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Dielectric studies under high pressure on strongly polar liquid crystals exhibiting monolayer smectic A phase

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Abstract

Dielectric studies have been performed at elevated pressures on two compounds of a homologous series possessing a strongly polar terminal group and three phenyl rings in their molecular structure. This is the first high pressure dielectric study on such systems that exhibit a monolayer smectic A phase. Also notable is the fact that these compounds show a dual frequency response, a promising feature for fast liquid crystal display devices. The low frequency relaxation recorded in the nematic and smectic A phases is attributed to the reorientation of the molecules about the short axis. The temperature and pressure dependence of the relaxation frequency of this mode as well as the involved activation parameters are discussed. At a given relative temperature the relaxation frequency decreases as the pressure is increased. However, the parameter that characterizes the temperature dependences of the relaxation frequency, viz., the activation enthalpy, has a very weak dependence on pressure. In contrast, the activation volume shows a linear decrease with temperature.
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1. Introduction

Dielectric spectroscopy is a powerful technique to get information about the molecular relaxation times of liquid crystal (LC) materials. This is especially true when the constituent molecules have a rigidly fixed dipole moment. With this in view investigations have been carried out on a large number of LC systems, but mostly restricted to measurements at atmospheric pressure [1]. While the first few dielectric studies under high pressure were on ferroelectric LCs [2–4], a significant amount of literature now exists following the pioneering work by the groups at Bochum and Cracow [5] on materials exhibiting the nematic (N) phase. The molecules investigated by them consist of two phenyl rings in the rigid core and with very few exceptions show, when it exists, a partially bilayer smectic A (Sm-A) phase. Molecules with three phenyl rings in the core are known to be rich in the mesomorphic sequence and could exhibit three different types of layer stacking in the Sm-A phase: monolayer, partially bilayer and bilayer [6]. The classification is based on

the ratio of the layer thickness (d) to the length of the molecule (l) in its most extended all-*trans* conformation—$d/l \approx 1$ for monolayer, $1 < d/l < 2$ for partially bilayer and $d/l \approx 2$ for bilayer. In this paper we present results on two compounds belonging to the same homologous series having three phenyl rings in their molecular structure and exhibiting a monolayer Sm-A phase.

2. Experimental

Measurements have been made on the sixth and eighth homologues of the series, 4-alkoxybenzoloxy-4′-cyanoazobenzenes [nOBCAB for short; for the molecular structure see supplementary material (SM)], whose transition temperatures at atmospheric pressure as recorded from polarizing microscopy observations are given below and are in agreement with the literature values [7]:

$n = 6$; 6OBCAB; N $\underset{125.3\,°C}{\longrightarrow}$ Sm-A

$n = 8$; 8OBCAB; N $\underset{98.8\,°C}{\longrightarrow}$ Sm-A
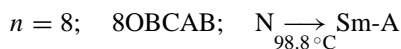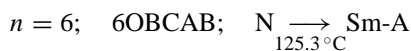
Notice that the compounds have a strong polar (C≡N) terminal group at one end and an alkoxy flexible tail at the other end.

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Also to be noted is the fact that unlike the compounds used by Würflinger and Urban [5], there are three phenyl rings in the core and further the rings are linked to each other through bridging groups. The latter is especially important as it can be expected to lower the relaxation frequency associated with the reorientation of the molecules about their short axis, a feature indeed seen in the room pressure investigations [8] of nOBCAB compounds. X-ray studies [8] have shown that for both the nOBCAB compounds the layer spacing (d) is constant over the entire temperature range in the Sm-A phase and further that the d/l ratio (l, the length of the molecule in its most extended configuration being measured using a molecular model) is about 0.95 establishing that the Sm-A phase is of the monolayer type.

The high pressure dielectric cell employed (see SM) is a modified form of the optical cell used in our laboratory [9] and is very similar to the one used earlier for the study of ferroelectric liquid crystals [4]. Essentially it consists of the sample contained in a Teflon gasket (thickness ∼0.06 mm) sandwiched between two steel cylinders, which also serve as electrodes, and enclosed in an elastomer tube. The elastomer tube also serves to prevent contamination of the sample by the pressure transmitting fluid (Plexol). Care was taken to make sure that the sample assembly was electrically isolated from the rest of the high pressure setup. The surface of the steel cylinders in contact with the sample was pre-treated with a silane solution to promote homeotropic alignment of the LC molecules. Screws threaded into the steel cylinders established electrical contact between the sample and the measuring equipment. The sample temperature was measured using a thermocouple in conjunction with a digital multimeter (Keithley DMM 2000). In this setup the sample pressure is the same as that in the plumbing line and thus could be measured with high precision using a Heise gauge. The precision in the determination of the temperature is reckoned to be ±10 mK, while that of pressure is ±3 bar. The dielectric parameters were determined in the frequency range 100 Hz to 1 MHz with the help of an impedance analyzer (HP4194A). The multimeter and the impedance analyzer were interfaced with a PC and the entire data acquisition process was controlled by a program written in Visual Basic. One drawback of this high pressure cell is that the Teflon gasket used to contain the sample is also present in the active area of the electrodes and thus contributes to the measured capacitance of the sample. Owing to the construction geometry it is neither possible to avoid this nor determine its exact contribution. Consequently calculation of the actual dielectric constant is not feasible. Hence we discuss the dielectric results in terms of the capacitance C' and $C'' = C'D$ (D being the loss factor), representing the real and imaginary parts of the dielectric constant.

3. Results and discussion

Fig. 1 shows the pressure–temperature (P–T) phase diagram for 8OBCAB determined using the optical transmission method; the diagram is qualitatively the same for 6OBCAB also (see SM). Since the clearing point (N-Iso) temperature is very high even at room pressure, we did not investigate the corresponding phase boundary at high pressures. The P–T diagram shows that both the
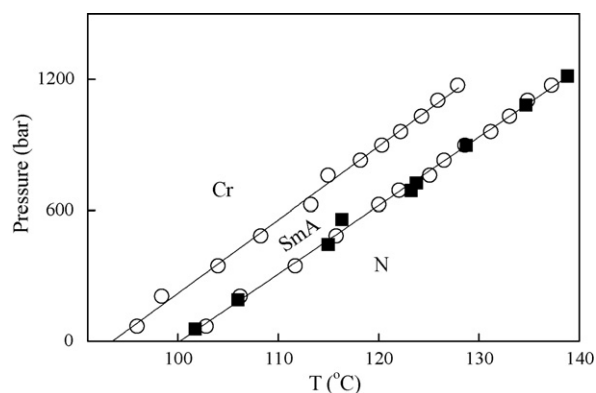

Fig. 1. Pressure–temperature (P–T) phase diagram for 8OBCAB obtained using optical transmission (open circles) and dielectric (filled squares) studies.

melting and the Sm-A–N transition temperatures increase linearly with pressure, although at slightly different rates – the slope dP/dT for the two boundaries are 33.6 bar/°C and 31.3 bar/°C, respectively – with the result that the range of the Sm-A phase increases with increasing pressure, a feature commonly found for the monolayer Sm-A systems.

From the temperature-dependent measurements carried out at room pressure both 6OBCAB and 8OBCAB are known to be positive dielectric anisotropy materials, i.e., $\Delta\varepsilon$ ($=\varepsilon_\parallel - \varepsilon_\perp) > 0$ through the N and Sm-A phases. A point that may be emphasized here is that both these compounds have the so-called "dual frequency" response [10]. In such materials at a frequency (f_c), which generally is not too different from the relaxation frequency corresponding to fluctuations about the short axis of the molecules, there is a crossover in the sign of $\Delta\varepsilon$; positive below f_c and negative above it (see SM). Technologically these systems are important since the sign of the electric torque acting on the molecules can be altered by changing the frequency of the applied electric field and thus controlling the orientation of the molecules. In fact, this is one of the solutions proposed to increase the speed of the liquid crystal display devices employing a nematic material. We shall later discuss about the influence of pressure on this aspect. The thermal variation of capacitance for the two materials at the lowest pressure investigated (∼50 bar) with the high pressure cell are shown in Fig. 2. The capacitance shows a clear increase upon transformation from the N to the Sm-A phase. (It must however, be remembered that the quality of alignment of the molecules could not be verified.) The transition temperatures obtained from such data are also shown in Fig. 1 and are in very good agreement with those from the optical transmission measurements.

The frequency dependence of C' and C'' for different temperatures in the N and Sm-A phases at a fixed pressure are shown in Figs. 3a and b and 4a and b for 6OBCAB and 8OBCAB, respectively; similar plots for different pressures at a constant temperature are given in Figs. 5a and b and 6a and b. To account for the quality of alignment which could be different at different pressures, the low frequency C' data at the pressures investigated has been normalized to a single value. Similarly for the C'' data the matching has been done by making the peak C'' value iden-
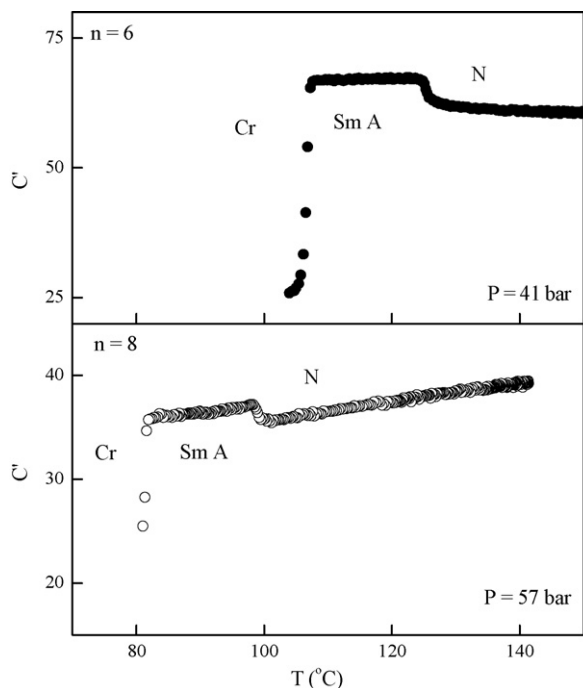
Fig. 2. Temperature dependence of the capacitance obtained in the cooling mode across the N–Sm-A and crystallization transitions at a pressure of 41 bar for 6OBCAB (top panel) and 57 bar for 8OBCAB (bottom panel). The N–Sm-A transition is marked by a clear step in the sample capacitance.
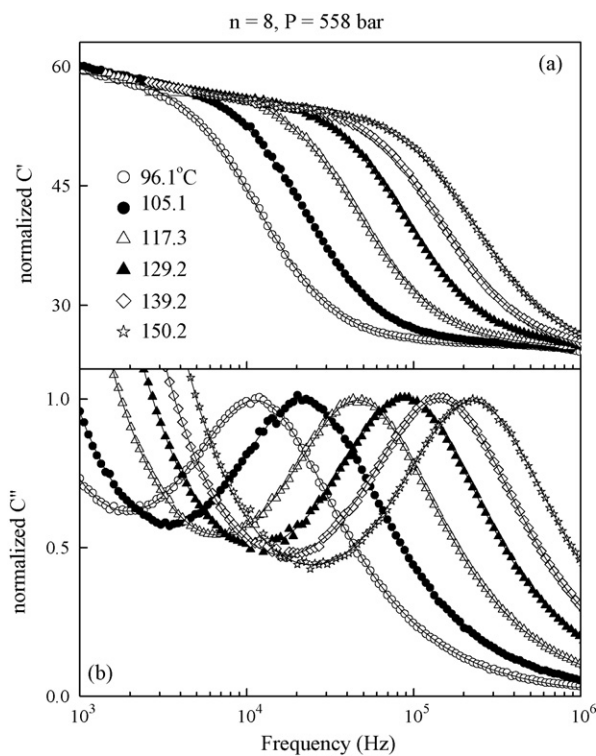

Fig. 4. Dielectric dispersion and absorption profiles for 8OBCAB at a constant pressure of 558 bar for different temperatures in the N and Sm-A phases.
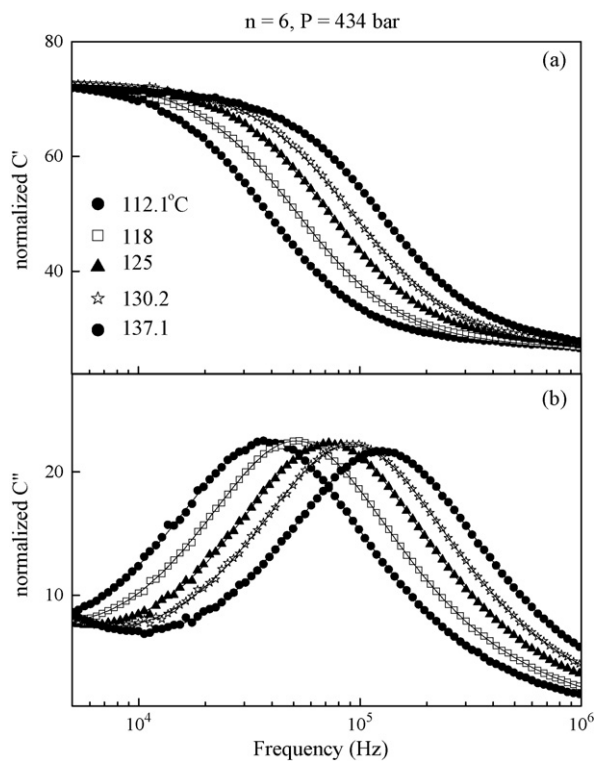

Fig. 3. Frequency dependence of the real (C', top panel) and imaginary (C'', bottom panel) parts of the dielectric constant for 6OBCAB at a fixed pressure of 434 bar and different temperatures in the N and Sm-A phases. The solid line through the symbols is the fit to the Havriliak–Negami equation. The relaxation frequency, which is essentially the middle point of the C' step change and the peak point of the C'' data, increases with increasing temperature.
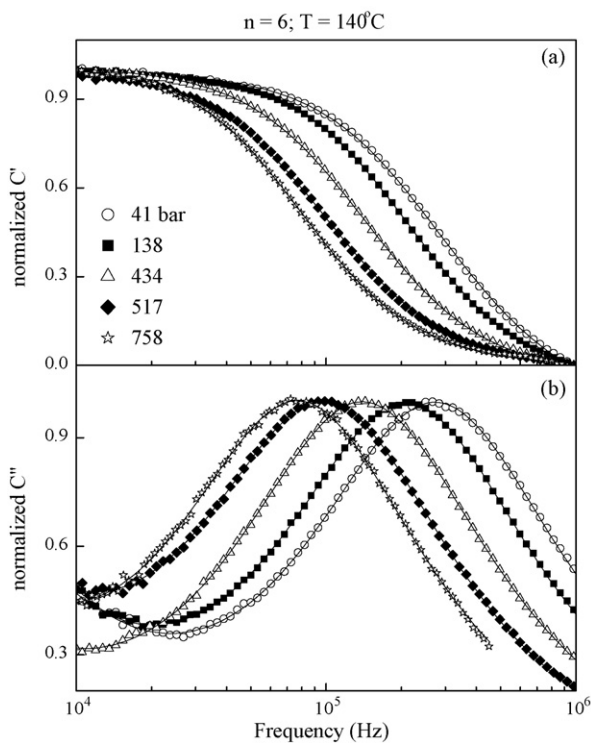

Fig. 5. Dielectric dispersion and absorption profiles for 6OBCAB at a fixed temperature for different pressures.
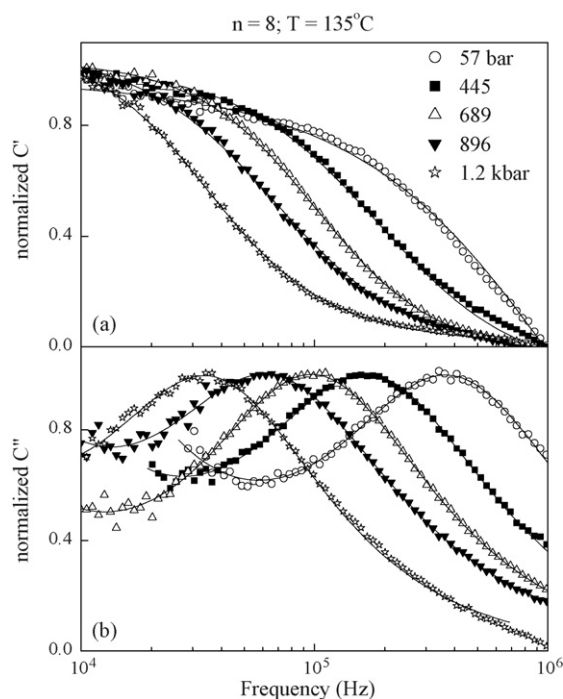
Fig. 6. Dielectric dispersion and absorption profiles for 8OBCAB at a fixed temperature for different pressures.

tical for each set. A feature that is immediately noticed in all the profiles is that there is a conductivity tail at low frequencies and a clear dielectric relaxation at each temperature and pressure. Considering the frequency range at which the relaxation occurs as well as the room pressure measurements with excellent homeotropic alignment of the molecules, the process is attributed to the rotations of the molecules about the short molecular axis. On a qualitative level it is observed that for the data set at constant temperature, the frequency at which the profile has a maximum in C'', taken to be a measure of the relaxation frequency, decreases with increasing pressure. On the other hand, at constant pressure, the relaxation frequency decreases when the temperature is decreased. These two features are compatible with the fact that the thermodynamic path traversed will take the material from the more disordered N phase to the ordered Sm-A phase. To quantitatively extract the relaxation frequency f_R, the raw C'' versus f (the measuring frequency) data were fit to the Havriliak–Negami equation [11]. Throughout the entire range of measurement of both the nOBCAB samples, only a single relaxation was seen and the profiles could be very well described by a Debye-relaxation. The temperature variation of f_R in the N and Sm-A phases for the two compounds at various pressures are given in Figs. 7 and 8. It is observed that f_R shows a smooth variation across the transition in both the samples, although a slight slope change occurs in the vicinity of the transition for 8OBCAB. The reason for the absence of a drastic change in f_R across the transition could be the following. For both the samples, the Sm-A–N transition is far away (∼150 °C) from the N-Iso transition at room pressure as well as at elevated pressures. Under such circumstances, i.e., when the ratio $T_{Sm-A–N}/T_{N-Iso}$ is ≪1, the Sm-A–N transition
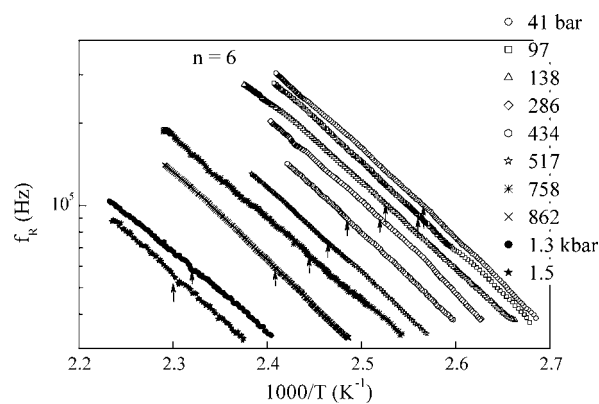

Fig. 7. Semilogarithmic plot of the temperature dependence of the relaxation frequency at different pressures in the N and Sm-A phases of 6OBCAB. The arrows indicate the N–Sm-A transition temperature at each pressure.

is expected to be second order with the nematic orientational order being saturated before the transition takes place from the N phase. (It may be remarked here that the thermal signature corresponding to the Sm-A–N transition is too small to be seen by the differential scanning calorimeter (see SM), a feature in agreement with the comment made above.) Since the director relaxation frequency in these phases is dependent on the magnitude of the orientational order parameter S, the saturation and the negligible change in S across the transition results in very small change in f_R. It may also be noted that at any given temperature application of pressure decreases the relaxation frequency. Recalling the feature mentioned earlier, namely, that these compounds exhibit a dual frequency response, the pressure dependence of f_R can be considered to be attractive from the display device point of view to tune the operating range of the device.

In a series of articles Urban and Würflinger [5,12–14] have established that the pressure and temperature dependences of the relaxation frequency are controlled by activation parameters, by defining

$$\text{activation volume} \quad \Delta^{\#}V = RT\left(\frac{\partial \ln\tau}{\partial P}\right)_T \tag{1}$$
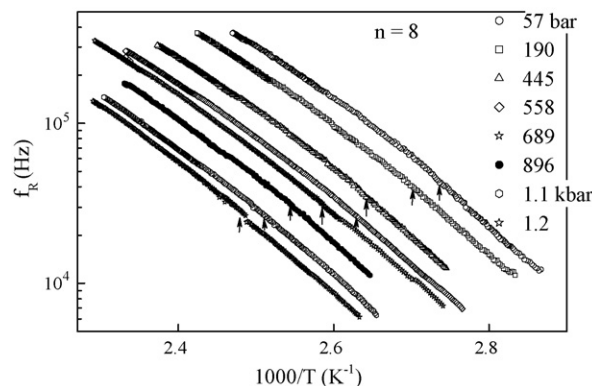

Fig. 8. Plot of the frequency of relaxation vs. 1/T for 8OBCAB. The arrows indicate the N–Sm-A transition temperature at each pressure.
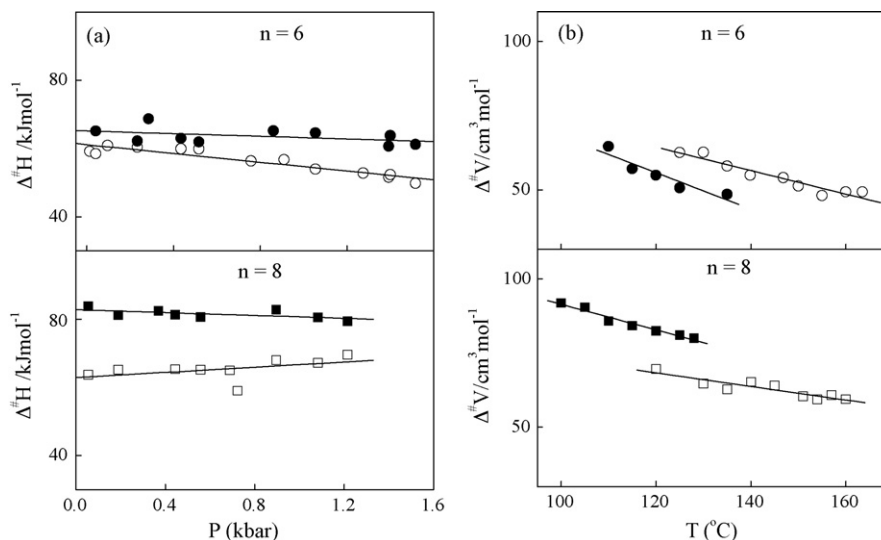
Fig. 9. (a) Pressure dependence of the activation enthalpy and (b) temperature dependence of the activation volume in the N (open symbols) and Sm-A (filled symbols) phases of 6OBCAB and 8OBCAB. The lines are merely guides to the eye.

and

activation enthalpy $\Delta^{\#}H = RT\left(\dfrac{\partial\ln\tau}{\partial T^{-1}}\right)_P$ (2)

where the relaxation time is given by $\tau = 1/2\pi f_R$. Notice that $\Delta^{\#}H$ is generally denoted as the activation energy. The pressure- and temperature-dependent f_R data shown in Figs. 7 and 8 have been fitted to Eqs. (1) and (2), respectively. Figs. 9a and b show the pressure and temperature dependences of the two activation parameters for the two samples in the N and Sm-A phases. Whereas in the Sm-A phase of both the compounds $\Delta^{\#}H$ shows a decrease with increasing pressure, in the N phase the behaviours are different—decreasing for 6OBCAB and weakly increasing for 8OBCAB. In contrast, $\Delta^{\#}V$ decreases with increasing temperature for all the cases. Generally, $\Delta^{\#}V$ has been reported to be decreasing with increasing temperature whereas $\Delta^{\#}H$ has been seen to show either a decrease or increase as pressure is increased. The activation volume is considered as the free volume that the molecule must have in order to perform the rotational jump over the potential barrier and thus can be expected to behave in the fashion experimentally observed. $\Delta^{\#}H$, on the other hand, is associated with the formation of dimers characteristic of molecules having a strongly polar terminal group, as in cyanobiphenyls as well as the compounds investigated by us. The diminution of $\Delta^{\#}H$ with increasing pressure has been argued to be indicative of reduction in the dimer formation with increasing pressure. However, since this parameter is seen to be either decreasing or increasing in the case of different materials, we guess that although the extent of dimer formation could certainly be a parameter, it alone cannot be deciding the behaviour. More experiments on different types of materials are required in this direction to clarify the matter. But what is clear from our work is that irrespective of the two-ring core or three-ring core in the molecular structure the behaviour at constant temperature and varying pressure or changing temperature at fixed pressure is quite similar. The fact that the smectic A phase is of the monolayer type unlike the partial bilayer type in cyanobiphenyls does not seem to make much difference in the pressure behaviour of the dielectric relaxation frequency.

In summary we have performed high pressure dielectric investigation on two compounds of a homologous series having a three-ring core molecular structure. The behaviour obtained in the smectic A and nematic phases as a function of temperature as well as pressure are in general agreement with a wealth of data available on materials having two-ring core structure.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.10.022.

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