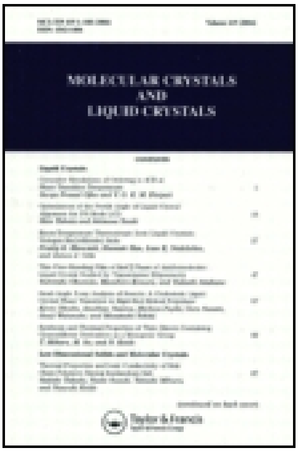

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Dielectric Spectroscopy of Some Nitro Phenyl Hydrazones, with Some Data at Elevated Pressures

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DIELECTRIC SPECTROSCOPY OF SOME NITRO PHENYL HYDRAZONES, WITH SOME DATA AT ELEVATED PRESSURES

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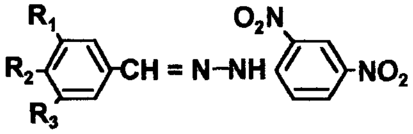
Abstract Dielectric measurements at ambient and elevated pressure confirm the proposal[1], that the two nitrophenylhydrazone compounds studied which display discotic phases, exist as dimers. The dipolar contribution to dielectric permittivity in the solid phase comes mainly from the alkoxy groups, and is augmented in the liquid phases by contributions from the hydrogen bonded o-NO_2 group. The two tailed material with a narrow mesophase exhibits erratic behaviour suggestive of the existence of meta-stable states in the solid phase. The use of a commercial ITO coated cell for the non-discotic compound revealed two separate artefacts which limited the value of the data.

INTRODUCTION

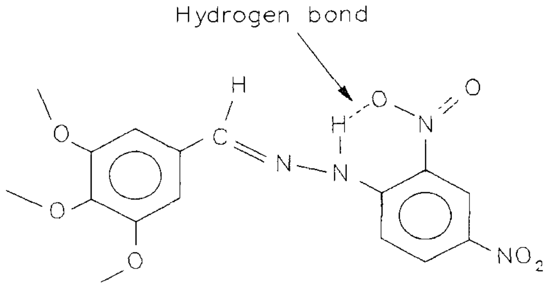
Dielectric measurements have been made on three nitrophenylhydrazones[1], two of which exist in a discotic liquid crystalline phase. These materials were prepared with a view to creating non-linear optical properties, with a strong electron acceptor NO_2 moiety, and a corresponding electron donor group. It became clear that the 2,4-dinitrophenylhydrazones exhibit liquid crystalline properties, and form a discotic phase. On the basis of X-ray and other measurements, it has been postulated that the existence of an intramolecular hydrogen bond is crucial to the existence of a mesophase. It was decided to explore the effect of elevated pressure to see if it would throw light on this feature of molecular structure. In addition a related material which does not form a liquid crystalline phase, was examined at ambient pressure in a conventional ITO coated glass liquid crystal cell. The purpose was to resolve some ambiguities in the measurements made on the discotic materials. Measurements were made at temperatures from ambient to above the melting points, and in the case of the discotics at pressures up to 200 MPa.

MATERIALS

The discotic molecules have the following structure,

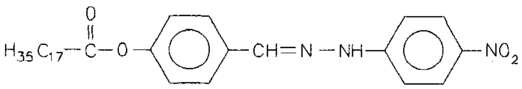


It has been proposed[1], that an intramolecular hydrogen bond forms, linking the o-NO_2 and the NH group. This creates a third ring and also causes the molecule to become flat and rigid.



The case where R_1,R_2 and R_3 = OC_8H_{17} corresponds to compound **13** of Paulus[1], 3,4,5-trioctyloxybenzaldehyde-2',4'-dinitrophenylhydrazone. It has a melting temperature of 96 C and clearing temperature of 135 C. The case where R_1 and R_2 = $OC_{16}H_{37}$, and R_3 = H, corresponds to compound 7 of Paulus[1], 3,4-dihexadecyloxybenzaldehyde-2',4'-dinitrophenylhydrazone. It has a melting temperature of 124 C and a clearing temperature of 130 C. Both compounds exhibit discotic hexagonal mesophases.

The third sample, 4-heptadecylcarboxyaldehyde-4'-nitrophenylhydrazone, has the following structure,



1/CO/18/B1

It is similar to compound **1** of Paulus[1], but the alkyl moiety contains an added carboxyl oxygen, and there is no o-NO_2 group, We will refer to it as compound **1'**. It has a melting temperature of 123 C, and exhibits no mesophase.

EXPERIMENTAL

The details of the experimental arrangements have been described elsewhere [2,3,4]. A Hewlett Packard 4192A low frequency analyser was used to measure the dielectric properties of the sample as a capacitance C (pF) in parallel with a conductance G (S) at a range of frequencies from 5 Hz to 13 MHz. For some measurements on compound **13** only, a Hewlett Packard 4191A radio frequency analyser, with a frequency span of 1 MHz to 1 GHz, was used[4]. Some measurements were made at ambient pressure in a thermostat through which a stream of air or nitrogen of known temperature was passed. The remainder of the measurements were made inside a pressure vessel the temperature and pressure of which were controlled and measured by computer[2].

The sample of **1'** was placed in a commercial ITO coated liquid crystal cell[5], with a geometric capacity C_0 of 13.1 pF and an electrode spacing of 10 μm. Such cells have the advantage of requiring very small amounts of sample, and allowing visual inspection of the contents. Against this there is the disadvantage that the resistance of the ITO coating in series with the dielectric, leads to a relaxation which is entirely spurious. In our case the equivalent series resistance of the coating was of the order of 3 - 4 kΩ, and so the effect vitiates data at frequencies above 100 kHz or so. When filled with material C_0 is known only approximately. The sample was introduced into the cell by melting under a vacuum.

One sample of compound **13** was placed between gold plated disc electrodes separated by silica fibres[4]. The estimate of C_0 was probably most accurate in this case. The remaining samples were placed between metal discs, spaced by glass spheres, again raising the temperature of the material above the melting point in a vacuum. In the case of compound **7** the discs were made of tool steel, and in the case of compound **13**, brass was used. To ensure isolation from the pressurising medium which was a synthetic hydraulic oil, Plexol, these latter two samples were encapsulated by heat shrinking a tube of polyolefin onto the assembly to seal the edges of the discs. The viscosity of compounds **7** and **13** when melted was low so that there was a strong tendency for them to escape from the test capacitor and testing was terminated when it became clear that the sample had been damaged.

RESULTS

The dielectric measurements of G(ω) and C(ω) can be discussed in terms of a complex relative permittivity $\varepsilon(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$. Taking the geometric capacitance of the sample as C_0, we have $C_0\varepsilon'(\omega) = C(\omega)$ and $C_0\varepsilon''(\omega) = G(\omega)/\omega$. The equilibrium permittivity ε_s, density ρ and high frequency permittivity ε_∞, normally approximated as the square of the refractive index n^2, can be related to an effective molecular dipole moment μ by the Kirkwood- Fröhlich equation,

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{4\pi N g \mu^2}{9kT} \quad \ldots\ldots\ldots\ldots (1)$$

where N the number density is related to the molecular weight M and Avogadro's number, $N = N_A\rho/M$ and g is a correlation coefficient.

The Havriliak Negami empirical relation can be used to characterise $\varepsilon(\omega)$,

$$\varepsilon\,(\omega) - \varepsilon_\infty = \frac{(\varepsilon_s - \varepsilon_\infty)}{(1 + (j\omega\tau)^{1-\alpha})^{\beta}} \quad \ldots\ldots\ldots\ldots (2)$$

from which the frequency at which $\varepsilon''(\omega)$ reaches a maximum f_{max} can be determined. The effects of pressure and temperature on f_{max} can be expressed as parameters of an activated state, the activation volume,

$$\Delta V{\ddagger} = -RT(\partial \ln f_{max}/\partial p)_T \quad \ldots\ldots\ldots\ldots (3)$$

and activation enthalpy,

$$\Delta H{\ddagger} = -R(\partial \ln T f_{max})/\partial T^{-1})p \quad \ldots\ldots\ldots\ldots (4)$$

COMPOUND 13 (three tailed)

The test capacitor using silica fibre spacers allowed reasonably accurate estimation of the the relative dielectric permittivity $\varepsilon'(\omega)$. For this material a good estimate of the equilibrium permittivity ε_s can be obtained from the value at 10 kHz. In fig (1) this has been plotted as a function of temperature. The relatively small difference between ε_s

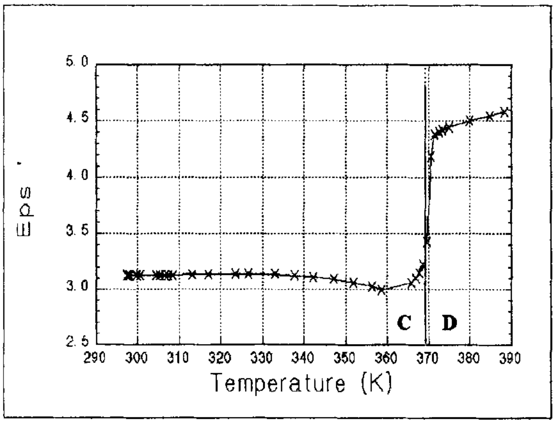


Fig 1. ε′ measured at 10 kHz for compound **13** in the crystalline, **C**, and discotic, **D**, phase.

and an estimate of around 2.2 for ε_{∞} based on high frequency measurements, suggests that the dipolar contribution comes chiefly from rotations involving the linking oxygen atoms of the three alkyl chains. At the melting temperature ε_s rises sharply as the discotic phase is entered.

In the discotic phase the relaxation process can be observed as a peak in $\varepsilon''(\omega)$, as in fig (2). The temperature sensitivity of this peak corresponds to $\Delta H\ddagger$ of 57.4 ± 2.8 kJ/mol. The half width of the loss peak is 2.1 decades. After an initial excursion of temperature to 109 C, it was noted that on reducing the temperature below the transition temperature of 96 C, to 89 C, the peak in ε″(ω) was still present in the solid phase, at a slightly lower frequency and of the same amplitude as at 103 C. But by the time ambient temperature was reached the peak had disappeared.

The same sample was placed in the pressure vessel at 110 C and compressed. The loss peak increased in amplitude and the frequency of the peak, f_{max}, fell until a pressure of 101 MPa was passed. At 152 MPa it appeared that the loss peak had moved to frequencies very much higher than 13 MHz which is the limit of the HP4192A instrument. This was accompanied by sharp drop in capacitance measured at 100kHz, from 139.5 pF to 102.7 pF, or 26 %. The exact pressure at which the transition took place is not known but this corresponds to a pressure sensitivity of the melting temperature dT_m/dp of up to 0.16 K/MPa. The plot of $\ln(f_{max})$ against pressure is linear, fig(3). Viewed in terms of activation volume, the slope of this plot corresponds to $\Delta V\ddagger$ = 46 ± 2 cm^3/mol. Further measurements were made at 131 C. At this temperature only one half of the loss peak is accessible to our instrumentation. Both $\varepsilon'(\omega)$ measured at 100 kHz and the peak value of ε″(ω) rise with pressure up to 225 MPa, after which point they decline though to a smaller extent than at 110 C. This suggests a pressure sensitivity of melting temperature of between 0.16 and 0.14 K/MPa. On reducing pressure, the $\varepsilon'(\omega)$ curve did not reproduce the behaviour when raising pressure but remained below the corresponding curve taken while raising pressure.

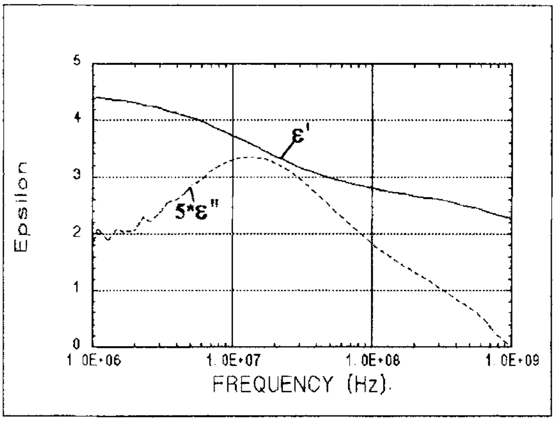


Fig 2. $\varepsilon'(\omega)$and $\varepsilon''(\omega)$ for compound **13** in the discotic phase at 0.1 MPa and 115.7 C. Note that values of $\varepsilon''(\omega)$ have been increased fivefold for plotting

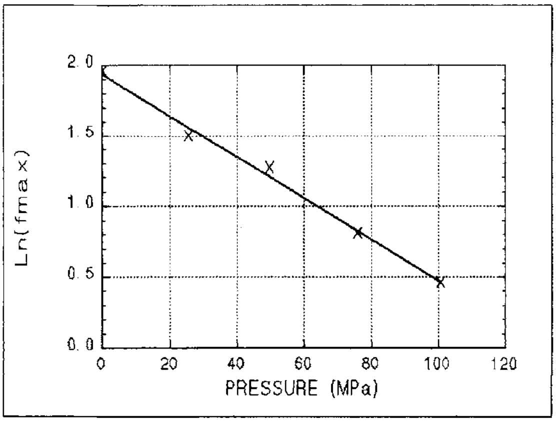


Fig.3 Ln(f_{max}) for compound **13** at 110 C and various pressures.

COMPOUND 7 (two tailed)

This compound has a narrow mesophase, from 124 to 130 C. It displays a very complex behaviour. Most of the data were obtained in the solid phase and were very dependent on the previous excursions of temperature and pressure. After the initial filling very large values of capacitance were measured at low frequencies with correspondingly large values of conductance. Following an excursion to 140 C this effect had largely disappeared, see fig (4). It was as if the material had been annealed. After this at ambient temperature a clear relaxation peak was observed at around 250 kHz. This peak persisted but with increasing frequency and amplitude as temperature was again raised above the melting point to 124 C. In the discotic phase the frequency of the peak rose steeply to 2.5 MHz. After an excursion to the isotropic state at 133 C the sample was returned to the solid state at 122 C. The loss peak remained with similar amplitude but at a reduced value of f_{max} of 1.4 MHz.

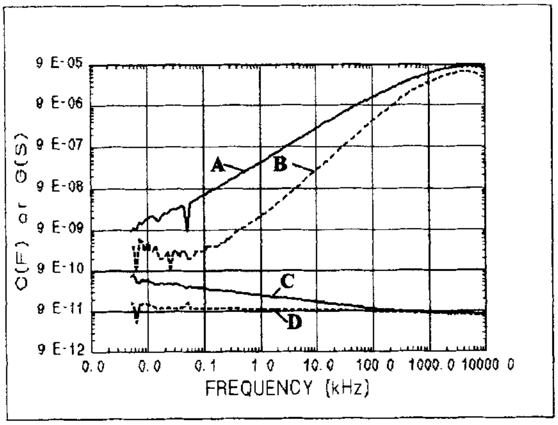


Fig.4. C(F) and G(S) for compound 7 at 25 C, before, **A** and **C**, and after **B** and **D**, temperature excursion to 140 C.

The sample was now placed in the pressure vessel and at ambient temperature there was no trace of a loss peak within our frequency window. This remained the case until the temperature was raised to 110 C, when a clear peak at 1.12 MHz emerged. After a return to ambient temperature this peak had disappeared. The temperature was now raised in one degree steps, and the peak did not return until the temperature again reached 95 C, when f_{max} had a value of 17.7 kHz, just distinguishable from the low frequency contribution caused by ionic conductivity. Fig. (5) shows the erratic behaviour of this peak, with f_{max} first increasing, then retreating into the shoulder caused by the contribution of ionic conductivity, then abruptly moving quickly to much higher values, reaching 1 MHz at 115 C. At 116 C it lay outside the measurement limit of 13 MHz.

The behaviour of the sample was now close to that of compound **13** at similar temperatures.

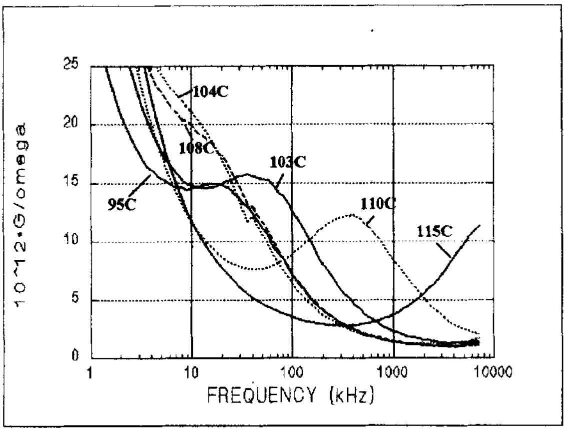


Fig. 5a. $10^{12}G/\omega$ for compound 7 at 0.1 MPa as temperature was raised in small steps. Note the erratic behaviour of f_{max}, rising from 95 to 103 C,then retreating to a shoulder from 104 to 108 C, then moving to much higher values at 110 and 115 C.

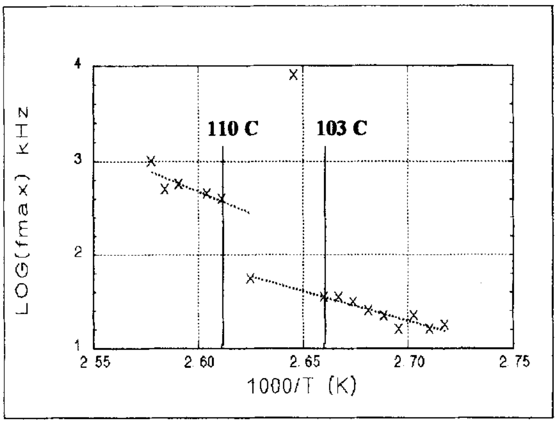


Fig. 5b. Values of f_{max} for compound 7 at 0.1 MPa, covering the temperature span of fig. 5a. Between 103 and 110 C the behaviour is anomalous.

At 120 C the pressure was raised in steps to 200 MPa, fig (6). At first the effect of pressure was to reduce f_{max} , but above 100 MPa the loss peak split into two peaks. At 175 MPa there was a return to a single peak , but at 200 MPa a pair re-emerged. These remained as pressure was reduced to ambient. This two peaked spectrum remained when the temperature was reduced to 110 C at ambient pressure, then as pressure was raised to 200 MPa and then reduced to ambient. Other such pressure excursions at 100 C and 90 C yielded very similar behaviour. It does not seem possible to make meaningful estimates of $\Delta H\ddagger$ or $\Delta V\ddagger$ from these measurements.

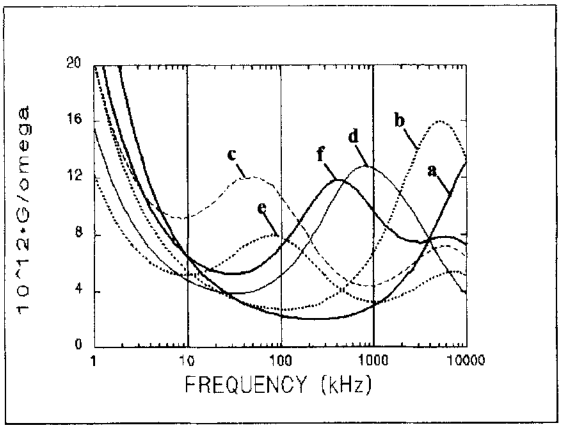


Fig.6 Plots of $10^{12}G/\omega$ for compound 7 at 120 C as pressure is raised and then lowereto ambient. Notice irregular alternation between one and two peaks, and between increases of f_{max} and decreases of f_{max} with a pressure increase.
a 0.1 MPa, **b** 100 MPa, **c** 125 MPa, **d** 175 MPa, **e** 200 MPa and **f** 0.1 MPa.

COMPOUND 1' (no mesophase)

The value of ε_s measured at 100 Hz and at ambient temperature was between 3.3 and 3.5. High frequency measurements were affected by the artefact which gave a relaxation process around 2.8 MHz as a result of the resistance of the ITO electrodes. A further effect was observed at elevated temperatures, which made it impossible to get reliable values of ε_s above ambient temperature.

A very large effect was found at low frequencies causing the value of capacitance to rise. This is attributed to electrode polarisation. If values of sample conductance are taken from regions where it remains essentially independent of frequency, and these are plotted against inverse temperature we find an Arrhenius energy of 157 ± 17 kJ/mol. This compares with a similar estimate for compound **13** of 185 ± 25 kJ/mol. Allowing for differences in geometry, compound **1'** has a fifty times greater conductivity than compound **13** at 110 C.

It has been proposed[1] that the strong electron acceptor nature of the para nitro group leads to strong charge separation effects in compounds **7** and **13** which causes pairs of molecules to align in an antiparallel manner. It is further postulated that the o-NO_2 group forms an intra-molecular hydrogen bond which makes the biphenyl group rigid and planar. The observed X Ray structure is thought to arise from columns of these rigid mesogens, surrounded by alkoxy tails and disposed in a hexagonal array. The strong tendency for the terminal p-NO_2 groups to be attracted to the oxidised electrodes can be expected to help align molecules with the long axis perpendicular to the surface, though how far this effect penetrates the bulk material is not known.

Three main contributions to ε_s can be expected . The o-NO_2 group with its hydrogen bond will have fairly large component of dipole moment perpendicular to the long axis of the mesogenic core. The individual oxygen atoms linking the alkyl chains to the benzene ring will also be capable of rotation, even in the solid phase. Finally the p-NO_2 group in molecules which are not paired in dimers could display a very large dipole moment in rotations of the molecule about its short axis, though such motion is not expected to be visible in the solid phase.

. The dielectric data lacks some precision because of uncertainty about the geometric capacitance of the test specimen and its density. Nevertheless it can be estimated that at ambient temperature, the equivalent dipole moment μ of **13** the three tailed compound, is of the order of 2 D. Each of the oxygen linkages connecting with the benzene ring has a dipole moment of 1.28 D [7]. If they responded quite independently this would yield a total moment of 2.2 D. In the discotic phase at say 105 C, there is a sharp rise in ε_s which corresponds to the addition of a further independent moment μ of 2.74 D. A probable source of such a contribution is the ortho nitro group. It is likely that the molecule performs rotations about its long axis so that the effective moment will depend on the orientation of this group, as well of course on whether the hydrogen bond remains intact. The effect of pressure on f_{max} in the discotic phase is consistent with this since the value of $\Delta V\neq = 46 \pm 2$ cm^3/mol is less than 10 % of the molar volume. For this compound there is no evidence of the very large effect that could be expected from the para nitro group and any associated charge separation effect, even in the isotropic phase.

Compound **1'** lacks the second nitro group which can form a hydrogen bond. Nevertheless even in the absence of a separation of charge between donor and acceptor groups the p-NO_2 group could still lead to the existence of dimers. Estimates of ε_s at ambient temperature suggest a value of μ of 1.9 D. The alkyl tail in this compound is joined to the benzene ring by a carboxyl group with a moment of 1.69 D[7]. Reliable data for ε_S in the molten state is not available.

All three compounds should show a strong tendency for the molecules to coat the electrodes with the p-NO_2 group attracted to the oxidised surfaces. The ITO cell used for **1'** should exhibit an especially strong effect. Although this low frequency effect is smaller with **7** and **13**, it is still present and makes estimation of ε_s difficult at elevated temperatures.

This leaves the behaviour of compound 7 unexplained. It must be remembered that most data for this material has come from the solid phase. It is possible that structures proposed from X Ray studies may not always exist and meta stable alternatives may also be possible. The crystallisation process as the discotic columns are assembled requires several constraints to be met. The charged molecules must first of all pair up. This pairing must allow for the correct alignment of the lateral dipole moment of the hydrogen bonded nitro group. The fact that this compound has an asymmetry in the arrangement of the two tails could complicate matters further. As long as the hydrogen bond is intact, rotation of one benzene ring relative to the other is not possible. Should it open, then the symmetry of the two tails could change as one benzene ring rotates relative to the other. Moreover the molecule would lose its planarity, and the possibility of inter as well as intra molecular hydrogen bonds could then exist. Given the various permutations of orientation of lateral o-NO_2 groups and of alkyloxy chains, the stacking of molecules in some ideal order may require time and even temperature cycling. Until such order is attained, meta stable states are likely to exist. What is perhaps surprising is the speed with which one mode, as characterised by a particular $\varepsilon'(\omega)$ spectrum, is replaced by a different mode, with either a quite different f_{max} or even two peaks in place of one. The anomalous behaviour of f_{max} with temperature in the span 103 to 110 C is easier to appreciate in fig. (5b). It seems not unlikely that the erratic effects of pressure to be seen in fig. (6) are related to this behaviour.

ACKNOWLEDGEMENTS

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REFERENCES

1 W.Paulus, H.Ringsdorf, S.Diele and G.Pelzl (1991) Liquid Crystals 9 807-819

2 W.G.Scaife and G. McMullin (1994) High Pressure Research to be published

3 G.McMullin, W.G.Scaife and R.Zentel (1994) Liquid Crystals to be published

4 H.Groothues (1992) Diplomarbeit University of Mainz

5 E.H.C. Co Ltd, Tokyo, Japan Type Y

6 S.U.Vallerien, F.Kremer and C.Boeffel (1989) Liquid Crystals 4 79-86

7.T.Klingbiel, D.J.Genova, T.R.Criswell and J.P.van Meter (1974) J.Amer.Chem.Soc. 96 7651-7655.