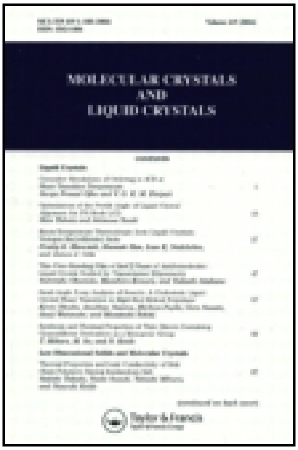


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electro-Optic Kerr Effect Investigations in a New Homologous Series of Liquid Crystal

Aloka Sinha [a] [c] , T. A. Prasada Rao [a] & Roman Dabrowski [b]

[a] Laser Lab, Department of Physics, Indian Institute of Technology, Madras, 600036, India

[b] Department Of Engineering, Chemistry and Physics, Institute of Chemistry, Military University of Technology, Warsaw, Poland

[c] Aloka Sinha. c/o Dr. Ranjan Bose, Department of Electrical Engineering, IIT Delhi, Hauz Khas, New Delhi, 110016, INDIA E-mail:

To cite this article: Aloka Sinha, T. A. Prasada Rao & Roman Dabrowski (2001): Electro-Optic Kerr Effect Investigations in a New Homologous Series of Liquid Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 369:1, 1-15

To link to this article: http://dx.doi.org/10.1080/10587250108030005

Mol. Cryst. Liq. Cryst., Vol. 369, pp. 1-15
Reprints available directly from the publisher
Photocopying permitted by license only

Electro-Optic Kerr Effect Investigations in a New Homologous Series of Liquid Crystal

ALOKA SINHA[a*], T.A. PRASADA RAO[a] and ROMAN DABROWSKI[b]

[a]Laser Lab, Department of Physics, Indian Institute of Technology, Madras 600036, India and [b]Department Of Engineering, Chemistry and Physics, Institute of Chemistry, Military University of Technology, Warsaw, Poland

(Received April 21, 2000; In final form April 21, 2000)

Measurements are reported for the first time for the D.C. Kerr response and the pretransitional behaviour of a new homologous series of liquid crystal 4′-(trans-4′-alkylcyclohexyl)-benzonitrile(for n=5 to 9) at and above the nematic-isotropic phase transition temperatures. The real part of the third order nonlinear susceptibilities($\chi^{(3)}$) have been determined for this homologous series of liquid crystals from the Electro-optic Kerr effect (EOKE) experiments at and above the nematic -isotropic phase transition temperatures. The variation of the Kerr constant with temperature has been discussed on the basis of the Landau-de Gennes model of nematic -isotropic phase transition. The Kerr relaxation time and other statistical parameters concerned with a nematic-isotropic phase transition like the latent heat of transition have also been determined using the Landau-de Gennes' theory of phase transition. The variation of the Kerr constant, the values of the third order nonlinear susceptibilities, the Kerr relaxation time and the latent heat of transition with the number of carbon atoms in the alkyl chain within the series have been discussed on the basis of an interesting effect called the "ODD-EVEN" effect. The results and discussions are presented.

Keywords: nematic liquid crystals; electro-optic Kerr effect; third order nonlinear susceptibilities; odd-even effect; phase transition; Landau-de Gennes' theory of phase transition

I. INTRODUCTION

Liquids crystals are becoming increasingly important as potential materials for optoelectronic devices[1–2]. Most of these devices are based on nonlinear optical

---

* Author for correspondence. Address: Aloka Sinha, c/o Dr. Ranjan Bose, Department of Electrical Engineering, IIT Delhi, Hauz Khas, New Delhi, 110016 INDIA. Email: alokasinha@hotmail.com

effects. Liquid crystals show giant optical nonlinearity in the phase transition regions.

It is of interest to study the effect of structure on the nonlinear optical properties of these materials to further molecular engineer new materials showing better nonlinear optical properties. One of the types of investigation into the structure-property relationship of the nonlinear optical properties of liquid crystals is to investigate a homologous series of liquid crystals[3–4]. In a homologous series, the group of molecules differs from one to the other homologue only by the number of methylene groups in the terminal substituent. There are two principal motivations behind this type of study. First, the search for technologically useful liquid crystals is directed toward materials of specific temperature ranges. The present lack of ability to predict such temperature ranges and coupled with the usual availability of a general synthesis procedure for a homologous series of liquid crystals, makes this type of investigation very fruitful. Very few pure liquid crystals have been found that are usable in display applications. Most of the display applications utilize a mixture of mesogenic compounds. These mixtures are based on a homologous series of liquid crystals in order to obtain eutectic mixtures and also to guard against material instabilities [5]. There is a second more fundamental reason for studying a homologous series of liquid crystals. In proceeding along a homologous series of liquid crystals, only very small changes in the molecular structure are made at each step. Thus, more specific conclusions would be possible when the effect of mesophase behaviour and properties are correlated with molecular size and shapes.

In this paper,we report for the first time the Electro-optic Kerr effect investigations in the 4′-(trans-4′-alkylcyclohexyl)-benzonitrile homologous series (the PCH series, for n =5 to n=9) [6]. The third order susceptibilities ($\chi^{(3)}$), which characterize the efficiency of these compounds for nonlinear optical applications have been determined. Since, these investigations have been carried out in the nematic – isotropic phase transition region (region for giant nonlinear optical properties), the validity of the Landau-de Gennes' theory[7] for the nematic – isotropic phase transition has been verified. The Kerr relaxation time, the latent heat of transition and the fictitious second order phase transition temperature have also been determined from the Landau-deGennes theory. The variation of the Electro-optic Kerr constant, the values of the third order nonlinear susceptibilities, the Kerr relaxation time and the latent heat of transition with the number of carbon atoms down the homologous series have been found to show the well known "odd-even" effect [8–10]. These variations have been explained on the basis of the variation of the nematic – isotropic phase transition temperatures with the number of the carbon atoms down the homologous series.

II. THEORY

Kerr law is given by [11]:

$$\Delta n = B\lambda E^2 \tag{1}$$

where Δn is the induced birefringence, B is the Kerr constant, λ is the probe wavelength and E is the applied electric field to the isotropic media.

By applying the symmetry properties [12], the nonvanishing elements of the third order susceptibility tensor $\chi^{(3)}$ in an isotropic media are related as:

$$\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221} \tag{2}$$

Also, applying the Klienmann symmetry[13] we get:

$$1/3\chi_{1111} = \chi_{1122} = \chi_{1212} = \chi_{1221} \tag{3}$$

Thus, there is only one nonvanishing element of the third order susceptibility tensor and can be related to the Kerr constant as [14]:

$$B = 24\pi/n\lambda[\chi_{1221}(-\omega_1, \omega_1, 0, 0)] \tag{4}$$

By Landau-de Gennes theory [7] for a nematic-isotropic phase transition in a conventional liquid crystal, the free energy can be expanded as a function of the nematic order parameter Q as:

$$\mathrm{F} = \mathrm{F_0} + \frac{1}{2}\mathrm{a}(\mathrm{T} - \mathrm{T}^*)\mathrm{Q}^2 - \frac{1}{3}\mathrm{bQ}^3 - \frac{1}{3}\frac{\Delta\varepsilon_0}{4\pi}\mathrm{E}^2\mathrm{Q} + \mathrm{O}(\mathrm{Q}^4) \tag{5}$$

where, a, b, c are the phenomenological constants characteristic of the transition and are assumed to be independent of temperature, T^* is a temperature below the nematic-isotropic transition temperature below which no stable isotropic phase can exist. $\Delta\varepsilon_0$ is the dielectric anisotropy in the perfectly ordered nematic phase. In the absence of an electric field there is no term linear in Q. This ensures that the state of minimum F in the absence of the electric field is a state of zero Q or the isotropic phase. Neglecting higher order terms in Q and by minimizing the free energy with respect to the field and using equation (1) we get [15]:

$$\mathrm{B_{DC}} = \frac{\Delta \mathrm{n_0} \Delta\varepsilon_0}{12\pi\lambda \mathrm{a}(\mathrm{T} - \mathrm{T}^*)} \tag{6}$$

Thus according to Landau-deGennes model of the nematic-isotropic phase transition, the variation of the inverse of the Kerr constant with temperature is linear with an intercept on the temperature axis which gives us the value of the fictitious second order transition temperature (T^*). The Kerr constant is predicted to diverge near the nematic -isotropic phase transition. The variation of Q(E) with time is given as [16–17]:

$$\nu \frac{\partial Q}{\partial t} = -\frac{\partial F}{\partial Q} \tag{7}$$

where, ν is the viscosity coefficient.

Under zero field conditions (i.e., the relaxation occurs in the absence of the electric field) and using the following equation

$$\frac{\partial Q}{\partial t} = -\frac{Q}{\tau} \tag{8}$$

and equation (7), the Kerr relaxation is given as

$$\tau = \frac{\nu}{a(T - T^*)} \tag{9}$$

The latent heat of transition (L) is given as [18–20]:

$$\nu = \frac{9}{2}\tau_{Kerr}(T - T^*)\frac{L}{T_{NI}} \tag{10}$$

Thus, the latent heat of transition can be determined from equation (10) by determining the Kerr relaxation time (τ_{Kerr}) and the orientational rotational viscosity (ν) at the transition temperature (T_{NI}).

III. EXPERIMENTAL PROCEDURE

The phase transition temperatures for the samples have been determined by differential scanning calorimetry(DSC) measurements. The molecular structures of the PCH homologous series of compounds are shown in Figure 1. All the studied liquid crystals have a nematic-isotropic phase transition as seen under the polarising microscope. The schematic diagram of the experimental set-up is shown in Figure 2. The liquid crystal samples are contained in Kerr cells consisting of polished aluminum electrodes of 10 mm path length and a 2 mm electrode separation. The electrodes themselves form the sides of the Kerr cells. The Kerr cells are designed such that minimum quantities of liquid crystal samples can be used without any wastage. The liquid crystal samples are heated directly by a Proportional Integral Differential (PID) controller. The temperatures of the sample could be maintained upto an accuracy of ± 0.1°C. The sample is maintained in the cell at the desired temperature for about 40 minutes before taking measurements.

A Helium-Neon laser of 5 mW power has been used as a probe beam. A photomultiplier tube (RCA IP-28) is used as a detector. High voltage pulses up to 8 kV have been used to induce birefringence in the medium. The high-voltage electric pulses that cause birefringence in the medium have been measured using a Tek-

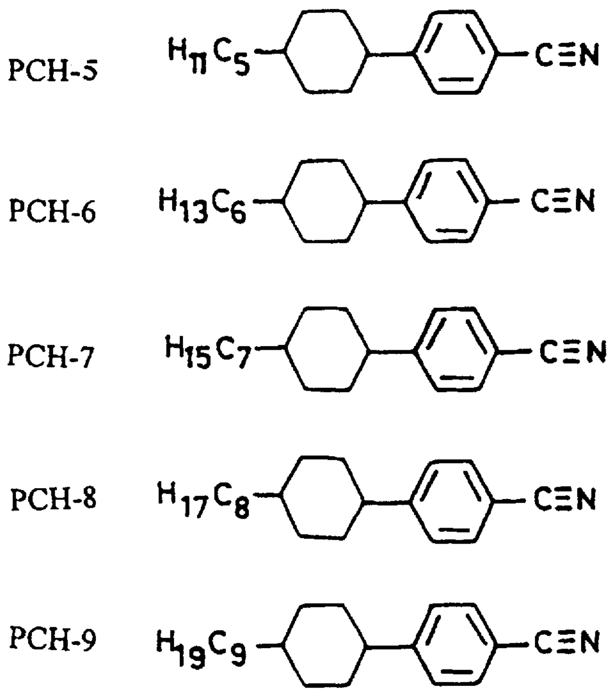


FIGURE 1 Molecular structure of the phenyl cyclohexane(PCH) homologous series of compounds

tronix P6015 high voltage probe with 1:1000 attenuation. Both the Kerr signal and the high voltage pulses are acquired on a Digital storage oscilloscope (Tek 2440) with 350MHz bandwidth and a sampling rate of 500MS/sec. The polarizer and the analyzer are adjusted such that they are crossed with each other, making an angle of 45° with the direction of the electric field.

The phase difference can be obtained from the experiment by using the relation [21]:

$$I = I_o \sin^2(\delta/2) \tag{11}$$

where I is the intensity when both the analyser and the polariser are crossed with respect to each other and I_0 is the intensity when the polariser and analyser are parallel to each other. The induced birefringence (Δn) which is related to the phase difference (δ) induced by the electric field is given by [17]:

$$\delta = 2\pi l \Delta n/\lambda \tag{12}$$

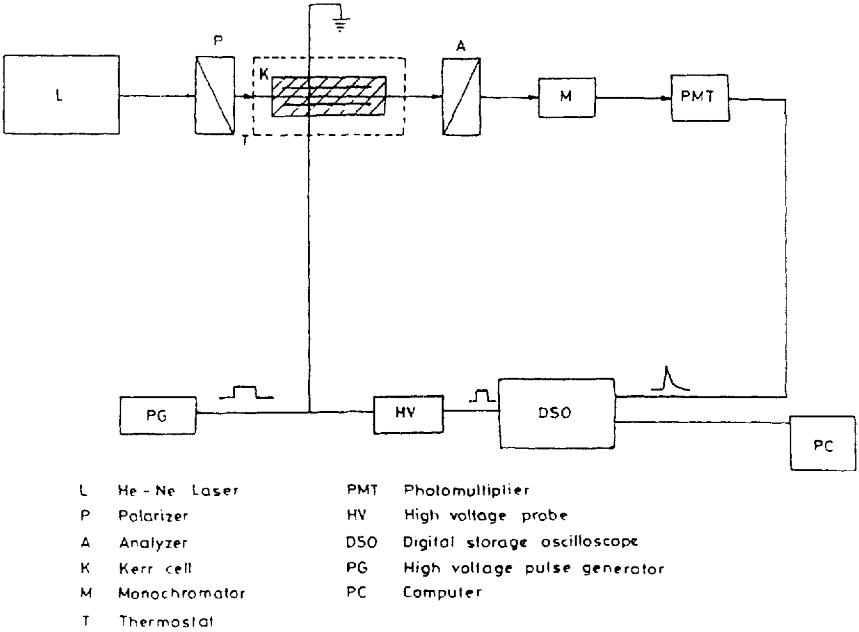


FIGURE 2 The experimental setup for the measurement of the Electro-optic Kerr constant (B_{DC})

where l is the length of the Kerr cell and λ is the probe wavelength. Thus the values of B_{DC} and hence $\chi^{(3)}$ for various temperatures have been obtained by using the above equations.

IV. RESULT AND DISCUSSION

The phase transition temperatures, determined from the Differential Scanning Calorimetry measurements are shown in table I. The values of the Kerr constant (B_{DC}) at the phase transition temperature and above have been determined from the plot of the induced birefringence with respect to the square of the electric field for each of the samples. Figure 3 shows the linear variation of the induced birefringence with the square of the electric field at the nematic-isotropic phase transition temperature for all the samples. The Kerr constant (B_{DC}) and the susceptibility values ($\chi^{(3)}$), have been determined for all the samples at the nematic-isotropic phase transition temperatures and are shown in table I. Figure 4 shows the variation of the Kerr constant and the inverse of the Kerr con-

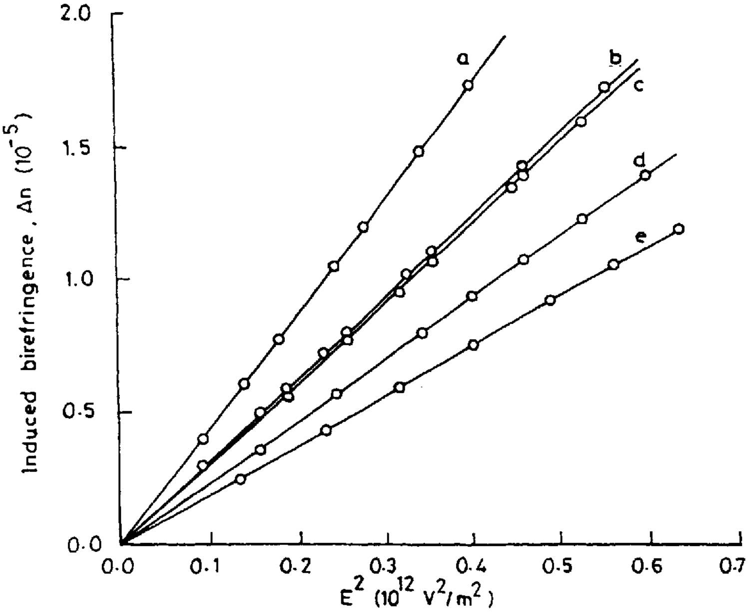


FIGURE 3 Variation of the induced birefringence(Δn) with the square of the electric field at T_{NI} for (a) PCH-6, (b) PCH-5, (c) PCH-8, (d) PCH-7 and (e) PCH-9

stant for one of the samples, i.e. PCH 8. Linear variation of the inverse of the Kerr constant with temperature confirms the validity of the Landau-deGennes theory for a nematic -isotropic transition. The Kerr relaxation times have been obtained at the phase transition temperatures by calculating the Landau-de Gennes phenomenological constant "a" from the equation (6).

TABLE I The B_{DC} and $\chi^{(3)}$ values at the nematic-isotropic phase transition temperatures for the PCH series of compounds

Sample	*T_{NI} (°C)*	*Refractive Index (at T_{NI})*	*B_{DC} (at T_{NI}) (10^{-12} m/V^2)*	*$\chi^{(3)}$ (at T_{NI}) (10^{-20} m^2/V^2)*
PCH-5	56.1	1.500	49.9	62.8
PCH-6	47.0	1.532	72.6	93.4
PCH-7	57.8	1.526	37.2	47.7
PCH-8	55.2	1.524	47.7	60.9
PCH-9	59.1	1.521	29.0	37.0

Knowing the experimental values of the Kerr constant at the phase transition temperature and using the values of anisotropy of refractive index (Δn_0) and the

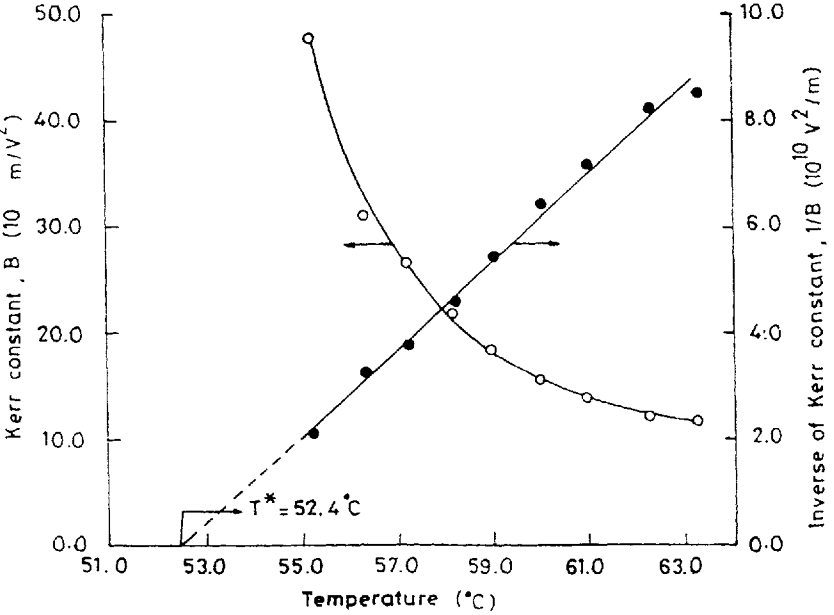


FIGURE 4 Variation of the Kerr Constant and the inverse of the Kerr constant with temperature for PCH-8

anisotropy of dielectric constant ($\Delta\varepsilon_0$) at the transition temperature from literature [6], the "a" values have been obtained. They are shown in Table II for all the samples. The Kerr relaxation times are then obtained from equation (9), using the calculated values of "a" and the experimentally determined values of the viscosity at the transition temperature. The values of the viscosity have been obtained from the Brooke field viscometer at T_{NI}. The obtained values of the relaxation time for all the PCH samples are shown in Table II. The relaxation times are in the microsecond range. This proves that the relaxation is not due to individual molecules. The fictitious second order transition temperatures (T^*) have been obtained by extrapolating the $(B_{DC})^{-1}$ straight line. The Landau-de Gennes phenomenological constants have been calculated earlier. Knowing the Landau-de Gennes phenomenological constant (a) and the orientational rotational viscosity(v), the values of the latent heat of transition for all the samples could be calculated and are shown in Table III. The determined values of the latent heat of transition are very small.

Figures 5, 6, 7 and 8 show the variation of the Kerr constant, the third order nonlinear susceptibilities, the Kerr relaxation time and the latent heat of transition with the number of carbon atoms respectively. All these variations show a pronounced "odd-even" effect.

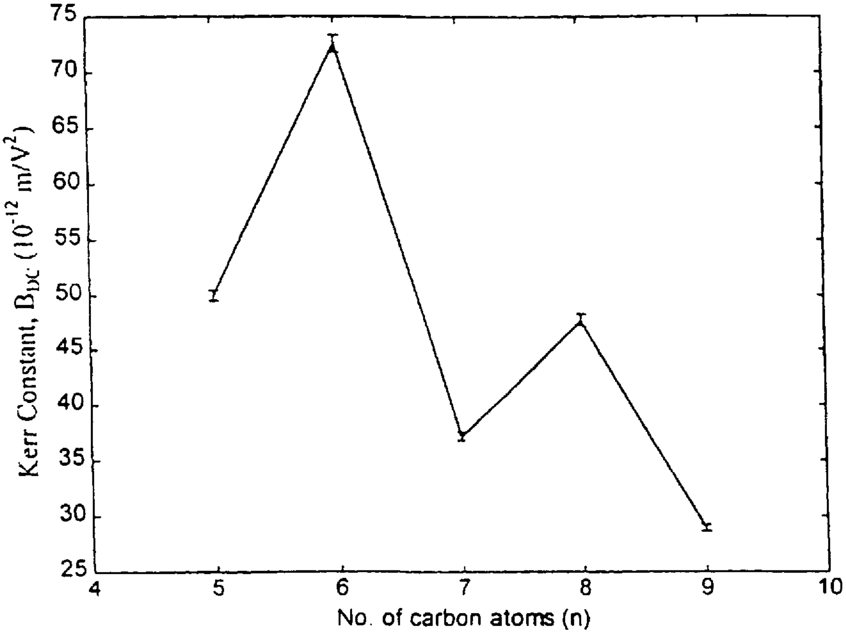


FIGURE 5 Variation of the Kerr constant with the number of carbon atoms for the PCH series

TABLE II The Kerr relaxation times and the phenomenological constant "a" for all the PCH samples at T_{NI}

Sample	T_{NI} (°C)	T^*	B_{DC} (at T_{NI}) (10^{-12} m/V^2)	Δn_o	$\Delta\varepsilon_o$	a (10^3 Jm^{-3}K^{-1})	ν (cP)	τ_{Kerr} (at T_{NI}) (μs)
PCH-5	56.1	54.6	49.9	0.104	16.8	3.9	23.2	3.9
PCH-6	47.0	44.4	72.6	0.120	10.0	2.5	27.8	4.1
PCH-7	57.8	56.0	37.2	0.106	15.6	4.7	26.9	3.1
PCH-8	55.2	52.4	47.7	0.110	9.8	3.3	32.3	3.4
PCH-9	59.1	57.4	29.0	0.120	7.0	6.3	32.0	3.0

TABLE III The latent heat of transition for the PCH samples at T_{NI}

Sample	T^*	a (10^3 Jm^{-3}K^{-1})	ν (cP)	L (10^6 J/m^3)
PCH-5	54.6	3.9	23.2	0.049
PCH-6	44.4	2.5	27.8	0.026
PCH-7	56.0	4.7	26.9	0.061
PCH-8	52.4	3.3	32.3	0.041
PCH-9	57.4	6.3	32.0	0.082

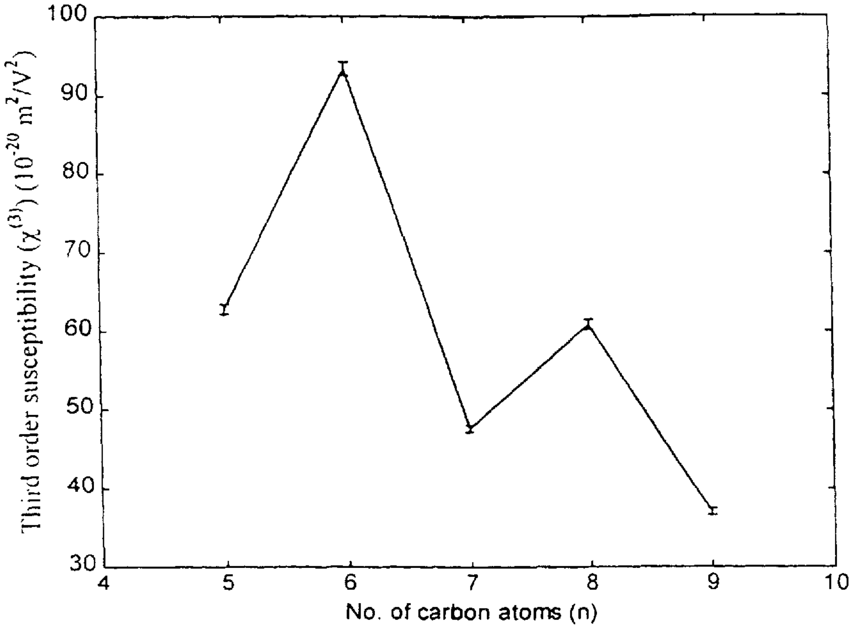


FIGURE 6 Variation of the $\chi^{(3)}$ values with the number of carbon atoms for the PCH series

V. CONCLUSION

All the studied liquid crystals belonging to the PCH homologous series show a giant optical nonlinearity in the nematic- isotropic phase transition region as can be seen from the $\chi^{(3)}$ values in table I. This is because of the weak nature of the first order nematic-isotropic phase transition and hence there is an existence of the short – range order in the isotropic phase even though the long range order is destroyed. This gives rise to highly correlated molecular re-orientational effects in the isotropic phase and can be distinguished from the usual individual molecular re-orientational effects[16, 22]. The linear variation of the induced birefringence (Δn) with the square of the electric field as shown in Figure 3 proves the validity of the Kerr law. The linear variation of the inverse of the Kerr constant with temperature as shown for one of the samples in Figure 4 proves the validity of the Landau-deGennes theory of phase transition. The relaxation time is in the microsecond range due to the formation of swarms of molecules near the isotropic-nematic phase transition temperature and is different from the characteristics of individual molecular reorientations as in the case of anisotropic liquids.

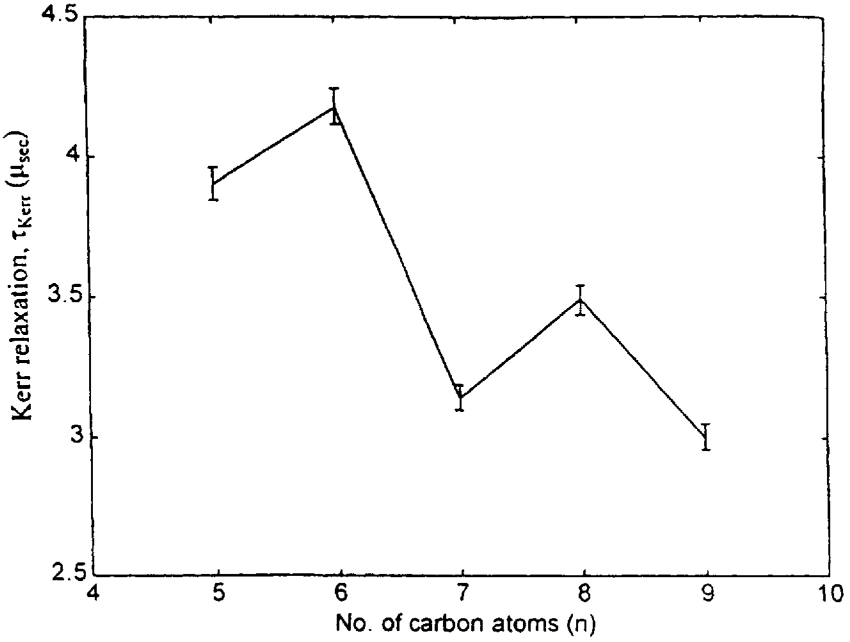


FIGURE 7 Variation of the Kerr relaxation time with the number of carbon atoms for the PCH series

These are typically of the order of a few picoseconds [23]. The small value of the latent heat of transition indicates the weak first order nature of the nematic- isotropic phase transition. In the present studies, the odd-even effect behaviour has been observed in the variation of the Kerr constant, third order susceptibilities, the Kerr relaxation time and the latent heat of transition with the number of carbon atoms in the side alkyl chains in the homologous series. All of them show the characteristic zig-zag alternation. The points corresponding to the even members (having an even number of carbon atoms in the side alkyl chain) and those corresponding to the odd members (having an odd number of carbon atoms in the side alkyl chain) lie on two separate smooth curves. From the present investigations, it has been observed that the Kerr constant and the relaxation time have a strong dependence on T_{NI}. So by understanding the variation in T_{NI} an explanation for the variation of the other parameters has been sought for.

The variation in T_{NI} (odd-even effect) with the number of carbon atoms in the side alkyl chain has been shown in Figure 9 and is opposite to that of the other parameters (like the Kerr relaxation time, Kerr constant etc.). In the case of T_{NI}, the odd members have a greater value whereas in the case of the other parameters

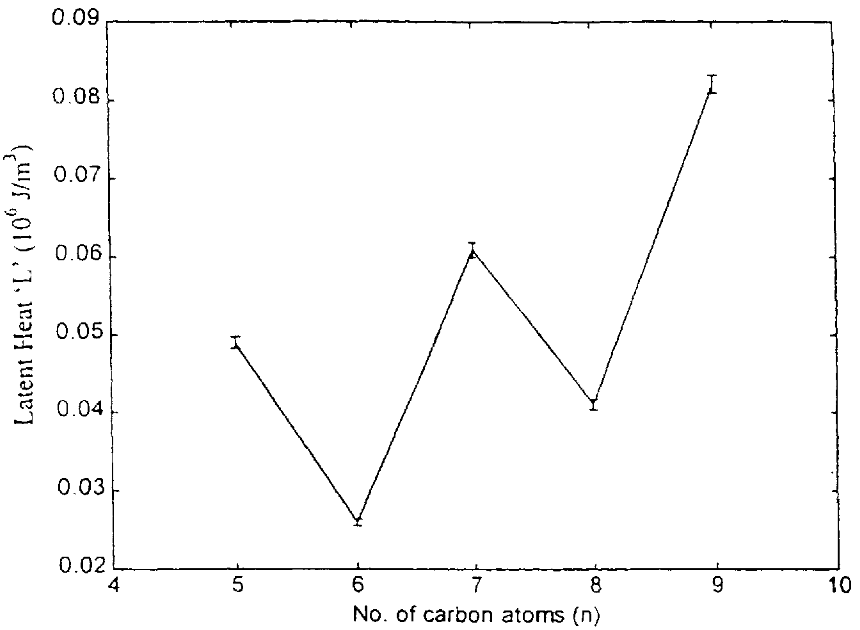


FIGURE 8 Variation of the latent heat of transition with the number of carbon atoms for the PCH series

(except the latent heat of transition) the even members have a greater value than the odd members. The alternation in the values of T_{NI} with the number of carbon atoms have been earlier correlated with the effects of increasing chain length on the anisotropy of molecular polarizability. The dependence of T_{NI} on the anisotropy of molecular polarizability ($\Delta\alpha$) has been derived by de Jeu *et al.* [8]. This relation has not been used in the present investigations for the calculations of T_{NI} but it is useful to understand the various factors which gives rise to the odd-even effect in T_{NI}. The relation is given as

$$T_{NI} = \frac{1}{4.54}\frac{4\pi^2}{(135)}\frac{(\Delta\alpha)^2 I}{k\,V^2} \tag{13}$$

where, I is the ionization potential and it represents the average excitation energy, V is the molar volume and k is the Boltzman's constant. $\Delta\alpha$ roughly corresponds to the molecular shape. Using the Rayleigh scattering technique, Lalanne *et al.* [24] investigated the anisotropy in polarisability in the case of the cyanobiphenyl homologous series (for n = 1 to 12) of compounds. From these studies it was observed that the anisotropy in polarizabilities increased with n upto n = 5.

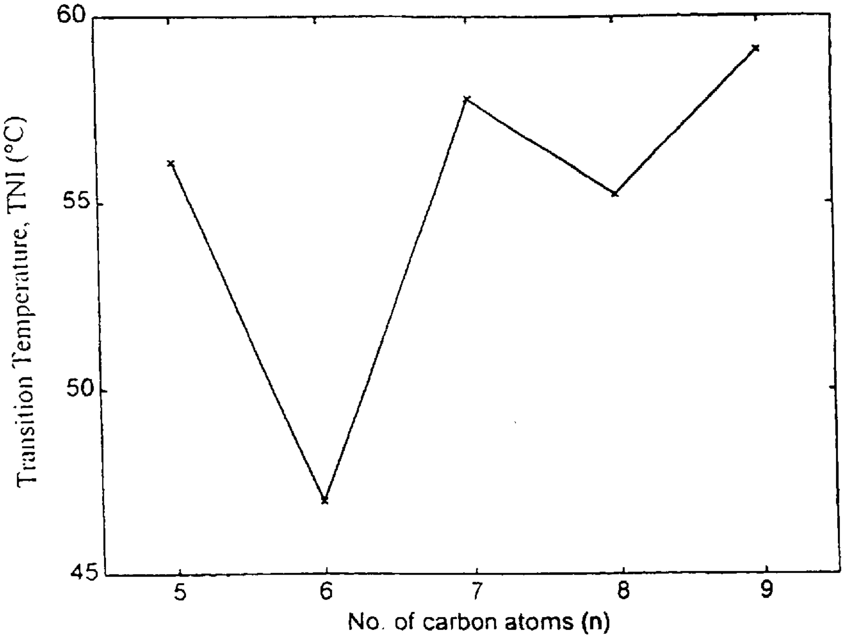
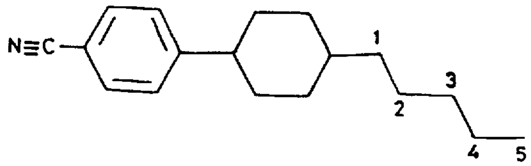


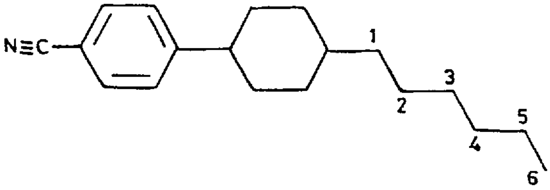
FIGURE 9 Variation of the nematic-isotropic phase transition temperatures with the number of carbon atoms for the PCH series

Beyond this for n = 5 to 12 an alternating behaviour was observed in the value of $\Delta\alpha$. Thus, an alternation in the value of the anisotropy in polarisability was observed down a homologous series.

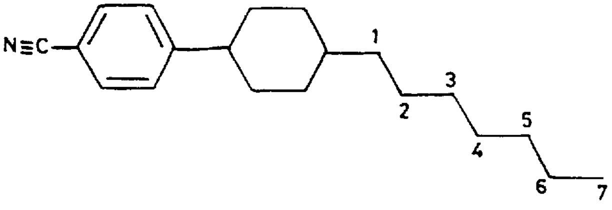
Assuming a rigid extended zig-zag chain for the side alkyl chain as shown in Figure 10, the axial polarisabilty ($\alpha_{\|}$) increases twice as much as the polarizability at right angles to the molecular long axis ($\alpha_{\perp}$) when passing from an even member to an odd member of the alkyl substituted series and $\alpha_{\|}$ and $\alpha_{\perp}$ increases almost equally when passing from an odd to an even member of the series. So the anisotropy in molecular polarizability is greater for the odd members than the even members at comparable molecular weight. From the relation (13), the values of T_{NI} are predicted to be higher for the odd members than in the even members. Since all the other parameters (except the latent heat) have an inverse relationship with T_{NI}, the even members show a higher value than the odd members for the other parameters. The latent heat of transition has a direct relationship with T_{NI} and hence shows a similar trend.



PCH-5



PCH-6



PCH-7

FIGURE 10 The rigid zig-zag extended molecular structure for the odd and the even members of the PCH series

References

1. **M.J. Samone, G. Khanarian and M.S. Kwiatek**, J. Appl. Phys. **75**, 1715(1994).
2. **I.C. Khoo**, Acta. Phys. Pol. A. **86**, 267(1994).
3. **P.P. Karat and N.V. Madhusudhana**, *Molecular Crystals and Liquid Crystals*, **36**, 51(1976).
4. **E.G. Hanson, Y.R. Shen and G.K.L. Wong**, Physical Review A,**14**, 1991(1976).
5. **H. Sorkin and A. Denny** *RCA, Rev.*, **34**, 308(1973).
6. **L. Pohl and U. Finkenzeller**(1977) *Physics Letters*, 60A, 421(1977).
7. **P.G. de Gennes and J. Prost**, The physics of liquid crystal, II edition, Oxford University Press, 1993.
8. **W.H. de Jeu and J. Van der veen**, *Molecular Crystals and Liquid Crystals*, **40**, 1(1977).
9. **P. Pines, D.J. Ruben and Allison**, *Physical Review letters*, **33**, 1002(1974).
10. **D.A. Pink**, *Journal of Chemical Physics*, **63**, 2533(1975).
11. **J. Kerr**, *Philosophical Magazine Ser.* **50**, 337(1875).

12. **P.N. Butcher and D. Cotter** *The elements of Nonlinear Optics*, Cambridge University Press, Cambridge, 1990, p. 141.
13. **D.A. Kleinmann**, *Physical Review*, **126**, 1977(1962).
14. **C.C. Wang**, *Physical Review*, **152**, 149(1966).
15. **Y.Poggi, J.C.Fillippini and R.Aleonard**, *Physics Letters*. **57**A, 53(1976).
16. **P.G. de Gennes**, *Molecular Crystals and Liquid Crystals*, **12**, 193(1971).
17. **E.G. Hanson and Y.R. Shen**, *Molecular crystals and liquid crystals*, **36**. 193(1976).
18. **M.A. Agafonov, S.G.Polushin, T.A.Rotinyan and E.I.Ryumtsev**, *Soviet Physics Crystallography*, **31**, 310(1986).
19. **E.I. Ryumtsev and S.G. Polushin**, *Molecular Crystals and Liquid Crystals*, **212**, 271(1992).
20. **Cheol Soo Park, N.A.Clark and R.D.Noble**, *Physical Review Letters*, **72**, 1838(1994).
21. **A.D. Buckingham and J.H. Williams**, J. Phys. E: Sci. Instrum. **22**, 790(1989).
22. **J.D.Lister and T.W. Stinson**, *Physical Review Letters*, **25**, 503(1970).
23. **J. Prost and J.R. Lalanne**, *Physical Review A*, **8**, 2090(1973).
24. **J.R. Lalanne, B.Lemaire, J.Rouch., C.Vaucamps and A.Proutiers**, *Molecular Crystals and Liquid Crystals*, **66**, 1(1981).