

This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 20 February 2013, At: 11:57

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>

Study of Reentrant Nematic and Smectic Phases Using Dielectric Relaxation

C. Legrand^{a b}, J. P. Parneix^{a b}, A. Chapoton^a,
Nguyen Huu Tinh^{a b} & C. Destrade^b

^a C.H.S., LA CNRS 287, P4, Université de Lille I,
59655, Villeneuve d'Ascq

^b C.R.P.P., Domaine Universitaire, 33405, Talence,
France

Version of record first published: 17 Oct 2011.

To cite this article: C. Legrand, J. P. Parneix, A. Chapoton, Nguyen Huu Tinh & C. Destrade (1985): Study of Reentrant Nematic and Smectic Phases Using Dielectric Relaxation, *Molecular Crystals and Liquid Crystals*, 124:1, 277-285

To link to this article: <http://dx.doi.org/10.1080/00268948508079483>

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.

Study of Reentrant Nematic and Smectic Phases Using Dielectric Relaxation†

C. LEGRAND, J. P. PARNEIX, A. CHAPOTON,‡ NGUYEN HUU TINH,
C. DESTRADE§

‡C.H.S., LA CNRS 287, P4, Université de Lille I, 59655 Villeneuve d'Ascq,
§C.R.P.P., Domaine Universitaire, 33405 Talence, France

(Received July 19, 1984)

Dielectric properties are reported of new pure substances exhibiting reentrant nematic and reentrant smectic phases. The quasistatic dielectric constants ($\epsilon'_\parallel, \epsilon'_\perp, \epsilon'_{is}$) and the dispersion of $\epsilon''_\parallel, \epsilon''_\perp$ and ϵ''_{is} in the radiofrequency range (5Hz–1GHz) have been investigated. The current experimental dielectric behaviours are examined and discussed using our experimental data.

INTRODUCTION

Many aspects of molecular motion and structure in mesophases can be revealed by dielectric characterization. Recently, this method has been used to investigate reentrant phases.^{1,2,3} We have continued these studies using other pure substances or mixtures exhibiting reentrant behaviour.⁴ We report here some new dielectric measurements on similar compounds recently synthesized in the C.R.P.P.^{5,6}

EXPERIMENTAL

The substances investigated with their chemical formulae and phase sequences are given in table 1. It can be noted that the compound

†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

DB₉ONO₂ shows a triple reentrant behavior while the compound 11ONBBA exhibits smectic C, F and G phases below the reentrant nematic phase.

The dielectric permittivity ($\epsilon^* = \epsilon' - j\epsilon''$; dielectric constant, ϵ' ; dielectric loss factor, ϵ'') was measured using two Hewlett-Packard Analyzers driven by a H.P. table computer (figure 1). The experiments were carried out at variable frequency and constant temperature. For a given temperature, the two components of the permittivity v.s. frequency were automatically deduced. The data were available in real time on a printer or a plotter (in the range 5Hz–

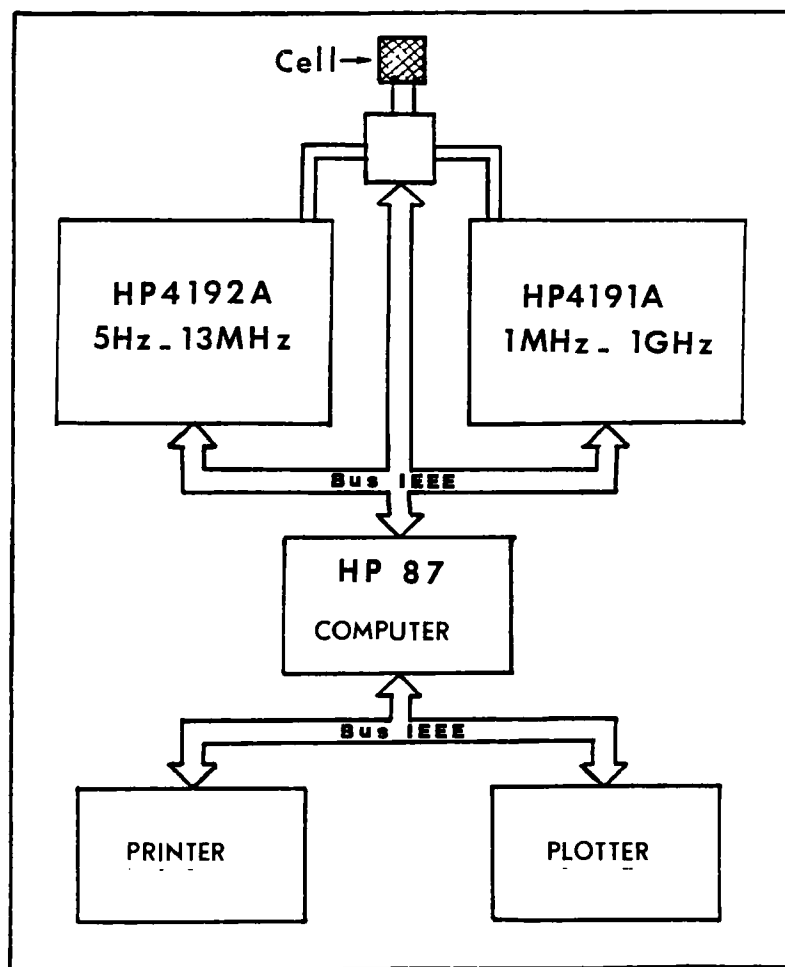


FIGURE 1 The $\epsilon^*(f)$ experimental set-up.

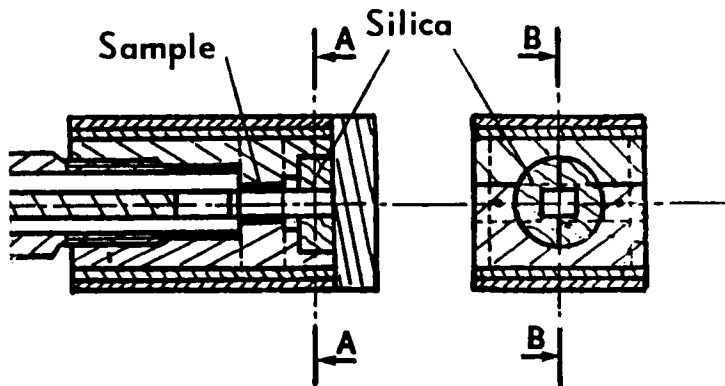


FIGURE 2 The experimental cell.

1GHz, 150 experimental points were produced in about two minutes). The experiments were made using a new parallel plate cell (figure 2). The sample was introduced into the cell by capillary action. The required sample volume was very small (lower than 5 mm^3). The cell was temperature controlled ($\pm 0.2^\circ\text{C}$) up to 200°C . A 1.2 T static magnetic field was applied to orientate the sample. It was estimated that the overall uncertainty in ϵ' was 2% and lower than 5% in ϵ'' .

RESULTS AND DISCUSSION

The variation of the static dielectric constants ϵ'_\parallel , ϵ'_\perp , ϵ'_{is} of 11ONBBA and DB_9ONO_2 with temperature are given in figures 3 and 4 re-

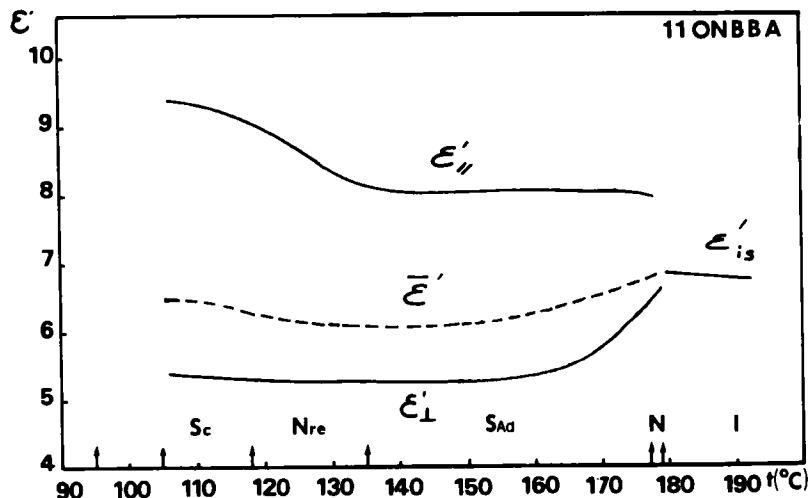


FIGURE 3 The static permittivities v.s. temperature of 11ONBBA.

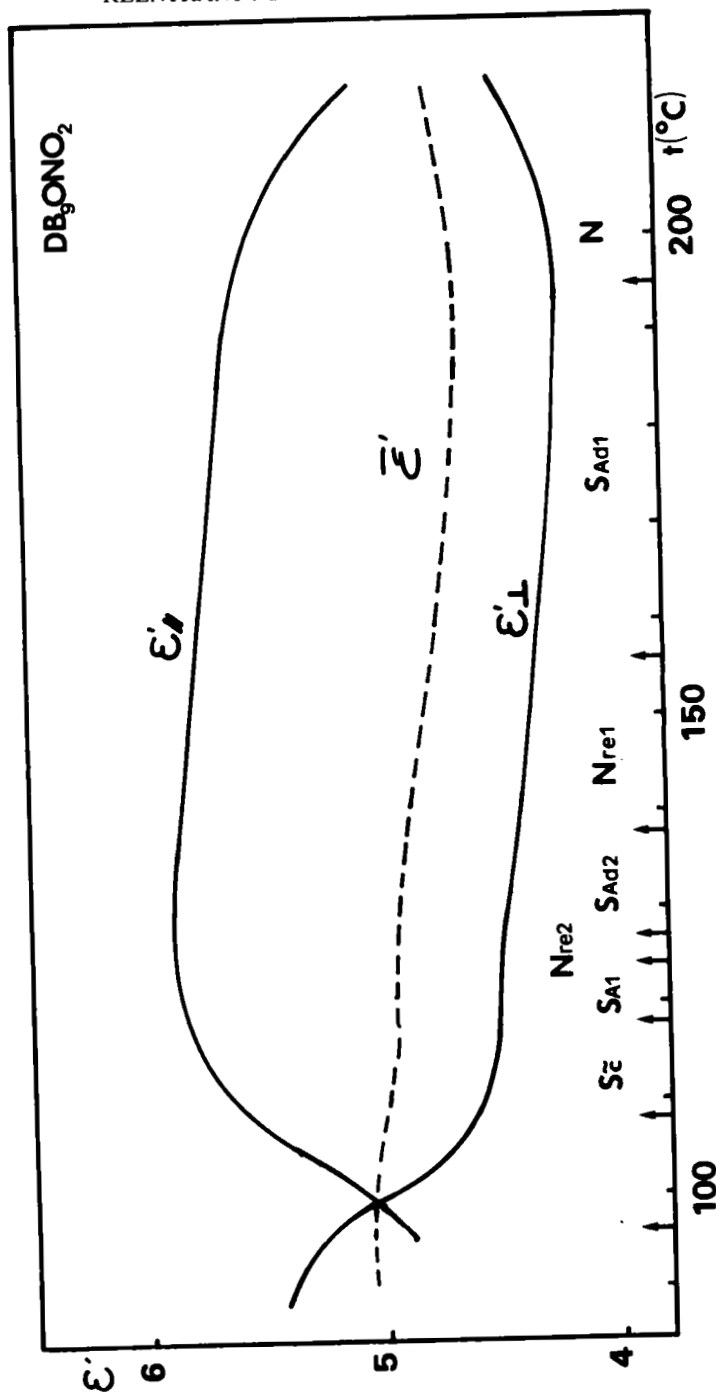


FIGURE 4 The static permittivities v.s. temperature of DB₃ONO₂.

spectively. The 11ONBBA dielectric anisotropy $\Delta\epsilon' = \epsilon'_\parallel - \epsilon'_\perp$ shows the usual trend where $\Delta\epsilon'$ increases in the high temperature nematic phase when T decreases, remains almost constant in the S_{Ad} phase and then increases in the low temperature nematic phase and in the smectic C phase. DB₉ONO₂ however, shows an unusual behaviour. The anisotropy of the mid-temperature reentrant nematic phase N_{re1} remains constant with temperature. This is perhaps related in some way with the existence of two adjacent S_{Ad} phases. When the temperature is decreasing, $\Delta\epsilon'$ decreases from the second reentrant nematic phase N_{re2} to the $S_{\bar{C}}$ phase where it changes sign.

Both compounds show similar dynamic behavior in their different mesophases. Typical Cole-Cole plots (ϵ' (ϵ'')) of the permittivities ϵ'_\parallel , ϵ'_\perp in the mesophases and ϵ'_{is} in the isotropic phase of 11ONBBA and DM₉ONO₂ are shown in figures 5 and 6 respectively.

As usual,⁷ one can observe a strong Debye relaxation mechanism for ϵ'_\parallel ("flip-flop" molecular orientation around a transverse axis) at low frequencies. In the perpendicular direction and in the isotropic phase, the dispersion observed is widely spread showing the existence of numerous relaxation mechanisms due to the rotational and librational motions of molecules. Note that the drastic increase of ϵ'' towards the very low frequencies is connected with the sample conductivity.

The most important results relate to the variation with temperature

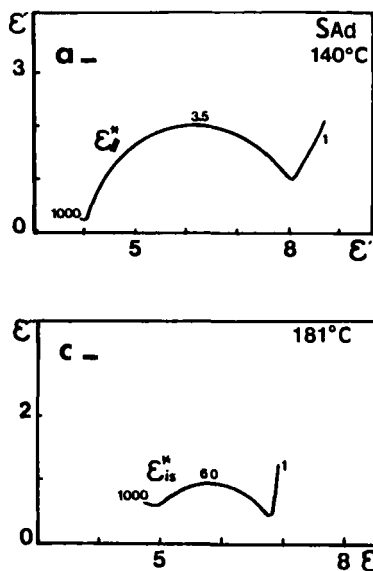


FIGURE 5 Cole-Cole plots of 11ONBBA.

- a ϵ'_\parallel in the S_{Ad} phase $T = 140^\circ\text{C}$
(F in MHz)
- b ϵ'_\perp in the S_{Ad} phase $T = 140^\circ\text{C}$
(F in MHz)
- c ϵ'_{is} in the isotropic phase $T = 181^\circ\text{C}$
(F in MHz)

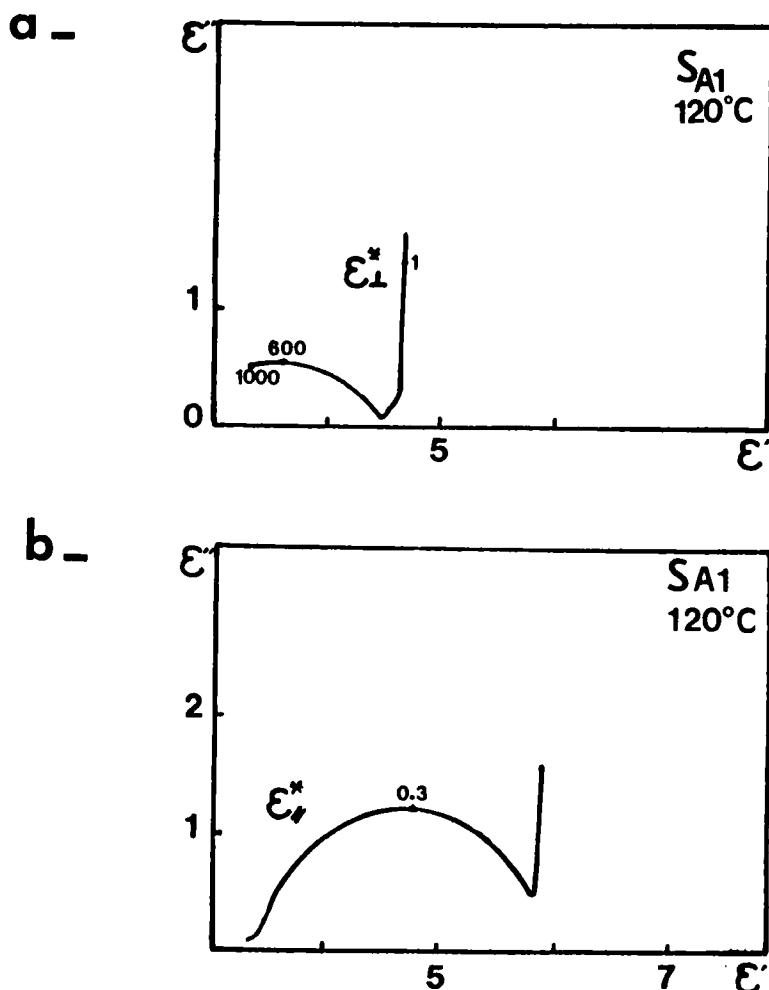


FIGURE 6 Cole-Cole plots of $DBONNO_2$.

a ϵ''_1 in the S_{A1} phase $T = 120^\circ\text{C}$ (F in MHz)

b ϵ''_1 in the S_{A1} phase $T = 120^\circ\text{C}$ (F in MHz)

of the critical frequency fc of the ϵ'' dispersion. Figures 7 and 8 show that the $\log fc$ v.s. $1/T$ plot is linear in each phase. Hence assuming an Arrhenius dependence $fc \sim e \exp \left(-\frac{W}{kT} \right)$, one can deduce the process activation energy W in each phase, from the straight line slope. The results are as follows:

11 ONBBA

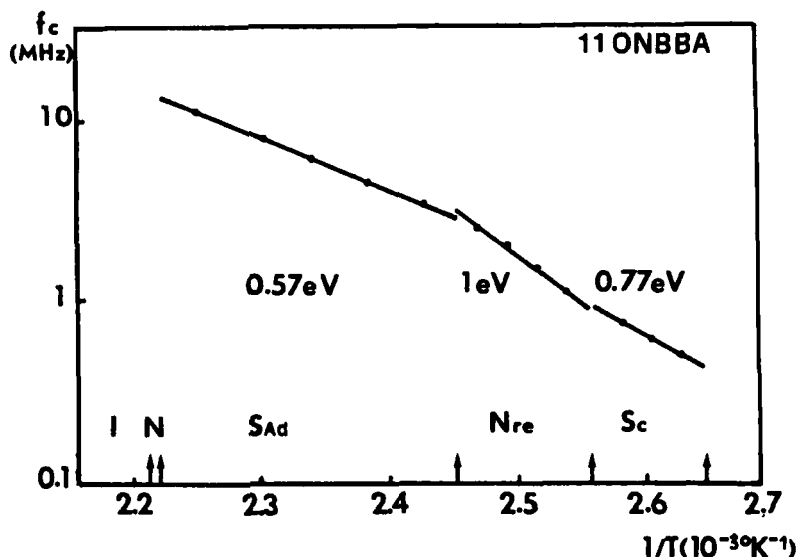


FIGURE 7 Relaxation frequencies v.s. the inverse temperature and activation energies for 11ONBBA.

The activation energies satisfy the following inequalities:

$$W_{Nre} \gg W_{SAd}$$

$$W_{Nre} > W_{SC}$$

The first inequality has been previously observed with compounds exhibiting reentrant^{1,2,4} or non reentrant phenomenon.⁸ The second one is rather usual. For a classical S_C phase it has been observed that $W_N \sim W_{SC}$.⁹



In this case, the inequalities are the following:

$$W_{SA1} \gg W_N > W_{SA2} > W_{Nre1} > W_{SA1}$$

These results seem to indicate that the molecular associations are different in the low temperature and high temperature nematic and S_{Ad} phases.

In all previous studies,^{1,2,3,4} concerning reentrant nematic phases, it has always been observed that: $W_{Nre} > W_N$. With DB_9ONO_2 , we

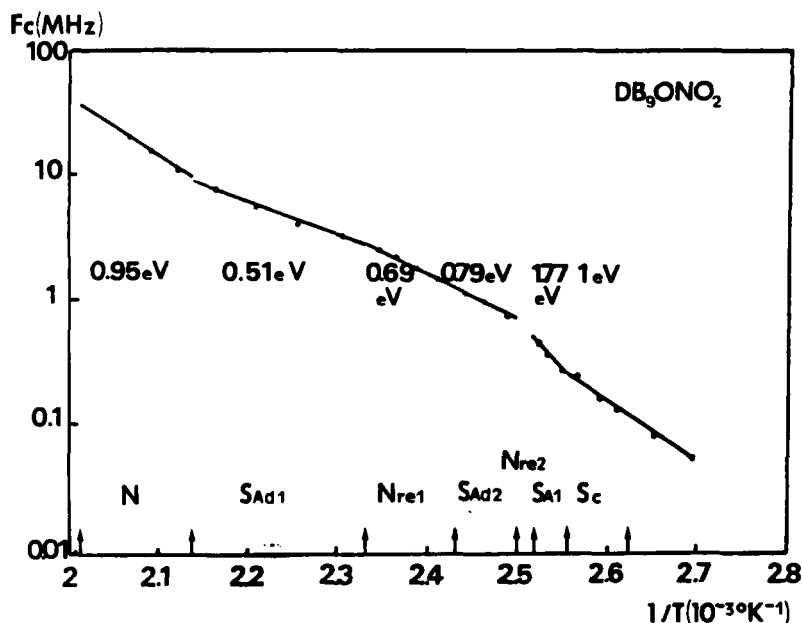


FIGURE 8 Relaxation frequencies v.s. the inverse temperature and activation energies for DB_9ONO_2 .

obtain $W_{Nre1} < W_N$. This can be connected with the appearance of a low temperature reentrant S_{Ad2} phase instead of a S_{A1} phase.⁶

This could also explain why $W_{SAd2} > W_{Nre1}$, when the reverse trend $W_{SAd} < W_N$ has always been observed.^{1,2,4,8}

Note that the W_{SA1} value is rather inaccurate due to the small temperature range of this phase (6°C). For the same reason, it was impossible to determine W_{Nre2} (3°C).

References

1. B. R. Ratna, R. Shashidar and K. V. Rao, *Proceedings of the Int. Liq. Cryst. Conf., Bangalore* (1979).
2. B. R. Ratna and R. Shashidar, *IXth Int. Liq. Cryst. Conf., Bangalore* (1982).
3. L. Benguigui and F. Hardouin, *J. Physique Lett.*, **42**, 111 (1981).
4. C. Legrand, J. P. Parneix, A. Chapoton, Nguyen Huu Tinh and C. Destradre *J. Physique Lett.*, **45**, 288 (1984).
5. Nguyen Huu Tinh and C. Destradre *to be published in this issue*.
6. Nguyen Huu Tinh, F. Hardouin and C. Destradre, *J. Physique*, **43**, 1127 (1982).
7. J. P. Parneix, *Thesis, Lille* (1982).
8. See for example, C. Druon and J. M. Wacrenier, *Mol. Cryst. Liq. Cryst.*, **98**, 201 (1983).
9. C. Druon and J. M. Wacrenier, *to be published in Mol. Cryst. Liq. Cryst.*