayed

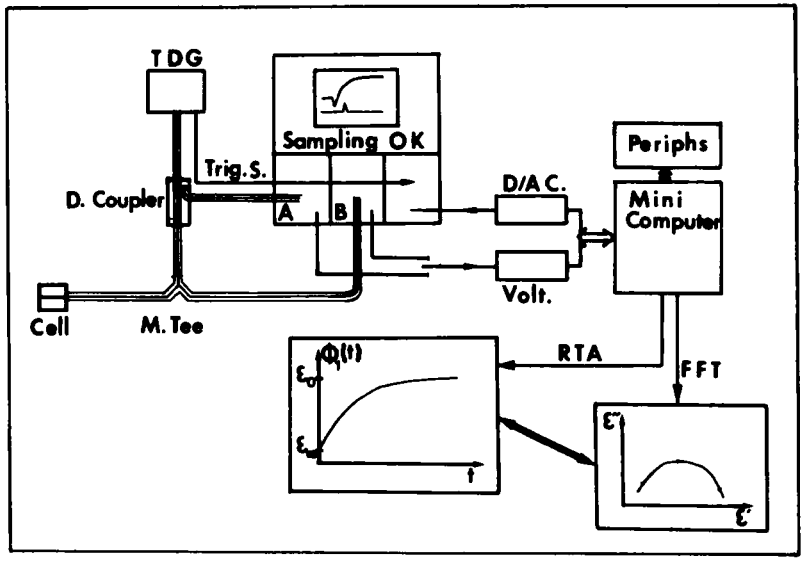


FIGURE 1 The two channel T.D.S. set-up: T.D.G.: Tunnel Diode Generator; R.T.A.: Real Time Analysis; F.F.T.: Fast Fourier Transform.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

waveforms is achieved using a mini-computer (HP9826 A) which drives a Digital/Analog converter and a fast voltmeter (via an IEEE bus). This system makes it possible to achieve a very fast signal acquisition (less than one second).

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

III REAL TIME ANALYSIS OF T.D.S. DATA

The method consists of giving a time response function which characterizes the dielectric behaviour of the investigated material. The response function $\phi(t)$ is related to the electrical charge Q(t) accumulated inside the sample and the time dependent voltage V(t) across the sample by:[4]

$$Q(t) = C\left[\epsilon_\infty V(t) + \int_0^t \phi\,(t - t')V(t')\,dt'\right] \qquad (1)$$

Where ϵ_∞ is the limiting high frequency permittivity and C the geometrical cell capacitance. V(t) and Q(t) are related to the incident and reflected waveforms. The capacitance C of the empty cell is determined by a calibration with standard liquids.

Equation (1) is solved numerically without any assumptions about the incident waveform or the relaxation process. Details of the way to achieve this resolution are given elsewhere.[6] The R.T.A. treatment immediately gives the high frequency limiting permittivity ϵ_∞ and the static permittivity ϵ_s.

IV EXPERIMENTAL RESULTS

To characterize anisotropic materials such as liquid crystals, special cells have been used.[7,8] The sample optical axis n was fixed using a strong static magnetic field (1.2 T). The dielectric characterization was measured in the two directions, with the measurement electric field parallel (E // n) and perpendicular (E $\perp$ n) to the axis n. The response functions were then deduced for each case: ϕ // (t) and ϕ $\perp$ (t) respectively.

1) The substances investigated

The chemical formula and the phase sequence of the compounds investigated using RTA are given in table I. All of them have a strong

TABLE I

The substances investigated: (1) R. J. Cox, IBM, San José (USA); (2) B.D.H. Chem. Ltd, Poole (UK); (3) M. Schadt, Hoffmann - La Roche, Basel (SWITZERLAND)

Compounds	Chemical formulae	Phase transitions
4-heptyl-4'-Cyanostilbene 7CS (1)	C_7H_{15}-⟨⟩-CH=CH-⟨⟩-CN	C52.5 S_{Ad} 64.6N95I
4-pentyl-4'-Cyanoter-phenyl T15 (2)	C_5H_{11}-⟨⟩-⟨⟩-⟨⟩-CN	C131N 230I
4-heptyl-4'-Cyanobenzoate 7CE (3)	C_7H_{15}-⟨⟩-COO-⟨⟩-CN	C44.6N 56.9I

longitudinal dipole moment. They differ mainly in the nature of the bridging group.

2) Real time analysis results

a - E // n direction

The parallel response functions ϕ // (t) obtained for E // n have a similar behavior for all the substances (Figure 2a).

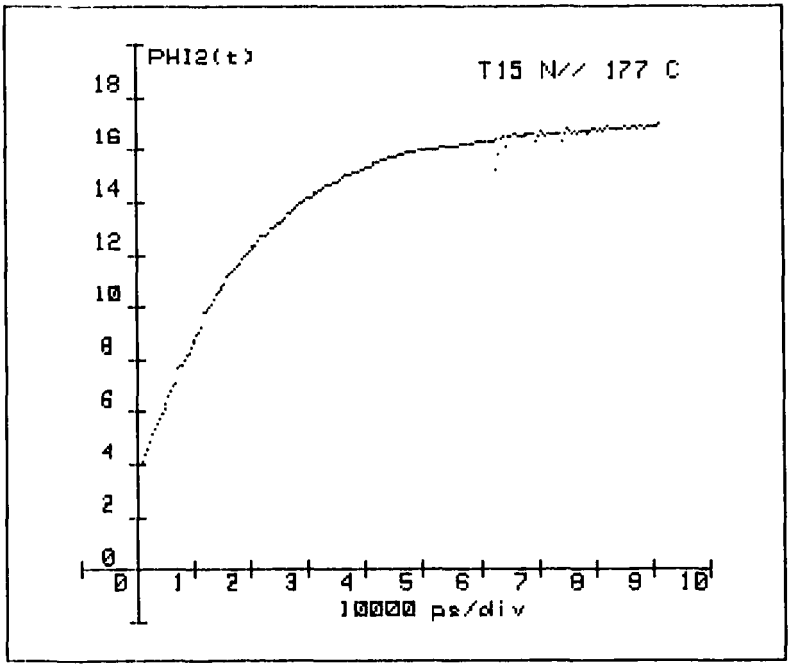


FIGURE 2a Parallel response function $\phi_{//}$ of T15 (nematic phase T = 177C)

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

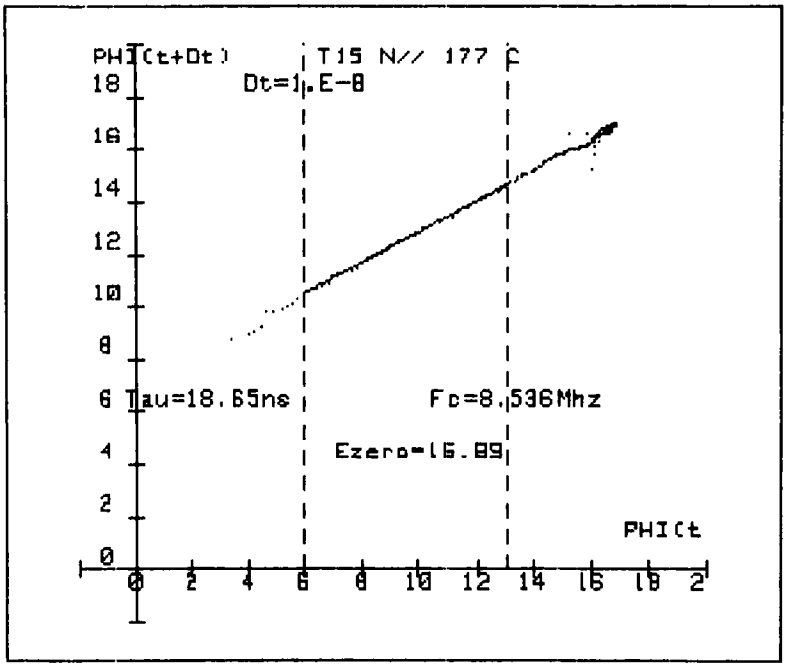


FIGURE 2b Csypkin representation for T15 parallel response function (nematic phase T = 177C)

They are nearly exponential at long times. The static and infinite permittivities can be directly obtained from this diagram[6]. An adequate representation (Csypkin representation) of the response function data $\phi(t + \Delta t)$ vs $\phi(t)$ enables us to obtain the long time relaxation and once more the static permittivity (Figure 2b).

b - E $\perp$ n direction

The perpendicular response function does not have a simple exponential behavior (Figures 3a–3b). This result is consistent with the frequency behavior.[9]

V DISCUSSION

As noted above, the main molecular difference between the compounds investigated lies in the nature of the bridging group. To complete the discussion we compare the dielectric properties of the series

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

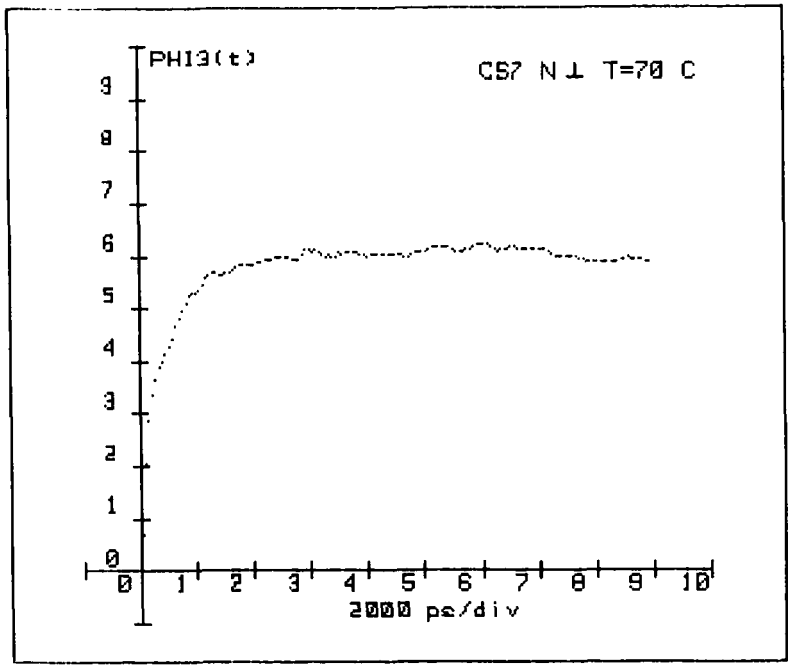


FIGURE 3a Perpendicular response function $\phi \perp$ of 7CS (nematic phase T = 70 C)

of homologous cyanobiphenyl (7CB) and cyanotolane (7CT) previously studied in our laboratory.[9,10]

1) Static permittivity

Typical static permittivity behavior vs temperature is given in figure 4. The dielectric anisotropy ($\Delta\epsilon' = \epsilon'_{//} - \epsilon'_{\perp}$) is strongly positive for all the compounds (Table II). Roughly the same value is obtained for 7CB – 7CT and 7CS. The polar central group of 7CE increases the overall dipole moment and then the static anisotropy increases ($\Delta\epsilon \simeq 16$).

2) Dynamic behavior

a - E // n direction

The long relaxation time is connected with the molecular orientation around a transverse axis. Assuming an Arrhenius dependence $\left(\tau \simeq \exp\left(\frac{W_N}{kT}\right)\right)$, the variation of the relaxation time τ vs. the in-

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

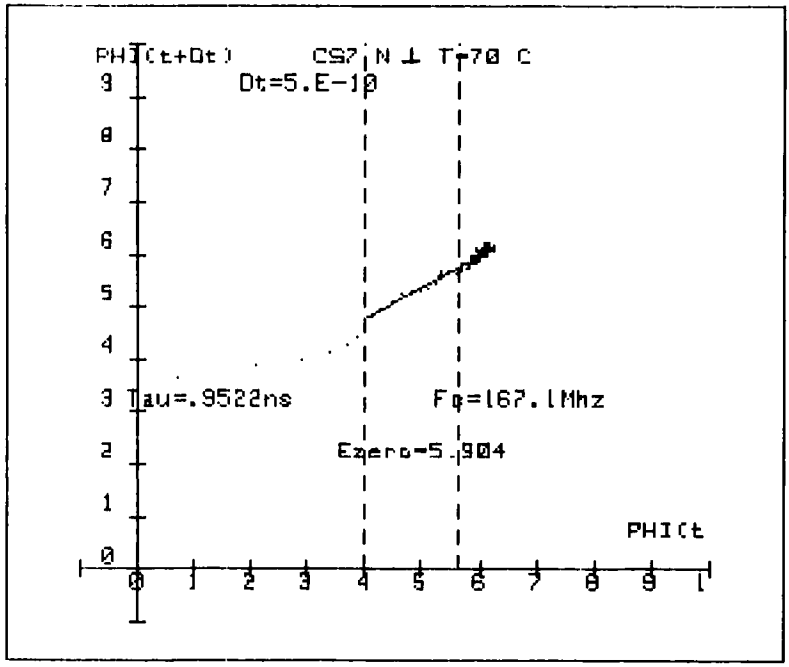


FIGURE 3b Csypkin representation for 7CS perpendicular response function (nematic phase T = 70 C)

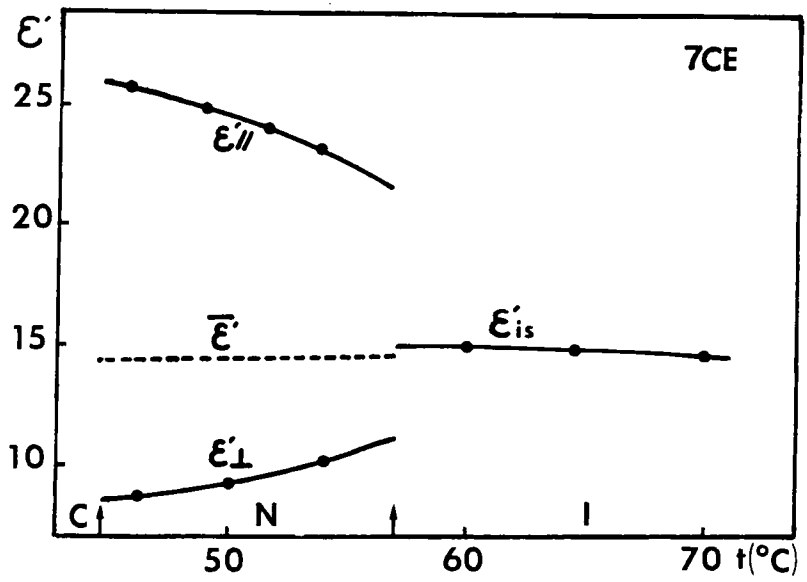
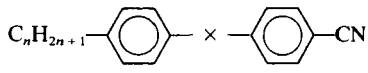


FIGURE 4 7CE Static permittivities vs Temperature

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

TABLE II

Experimental results for the cyanomesogenic series : static anisotropy $\Delta\epsilon' = \epsilon'_{//} - \epsilon'_{\perp}$; dynamic behaviour in the parallel direction at constant reduced temperature $T/_{TNI} = 0{,}98$



Substances	7CS	T15	7CE	7CB	7CT
X	—CH = CH—	— —	—COO—	-	—C ≡ C—
$\Delta\epsilon'$	11	12	16	10	9,5
$\tau_{//(ns)}$	11,4	4,8	53	26,5	26,5
$W_{N(ev)}$	0,77	0,56	0,88	0,54	0,98

verse temperature gives the activation energy W_N of the process.[7] Table II summarizes the data obtained for the different compounds. It can be noted that the 7CB and T15 have a lower activation energy ($\simeq$0,5 eV) than the other compounds ($\simeq$ 0,8 eV).

For the 7CS compound, the activation energy of the smectic phase,

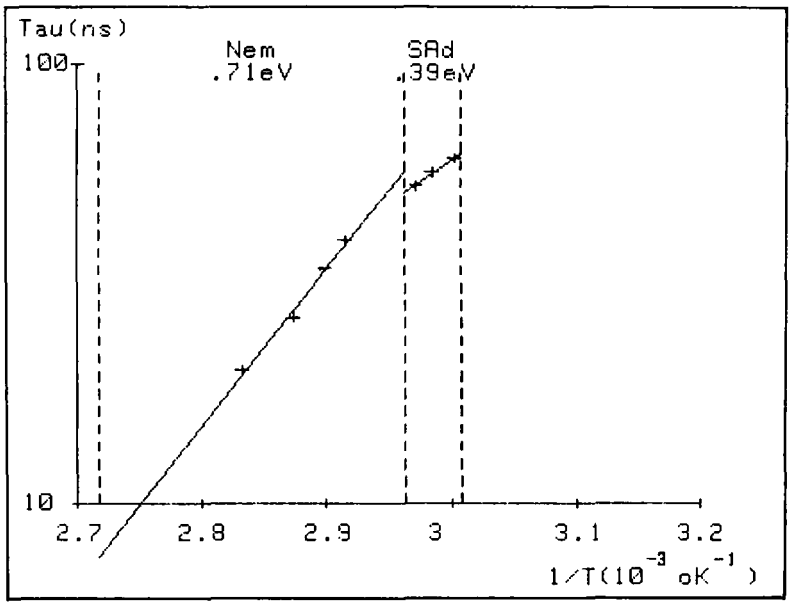


FIGURE 5 7CS Relaxation Times vs inverse temperature

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013

(S_{Ad}) is smaller than that of the nematic (figure 5). This can be interpreted in terms of a disymetric potential.[11]

b - E ⊥ n direction

The non-exponential behavior of the perpendicular response function can be attributed to the existence of several mechanisms such as transverse rotation or libration.[9]

References

1. H. Fellner - Felldegg, *J. Phys. Chem.*, **73**, 616, March (1969).
2. A. Sugget, "*Dielectric and Related molecular processus,*" *Burlington, London* (1979).
3. T. K. Bose, R. Chahine, M. Merabet and J. Thoen, *to be published, J. Physique* (August 1984).
4. R. H. Cole, *J. Phys. Chem.*, **79**, 1459 (1975).
5. R. Chahine and T. K. Bose, *J. Chem. Phys.*, **65**, 2211 (1976).
6. M. Elkadiri, J. P. Parneix and A. Chapoton, *to be published in IEEE, Inst. and Meas.*, (March 1985).
7. J. P. Parneix, *Thesis Lille* (1982).
8. C. Druon and J. M. Wacrenier, *J. Phys. E.*, **16**, 151 (1983).
9. C. Legrand, *3d cycle Thesis, Lille* (1984).
10. D. Lippens, J. P. Parneix and A. Chapoton, *J. Physique*, **38**, 1465 (1977).
11. C. Druon and J. M. Wacrenier, *Mol. Cryst. Liq. Cryst.*, **88**, 99 (1982).

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:58 20 February 2013