THE EFFECT OF POLAR SUBSTITUENTS ON DIELECTRIC AND OPTICAL TRANSMITTANCE PROPERTIES OF TWO λ-SHAPED MESOGENIC WITH BROMO AND CHLORO SUBSTITUENTS –A COMPARATIVE STUDY

P. B. Chand* and **R. Manohar***

*Department of Physics, Siddhanath Science Campus, Tribhuvan University, Mahendranagar, Kanchanpur, Nepal.
**Department of Physics, Lucknow University, Lucknow, India.

Abstract: Dielectric properties of two ë-shaped mesogenic compounds 4-((2-bromo-4-nitrophenyl)diazenyl)-1,3-phenylene bis(4-(tetradecyloxy)benzoate) (14MV) and 4-((2-chloro-4-nitrophenyl)diazenl)-1,3-phenylene bis(4-(decyloxy)benzoate) (10-OCPNDE) have been studied as a function of temperature and frequency. The bromo substituents compound exhibits smectic C phase but chloro substituents compound smectic A phase. Our interest is to compare the macroscopic properties of the two compounds of same category but different functional group i.e Br or Cl. With this aim, the dielectric permittivity with temperature and frequency has been determined for both the compounds in planar alignment at frequency range 100Hz-1MHz. In this paper, we reported the dielectric behaviour of the effect of bromo and chloro substituents on mesomorphic two ë-shaped mesogenic homologous series with bromo and chloro substituents.

Key words: λ-shaped liquid crystals; Polar substituents; Dielectric properties; Cole-Cole plot.

1. INTRODUCTION

Liquid crystals (LCs) are very common and important mainly because of their unique properties, including the selective reflection of light and ferroelectricity, and their potential application in numerous areas, especially in the fields of optics, electro-optics, thermo-conducting materials and fast switching (Zhang *et al*, 2007; Chong *et al*, 2007). Materials, thus, need to be designed to be chemically and optically stable, possess wide temperature range for their liquid crystal phases, have low melting points, low viscosities, suitable birefringence's, desirable dielectric properties, low conductivities. Lot of efforts has been made to understand and improve upon the characteristics of liquid crystals. Thus in addition to conventional nematic liquid crystals, ferroelectric liquid crystals, electroclinic liquid crystals, polymer dispersed liquid crystals etc. have been developed and attempts have been made to use them in devices. The researchers want to improve the properties of liquid crystals and various attempts have been made to develop better liquid crystals with unconventional molecular shapes and changing the different side chain. As a consequence, the design of nematogens is now focused on creating materials based on fluorinated systems because they have low conductivities and viscosities, and suitable position of fluoro substituents allow them to have appropriate dielectric anisotropies for applications (Hirschmann *et al*, 1998; Hall *et al*, 1997).

The study of dielectric and optical properties of liquid crystals is important from the theoretical point of view as well as for tailoring and optimizing material characteristics for electro-optic applications. Because the mesogenic properties of thermotropic liquid crystals are temperature dependent the study of the thermal variation of their properties is of great interest and significance. Dielectric studies of liquid crystals are important as they provide information about the molecular structures, intermolecular interaction and molecular dynamics (Meier *et al*, 1975). In addition to classical thermotropic liquid crystal phases of rod-like (calamatic) mesogens, distinct novel phases have recently been reported (Sekine *et al*, 1997; Pelzl *et al*, 1999; Diez *et al*, 2003) for mesogens of bent-core molecular structure, so called 'banana-phases'. The shape of the constituent molecule in liquid crystals is a vital factor in determining the mesophases properties.

The driving force of mesophase formation is a fundamental topic in the investigation of molecular assembly systems. Supramolecular assemblies composed of oligomeric liquid crystals are current topics in the design of new liquid crystalline materials (Goodby *et al*, 1998; Saez *et al*, 2005).

Author for Correspondence: P. B. Chand, Siddhanath Science Campus, Mahendranagar, Kanchanpur, Nepal, purnachandmnr@hotmail.com.

Dimeric liquid crystals are attractive because they exhibit different properties from the corresponding low molecular mass mesogens. For example, the transitional properties of dimeric liquid crystals are known to depend on the length and parity of the flexible spacer. Many types of dimeric and trimeric mesogenic molecules have been reported (Imrie *et al*, 1998; Imrie *et al*, 2002).

Recently, molecular topology (Goodby *et al*, 1998) and microsegregation (Tashierske, 1998; Tashierske, 2001) have attracted much attention as the origins for producing novel self-organizing systems. For example, "Janus-like" supermolecular liquid crystals, with molecular weights in excess of 4000D, have been introduced as a new style of molecular topology, and have been found to exhibit chiral nematic and chiral smectic C (SmC*) (Saez *et al*, 2003.). In addition to molecular motion, it is also important to understand the microscopic behaviour of liquid crystalline molecules. Akhisa Yamguchi et al. (Yamaguchi *et al*, 2005) have reported the ë-shaped mesogenic molecule. The ë-shaped molecular topology is expected to produce a characteristic effect since two different non-symmetric dimeric molecular configuration i.e. one is a straight shaped configuration and the other a bent structure coexist in a single mesogenic molecule. Many types of liquid crystals with unconventional molecular shapes have been reported (Demus, 1998). For example, Göring et al. (Vorländer *et al*, 1932) reported tuning-fork shaped molecules which show undulated smectic structures and Attard et al. reported Y-shaped molecules in which three mesogenic groups are symmetrically attached to phenyl ring. On the other hand, U-shaped dimeric liquid crystals have been investigated by several groups ((Vorländer *et al*, 1932; Matsuzaki *et al,* 1993; Kato *et al*, 1992; Attard *et* al, 1997). Attard and Douglass reported property structure correlations of the dimeric liquid crystals derived from phthalic acid, providing important understanding about the U-shaped liquid crystals systems (Attard *et* al, 1997).

In the present paper, the results of dielectric measurements have been reported for two ë-shaped compounds i.e. 14MV (4-((2-broom-4-nitrophenyl) diazenyl)-1,3-phenylene bis(4-(tetradecyloxy)benzoate)) and 10-OCPNDE (4-((2-chloral-4-nitrophenyl)diazenl)-1,3-phenylene bis(4-(decyloxy) benzoate)) samples. We have reported the effect of halogens on ë-shaped molecules and compared two similar ë-shaped molecules containing bromo and chloro halogens group.
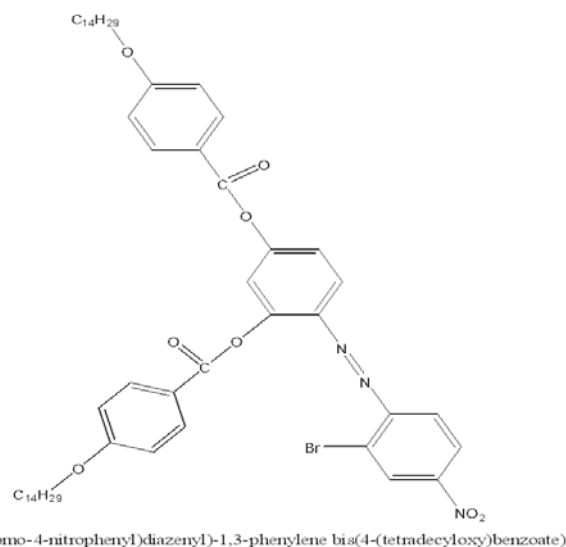
2. EXPERIMENTAL DETAILS

2.1 Materials:

The materials (4-((2-broom-4-nitrophenyl) diazenyl)-1,3-phenylenebis(4-tetradecyloxy)benzoate)) (14MV) and (4-((2-chloral-4-nitrophenyl) diazenl)-1,3-phenylene bis(4-(decyloxy)benzoate)) (10-OCPNDE) for investigation are newly synthesized and shows SmC in 14MV and SmA in 10-OCPNDE.The molecular structure of the samples are given as

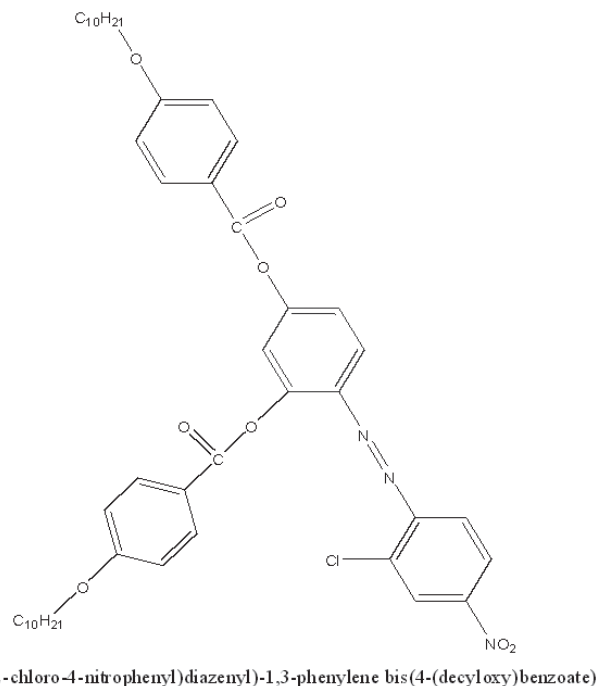**(a) 14MV**

Molecular Structure

Phase transition Scheme

4-((2-bromo-4-nitrophenyl)diazenyl)-1,3-phenylene bis(4-(tetradecyloxy)benzoate)

(b) 10-OCPNDE

$$Cr \xrightarrow{88\,°C} Sm\,C \xrightarrow{132\,°C} Iso$$

Molecular Structure

Phase transition Scheme

4-((2-chloro-4-nitrophenyl)diazenyl)-1,3-phenylene bis(4-(decyloxy)benzoate)

The complex dielectric permittivity $\mathring{a}^* = \mathring{a}' - j\,\mathring{a}''$ in different

$$Cr \xrightarrow{68\,°C} SmA \xrightarrow{121\,°C} Iso$$

mesophases of the planar aligned samples have been measured in the frequency range of 100 Hz to 1 MHz using impedance/gain phase analyser(model 4192A). The planar orientation of

the sample has been achieved by depositing a thin layer of polyamide nylon on to ITO –coated glass electrodes (sheet resistance ~ 10 Ù) and then rubbing the electrode surface unidirectionally with soft cotton. For a homeotropic alignment of the samples, electrodes were coated with the lecithin. Two plates of the dielectric cell were separated by mylar spacers of thickness 5 ìm in present studies.

Dielectric cells (active capacitance ~ 100 pF) were calibrated at room temperature by using standard liquid benzene. The temperature of the sample for optical and dielectric studies has been controlled by Julabo-F25 model having accuracy of ± 0.1°C and resolution limit 0.003°C. Dielectric data have been acquired during heating of the sample from its crystal phase. Instrumental uncertainty in the basic measurement of capacitance(C) and conductance (G) in the frequency range concerned is less than 0.2 % and hence in the determination of permittivity (å′) and loss (å″) from C and G is less than ± 1 %. The optical transmittance of the samples has also been investigated (Chand, 2009)

3. RESULT AND DISCUSSIONS

In the present paper we have measured the dielectric data in the heating cycle for two similar type of ë-shaped molecules i.e. (4-((2-broom-4-nitrophenyl)diazenyl)-1,3-phenylene bis(4(tetradecyloxy) benzoate)) and (4-((2-chloral-4-nitrophenyl) diazenl) -1,3- phenylenebis (4(decyloxy) benzoate)) and compared their results. In the case of present

sample dielectric data measured below 1 kHz are affected due to ionic conductance and electrode polarization effect (Srivastava *et al*, 1991) whereas data above 100 kHz are influenced due to the combined effect of lead inductances and electrode surface resistance (Srivastava, 1993; Dhar, 2004).
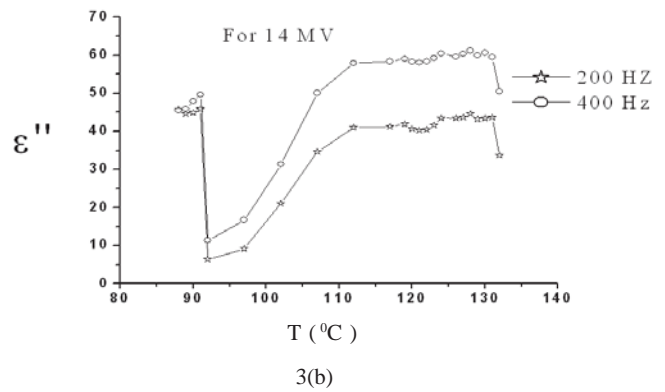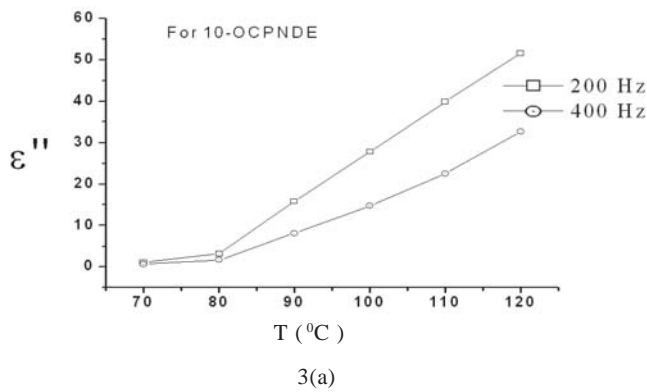
The temperature dependence of the dielectric permittivity (ε′) for both 10-OCPNDE and 14MV samples having λ-shaped molecules are shown in Fig. 1 at two different frequencies i.e. 200 Hz and 400 Hz. It is clear from Fig. 1(a) that the dielectric permittivity for 10-OCPNDE increases with increase in temperature in SmA phase. It is almost constant up to 80°C and beyond 80°C it increases slightly more with further increase in temperature. While in case of 14MV sample the Fig. 1 (b) shows that it increases uniformly up to 90°C and beyond 90ºC it suddenly decreases and again increases up to 117°C in SmC phase. It has been observed that the dielectric permittivity of both samples 10-OCPNDE and 14MV increases in smectic phase with increase in temperature. It is also observed that the dielectric permittivity is smaller in SmA phase of 10-0CPNDE in comparison to SmC phase of 14MV. The dielectric permittivity decreases with increasing frequency in both the samples. It is also supported by polar effects of the samples, because chlorine has higher polarity than bromine. The higher value of dielectric permittivity at higher temperature indicates that the molecular dipole have more freedom of movement as we increase the temperature.
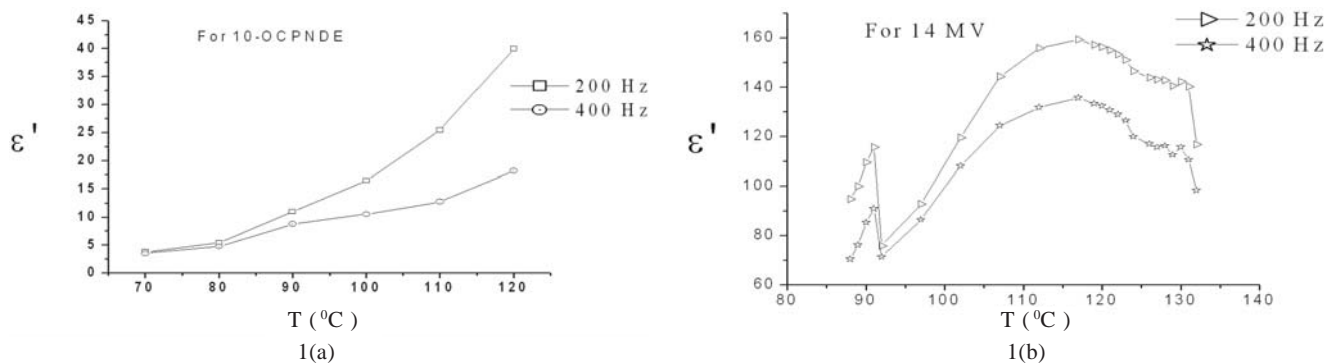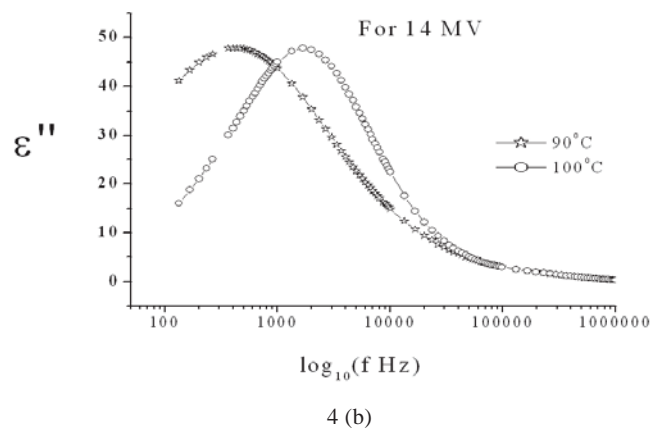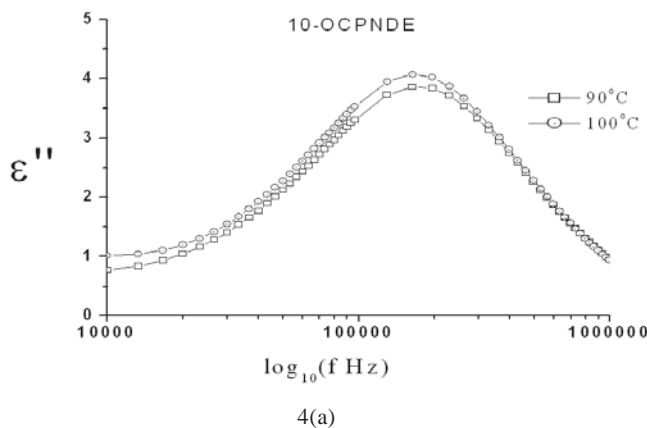

Figure 1: The variation of dielectric permittivity with temperature for (a) 10-OCPNDE and (b) 14MV samples at different frequencies i.e. 200 Hz and 400 Hz respectively.
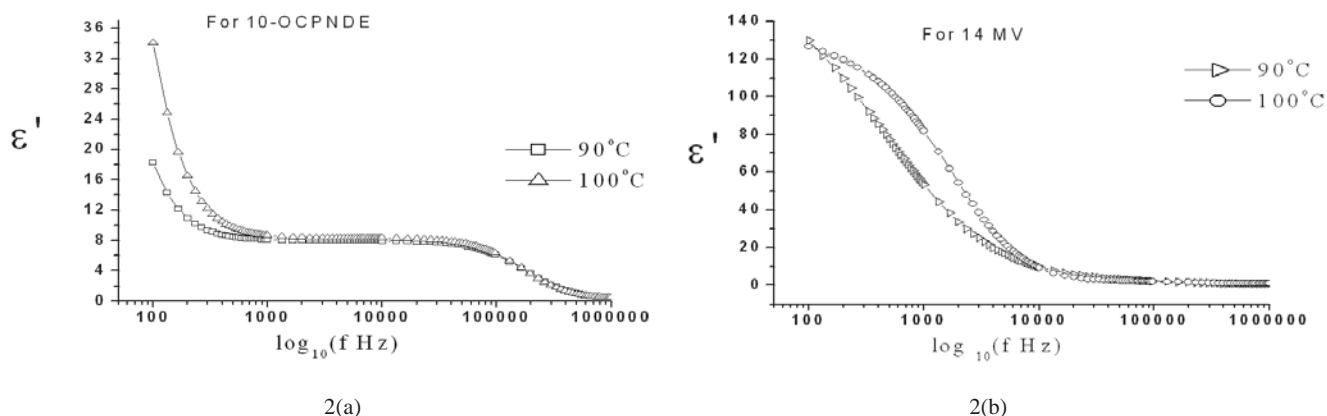
Figure 2: The variation of dielectric permittivity with $\log_{10}$ of frequency for (a) 10-OCPNDE and (b) 14 MV samples at different temperatures i.e.90ºC and 100ºC respectively.

3(a)

3(b)

Figure 3: The variation of dielectric loss with temperature for (a) 10-OCPNDE and (b) 14MV samples at different frequencies i.e. 200 Hz and 400 Hz respectively.

4(a)

4 (b)

Figure 4: The variation of dielectric loss with $\log_{10}$ of frequency for (a) 10-OCPNDE and (b) 14MV samples at different temperatures i.e.90°C and 100 °C respectively.

The frequency dependence of dielectric permittivity for 10-OCPNDE and 14 MV samples in smectic phase is given in Fig. 2. It is clear from Fig. 2 (a) that the dielectric relaxation for 10-OCPNDE sample occurs at high frequency side near 100 kHz and increases with increasing the temperature in SmA phase. It is interesting to note that in the lower region of frequency the dielectric permittivity decreases sharply and its nature of variation remain almost independent of temperature showing only a slight decrease in its numerical value. Fig. 2 (b) shows the dielectric relaxation for 14 MV and it occurs at low frequency side near1 kHz and increases with increasing the temperature in SmC phase.

The temperature dependence of dielectric loss (ε″) for 10-OCPNDE and 14MV samples is shown in Fig. 3. Fig 3(a) shows that the dielectric loss for 10-OCPNDE increases with increasing temperature and decreases with increasing the frequency in SmA phase. It increases slightly up to 80°C and then increases uniformly with further increase in temperature beyond 80°C. While Fig. 3 (b) shows that the dielectric loss for 14MV increases with increasing temperature and also increases with increasing frequency. It increases uniformly up to 90°C then suddenly decreases and again increases uniformly up to 112°C and beyond 112°C it remains almost constant on further increasing temperature. This type of molecular behaviour is also supported by the relaxation frequency versus temperature curve (discussed later) of the

sample in SmC phase [Fig. 6 (b)].

The variation of dielectric loss with $\log_{10}$ of frequency for 10-OCPNDE and 14MV samples is shown in Fig. 4. Fig. 4 (a) indicates that the dielectric absorption occurs at high frequency side near 100 kHz and the absorption peaks shift towards lower frequency side as the temperature increases. The dielectric loss initially increases with frequency and reaches a peak. Then it decreases and becomes almost constant after the frequency of about 1 MHz. It increases with increasing temperature in SmA phase. Fig. 4 (b) shows the absorption curve for 14MV. It occurs at low frequency side near 1 kHz and the absorption peaks shift towards higher frequency side as the temperature increases. It is also observed that the dielectric loss rises with rise in temperature and frequency.

We have determined the relaxation frequency of the samples using the Cole-Cole presentation. The Cole -Cole dispersion equation may be given as (Hill et al, 1969, Bottcher et al, 1978)

(1)

Here $\delta\varepsilon'$ is dielectric strength of material; $å'(\infty)$ is high frequency of electric permittivity of free space and α is distribution parameter. If α is small the above equation will satisfy the Debye type of relaxation phenomenon, and as á

5 (a)   5(b)
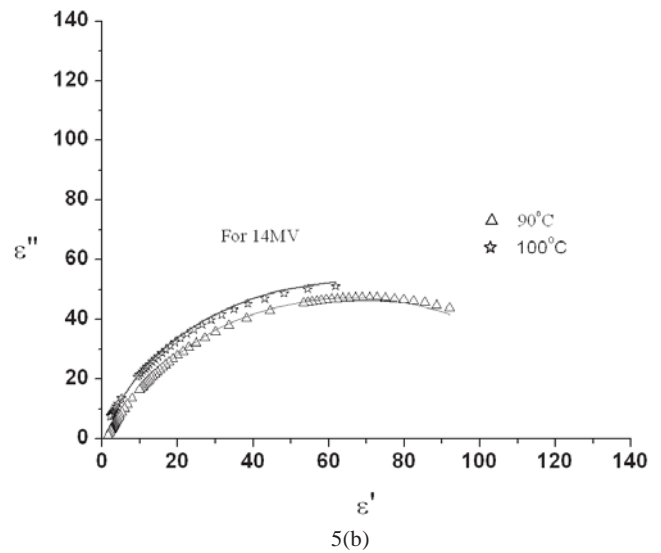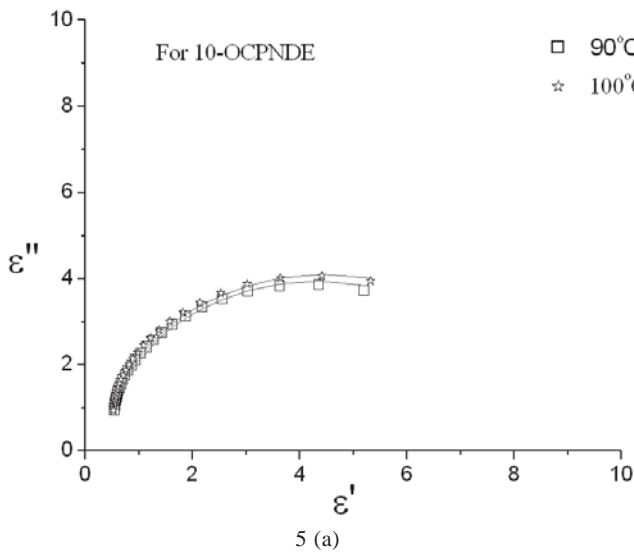
Figure 5: The Cole-Cole plots for (a) 10-OCPNDE and (b) 14 MV samples at different temperatures i.e.90ºC and 100ºC respectively.

increases beyond 0.5 the above equation suggests the existence of more than one relaxation process (Majumder et al, 1994).

Generally, the measured dielectric data for such type of sample holder are affected due to ionic conductance and electrode polarization effect in low frequency region (Srivastava et al. 1991)whereas data are affected due to the combined effect of lead inductances and electrode surface resistances in high frequency region (Srivastava 1993; Dhar, 2004; Gouda, 1992). Therefore the experimental results must required a low and high frequency correction. On separating real and imaginary part of the equation (1) one may get after adding high and low frequency correction parameters

$$\varepsilon' = \varepsilon'(dc) f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon'[1 + (2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)]}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)} \quad (2)$$

&

$$\varepsilon'' = \frac{\sigma(dc)}{\varepsilon_0 2\pi f^k} + \frac{\delta\varepsilon'(f\tau)^{(1-\alpha)} \cos(\alpha\pi/2)}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)} \sin(\alpha\pi/2)} + Af^m \quad (3)$$

Here σ (dc) is ionic conductance; ε_o is free space permittivity; k is the fitting parameter and ω is angular frequency. The term ε (dc)/f^n and σ (dc)/ $\varepsilon_o\omega$ are added in above equations for low

frequency effect due to the electrode polarization, capacitance and ionic conductance. The term Af ^{m} term is added in equation (3) for high frequency effect due to the ITO resistance and lead inductance. By the least square fitting of above equation into experimental data we have removed the low and high frequency errors.

Fig. 5 represents the variation of dielectric loss with dielectric permittivity for 10-OCPNDE and 14MV samples at different temperature 90ºC and 100ºC respectively. Fig. 5 (a) shows the Cole-Cole plots for 10-OCPNDE in SmA phase. It is observed that the centre of arcs shift towards ε' axis as the temperature increases. A similar behaviour is also shown in Fig. 5 (b) for 14MV at 90°C and 100°C temperatures in SmC phase. Using Cole-Cole plots dielectric parameters such as distribution parameter, relaxation frequency and dielectric strength have been calculated.

Fig. 6 represents the variation of relaxation frequency with temperature. It is clear from Fig. 6(a) that the relaxation frequency decreases uniformly up to 90ºC and beyond 90ºC it remains almost constant in SmA phase while in the case of 14MV, it increases uniformly up to 90ºC and beyond 90ºC it suddenly increases and then decreases uniformly and remains almost constant beyond 110ºC in SmC phase. The same type

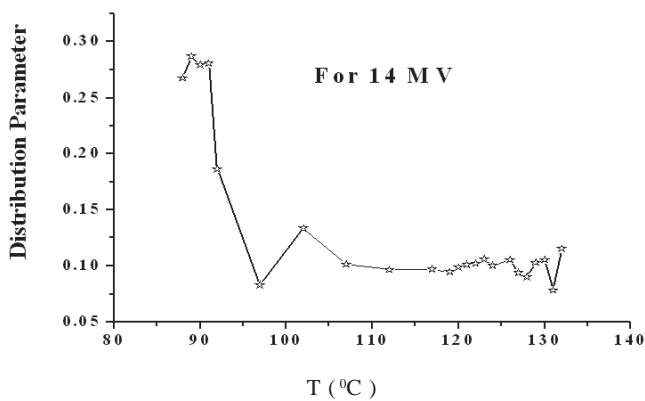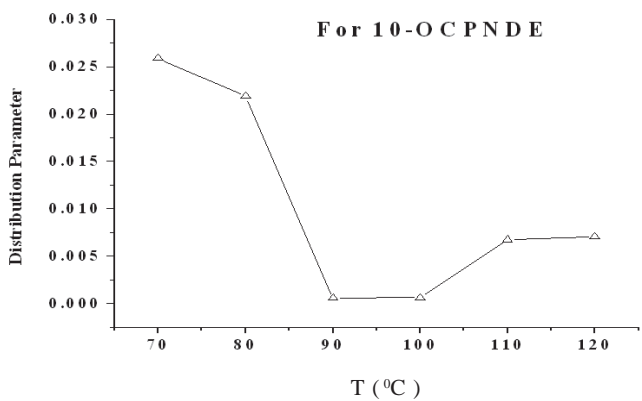6(a)   6(b)
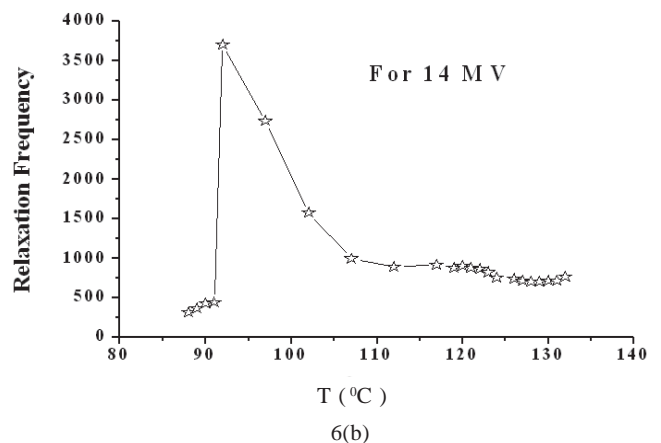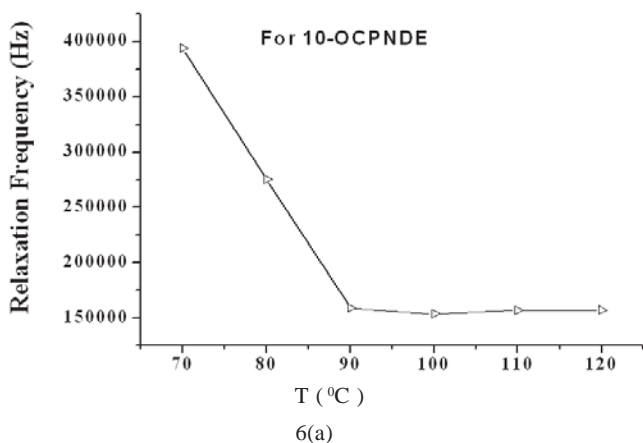
Figure 6: The temperature dependence of relaxation frequency for (a) 10-OCPNDE and (b) 14MV samples.

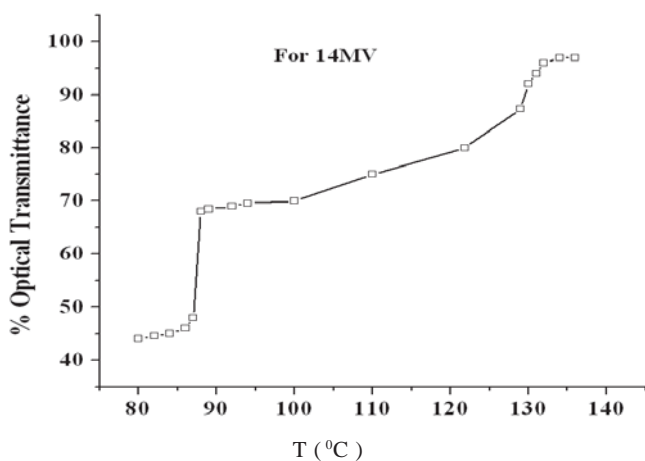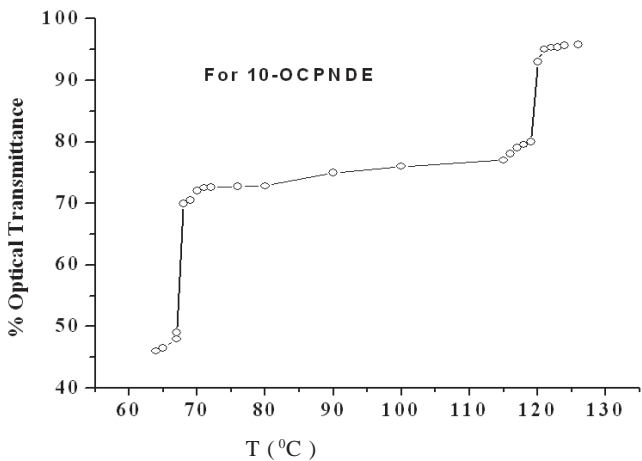7(a)   7(b)
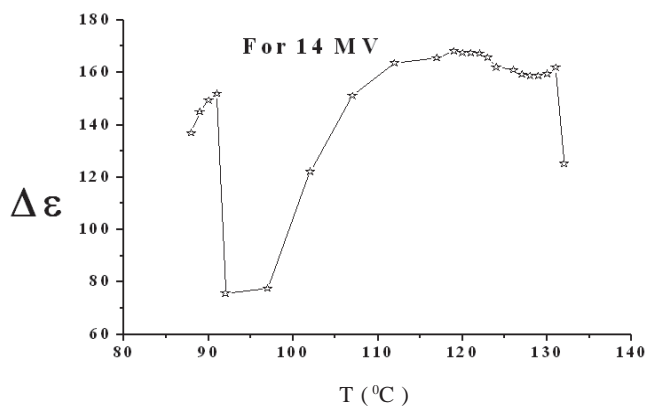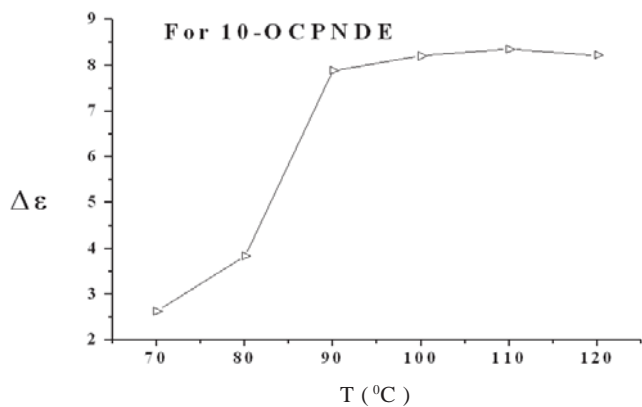
Figure 7: The temperature dependence of dielectric strength for (a) 10-OCPNDE and (b) 14 MV samples.

8(a)   8(b)

Figure 8: The temperature dependence of distribution parameter for (a) 10-OCPNDE and (b) 14MV samples.

9(a)   9(b)

Figure 9: The % optical transmittance versus temperature for (a) 10-OCPNDE and (b) 14MV samples.

of trend is observed in figures 1 and 2.

Fig. 7 shows the variation of dielectric strength (Äå) with temperature for 10-OCPNDE and 14MV samples. Fig. 7(a) represents the temperature dependence of dielectric strength for 10- CPNDE sample in SmA phase. It increases up to 90°C and beyond 90°C it is almost constant. Similar behaviour is also observed for 14MV sample in SmC phase. The magnitude of dielectric strength for 14MV is higher than that of 10-OCPNDE sample.This type of behaviour is also supported

by figure 1.

Fig. 8 shows the temperature dependence of distribution parameter for 10-OCPNDE and 14MV samples. The magnitude of distribution parameter of 10-OCPNDE is smaller than that of 14MV.

Fig. 9 (a) and Fig. 9(b) show the plots of normalized % optical transmittance of 10-OCPNDE and 14MV samples respectively. The % optical transmittance curve show a sharp increase at 88°C and 132°C indicating crystal to smectic

transition phase and smectic to isotropic transition phase for the sample 14MV. For the second sample i.e. for 10-OCPNDE, the % optical transmittance is changing abruptly at 68°C for crystal to smectic transition phase and at 121°C for smectic to isotropic phase transition.

The transition temperature as obtained using optical transmittance study matches with literature data.

4. CONCLUSION

1. The sample 10-OCPNDE (4-((2-chloral-4-nitrophenyl)diazenl)-1,3-phenylene bis(4-(decyloxy)benzoate)) has smectic A(SmA) phase while that of 14MV (4-((2-broom-4-nitrophenyl)diazenyl)-1,3-phenylene bis(4-(tetradecyloxy)benzoate)) has smectic C (SmC)phase. The dielectric permittivity of 10-OCPNDE sample is smaller than that of 14MV sample.

2. The dielectric absorption for 10-OCPNDE sample occurs at high frequency side near 100 kHz and the absorption peaks shift towards lower frequency side as the temperature increases. It increases with increasing temperature in SmA phase. While that in case of 14MV, it occurs at low frequency side near 1 kHz and the absorption peaks shift towards higher frequency side as the temperature increases. It is also observed that the dielectric loss rises with rise in temperature and frequency. The reason for this may bedue to Cl functional group attached to the sample10-OCPNDE is more polar than the Br functional group attached with sample 14MV.

3. The relaxation band in Cl attached compound 10-OCPNDE occurs in high frequency range while the relaxation frequency of Br attached sample 14MV lies in low frequency range in comparison to earlier one.

4. The optical transmittance study clearly indicates phase transition temperature of both the samples by sharp change in optical transmittance. The transition temperatures are in agreement to literature data.

5. REFERENCES

Attard, S. and Douglass, A.G. 1997. *Liq. Cryst.* **22**: 349.

Bottcher, C. J. F. and Bordewijk, P. 1978. *Theory of Electric Polarization*, Elsevier: Amsrerdam, Vol. II: 62-70.

Chand, P.B. 2009. Dielectric and optical studies of some mesogens of different molecular shapes. Ph.D. Thesis, Department of Physics, Lucknow University, Lucknow, India.

Chong, T.T., Heidelberg, T., Hashim, R., Gary, S. 2007. *Liquid Crystals* **34**: 267.

Demus, D. 1998. in *Handbook of Liquid Crystals*, ed. by D. Demus, J. W. Goodby, G. W. Gray, H. –W. Spiess and V. Vill, Wiley-VCH. Weinheim, vol. 1, ch.VI: 133-187.

Dhar, R. 2004. *Indian J. Pure Appl. Phys*. **42**: 56-61.

Diez, S., Dunmur, D., Panagiota, M. R. De Lafuente, Karahaliou, K., Mehl, G., Meyer, T., Jubindo, M. A. and Photinos, D.J. 2003. *Liquid Crystals* **30**(9): 1021-1030.

Goodby, J.W., Mehl, G.H., Saez, I.M., Tuffin, R.P., Mackenzie, G., Auzely-Velty, R., Benvegu, T. and Plusquellec, D. 1998. *Chem. Commun.* 2057.

Gouda, M. 1992. Dielectric relaxation spectroscopy of chiral liquid crystals, a Ph.D. thesis submitted to Department of Physics, Chalmers University of Technology, Goteberg.

Hall, W., Hollingshurst, J. and Goodby, J.W. 1997. *Hand book of Liquid Crystal Research*, edited by P.J. Collings and J.S. Patel, Oxford University Press, New York and Oxford, 17-70.

Hill, N. E., Vaughan, W.E., Price, A.H. and Davies, M. 1969. *Dielectric Properties and molecular behavior* (Van Nostrand Reinhold) London.

Hirschmann, H. and Hirschmann, V. 1998. TN, STN, *Displays in the hand book of Liquid Crystals* Vol.2B: Low molecular Weight Liquid Crystals, edited by D. Demus, J.W. Goodby, G.W. Gray, H.W. Spiess and V. Vill, Wiley-VCh, Weinheim, Ch III 3.1: 199-299.

Imrie, T., Henderson, P.A. 2002. *Curr. Opin. Colloid interface Sci.* **7**: 298.

Imrie, T., Luckhurst, G.R. 1998. In the *Handbook of Liquid Crystals,* Vol.1, D. Demus, J. W. Goodby, G. W. Gray, H. –W Spiess, V. Vill (Eds), Vol.1: 801-803.

Kato, T., Adachi, H., Fuzishima, A. and Frechet, J.M.J. 1992. *Chem. Lett.*, 265.

Majumder, T. P., Mitra, M. and Roy, S. K.1994. *Physical Review E* 50, 4796-4800.

Matsuzaki, H. and Mmatsunaga, Y. 1993. *Liq. Cryst.* **14**: 105.

Meier, G., Sackman, E.S. & Gramaier, D.G. 1975.*Application of liquid crystals* (Spinger-Verlog).

Pelzl, G., Diele, S., Weissflog, W. 1999. *Adv. Mater*. **11**: 707.

Saez, M. and Goodby, J.W.2003. *Chem. Commun.,* 1726.

Saez, M., Goodby, J.W. 2005 *J. mater. Chem.* **15**: 26.

Sekine, T., Niori, T., Sone, M., Watanabe, J., Choi, S.W., Takanishi,Y., Takazoe, H. 1997. *Jpn. J. Appl. Phys*. **36**: 6455.

Srivastav, S. L. and Dhar, R.1991. *Indian J. Pure and Appl. Phys*. **29**: 745-751.

Srivastava, S. L. and Dhar,R. 1991. *Indian J. Pure Appl. Phys*. **29**: 745.

Srivastava, S. L.1993. *Prc. Nat. Acad. Sci.* (India). **63**: 311.

Tashierske, C. 1998. *J. Mater. Chem*. **8**: 1485.

Tashierske, C. 2001. J. Mater. Chem. **11**: 2647.

Vorländer, D. and Apel, A.1932. *Chem. Ber*. **65**: 1101.

Yamaguchi, A., Nishiyama, I., Yamamoto, J., Yokoyama, H. and Yoshizawa, A. 2005. *J. Mater. Chem.* **15**: 280-288.

Zhang, B., Xiao, W., Cong, Y. and Zhang, Y. 2007. *Liquid Crystals* **34**(10): 1129-1136.

***