Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Effect of substituents and alkoxy chain length on the phase behaviour and optical properties of 4-substituted-phenyl 4-alkoxybenzoates

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Online publication date: 12 May 2010

To cite this Article Roushdy Corresponding author, M.(2004) 'Effect of substituents and alkoxy chain length on the phase behaviour and optical properties of 4-substituted-phenyl 4-alkoxybenzoates', Liquid Crystals, 31: 3, 371 — 375
To link to this Article: DOI: 10.1080/02678290310001655258
URL: http://dx.doi.org/10.1080/02678290310001655258

LIQUID CRYSTALS, VOL. 31, NO. 3, MARCH 2004, 371–375

Effect of substituents and alkoxy chain length on the phase behaviour and optical properties of 4-substituted-phenyl 4-alkoxybenzoates

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(*Received 26 May 2003; in final form 27 October 2003; accepted 27 October 2003*)

The refractive indices as functions of temperature were measured for 4-substituted-phenyl 4-alkoxybenzoates in which one substituent is a terminal alkoxy group with the number of carbon atoms kept constant (at $n=6$, 8, 14, or 16), while the other terminal substituent was either CH_3O, CH_3, Cl, CN or NO_2. Polarizing optical microscopy was also used to identify mesophases and measure their transition temperatures. The results are discussed in terms of electronic polarizability effects.

1. Introduction

The liquid crystalline state of matter is a fascinating subject for both basic and technological reasons. In order to correlate the stability of mesophases with the molecular structures of the liquid crystalline compounds, extensive studies by Gray and others have been previously presented [1–4]. Since then, there have been many investigations of the effects of substituents and of the alkoxy chain length on phase behavior [5–8]. These results have led to the conclusion that intermolecular forces due to dipole–dipole interactions (involving both permanent and induced dipoles), which generally depend on the specific units within the molecule, are very important in determining the mesophase stability. Recently, the effect of substituents and the alkoxy chain length on the phase behavior of some 4-substituted-phenyl 4-alkoxybenzoates (**I***n*a–e) was studied by using differential scanning calorimetry (DSC). The thermal stability of the compounds in this series was related to the polarizability anisotropy of bonds to the small substituents *X* [9].

It is well known that the refractive index of a medium is related to its dielectric constant and the polarizability of its molecules [10]. Therefore, refractive index measurements may be useful in giving more information on the effect of the polarity of terminal substituents as well as of the length of the alkoxy chain on the stability of mesophases.

Liquid crystals are birefringent; uniaxial phases, for example nematic or smectic A phases, have two different refractive indices, the extraordinary $\boldsymbol{n}_e$ and ordinary $\boldsymbol{n}_o$. According to each of these, respectively, light polarized parallel or perpendicular to the preferred direction of the phase propagates. Figure 1 shows [11] the temperature dependence of both $\boldsymbol{n}_e$ and $\boldsymbol{n}_o$ for a typical nematic liquid crystal.

The aim of the present study is to investigate the optical properties of a number of liquid crystals by the measurement of their refractive indices as a function of temperature. This is in order to cast more light on the effect of substituents, as well as of the chain length, on their phase behaviour. For this study, the 4-substituted-phenyl 4-alkoxybenzoates, **I***n*a–e were used (see the table). Substituents *X* (methoxy, methyl, chloro, cyano and nitro) were chosen to cover a wide range of electronic and

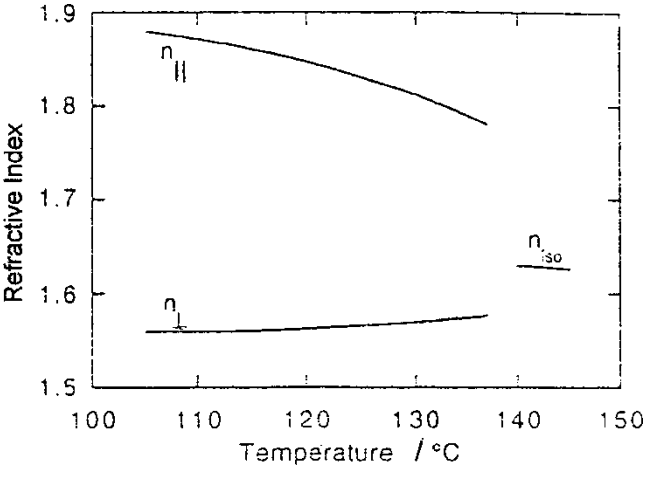

Figure 1. Refractive indices for a typical nematic liquid crystal: $n_{\|}$ and $n_{\perp}$ refer to n_{ex} and n_o, respectively.

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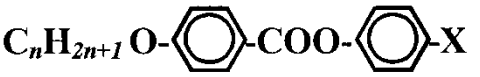
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290310001655258

Table. Thermodynamic properties for the investigated compounds, on cooling: T is in °C, ΔH_C in kJ mol^{-1} and ΔS_C in J mol^{-1} K^{-1}; ( ) indicates a monotropic transition.



(I*na–e*)

I6 n=6; I8 n=8; I14 n=14; I16 n=16

I*a* X=CH_3O; I*b* X=CH_3; I*c* X=Cl; I*d* X=CN; I*e* X=NO_2

Compound	n	X	T_{CrSmA}	T_{CrN}	T_{CrI}	T_{SmAN}	T_{SmAI}	T_{NI}	ΔH_c	ΔS_c
I 6a	6	CH_3O	—	—	95.0	—	—	(74.5)	0.50	1.44
I 6b	6	CH_3	—	—	66.7	—	—	(53.0)	—	—
I 6c	6	Cl	—	—	89.9	—	—	(68.5)	—	—
I 6d	6	CN	—	72.0	—	—	—	80.5	0.38	1.02
I 6e	6	NO_2	—	—	68.0	—	—	(55.0)	0.19	0.58
I 8a	8	CH_3O	—	—	85.0	—	—	(75.0)	0.61	1.75
I 8b	8	CH_3	—	—	61.8	—	—	(51.5)	0.94	2.91
I 8c	8	Cl	—	—	79.4	—	(75.5)	—	3.62	10.4
I 8d	8	CN	—	78.0	—	—	—	83.0	0.79	2.23
I 8e	8	NO_2	53.1	—	—	62.6	—	67.0	0.37	1.09
I 14a	14	CH_3O	—	—	96.3	—	(74.0)	—	—	—
I 14b	14	CH_3	—	—	71.1	—	(61.5)	—	1.24	3.72
I 14c	14	Cl	—	—	79.8	—	(76.0)	—	3.85	11.03
I 14d	14	CN	78.0	—	—	—	94.0	—	3.42	9.32
I 14e	14	NO_2	74.6	—	—	—	85.8	—	2.84	7.92
I 16a	16	CH_3O	—	—	96.1	—	(75.0)	—	2.10	6.03
I 16b	16	CH_3	—	—	77.7	—	(60.6)	—	4.01	12.02
I 16c	16	Cl	—	—	84.7	—	(74.0)	—	4.90	14.12
I 16d	16	CN	85.9	—	—	—	95.0	—	4.63	13.34
I 16e	16	NO_2	79.4	—	—	—	87.5	—	3.70	10.28

dipolar characteristics, while the chain lengths (n=6, 8, 14, and 16 carbon atoms) were selected to induce different mesophases (nematic and smectic).

The table shows the molecular structure, the phase types, the transition temperatures and the heats of transition of these compounds. Polarizing microscopy was also used for mesophase identification as well as for measuring transition temperatures.

2. Experimental

2.1. *Materials*

The preparation of the compounds listed in the table has been described previously [9]; here the compounds were characterized by infrared spectroscopy and their transition temperatures were determined by DSC.

2.2. *Refractive index measurements*

Measurements of refractive index in the temperature range 40–100 ± 0.2°C were performed using an Abbe 60 refractometer attached to an ultra-thermostat. Refractive index measurements at temperatures other than 20°C were corrected to compensate for the change of refractive index of the prism brought about by the working temperature, since the instrument was initially calibrated for 20°C. This correction amounted to 0.0000078 per °C. Unfortunately, extraordinary refractive index values, in the liquid crystalline phases for the compounds under test, were too high to be measured by the available refractometer. Because most of the compounds under test show their mesophases monotropically, ordinary refractive index measurements were recorded while cooling from the isotropic phase to the mesophases.

2.3. *Polarizing optical microscopy*

Identification of the mesomorphic phases and determination of their transition temperatures were performed using a Wild M7S polarizing microscope attached to an MPS51photo camera and a home-made hot stage. The working temperature of the hot stage ranged from room temperature to 300 ± 0.5°C. With respect to the textures presented in this study, no special surface treatments were made to the glass microscope slides or the cover slips beyond wiping with lens tissue.

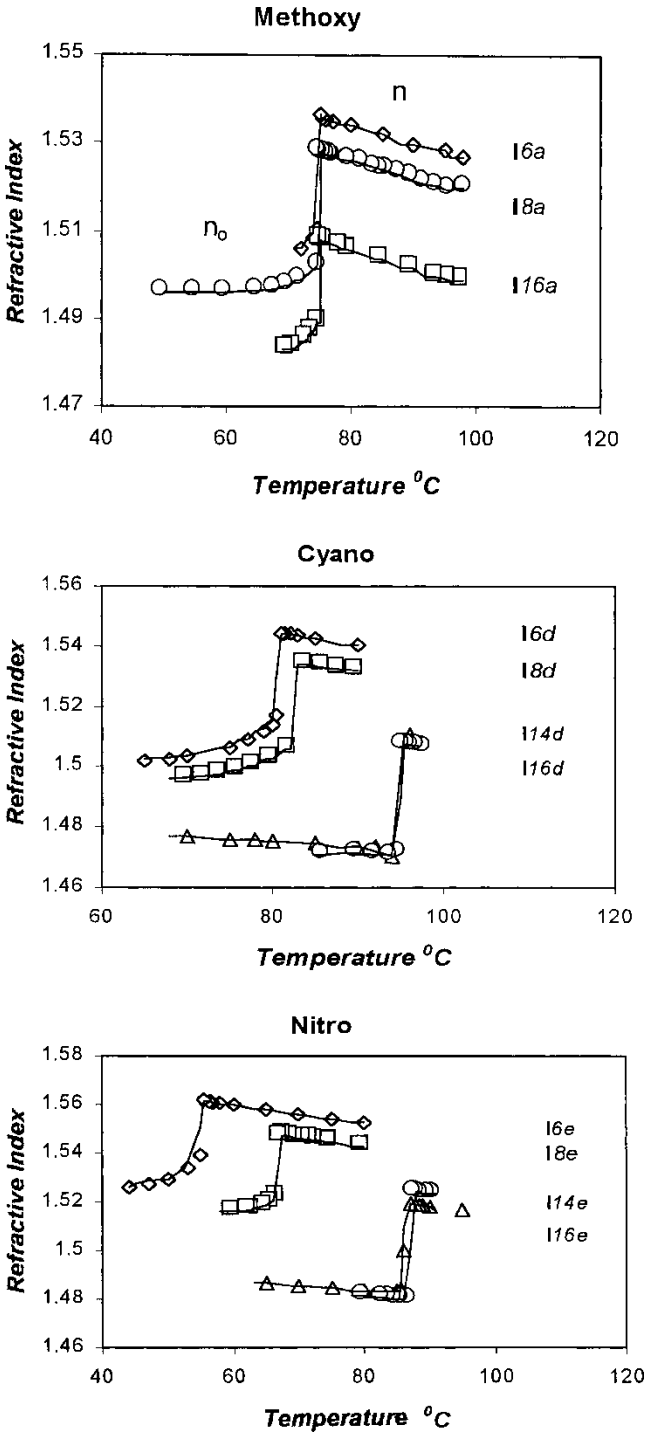


Figure 2. Refractive indices as function of temperature for **I***n*a–e.

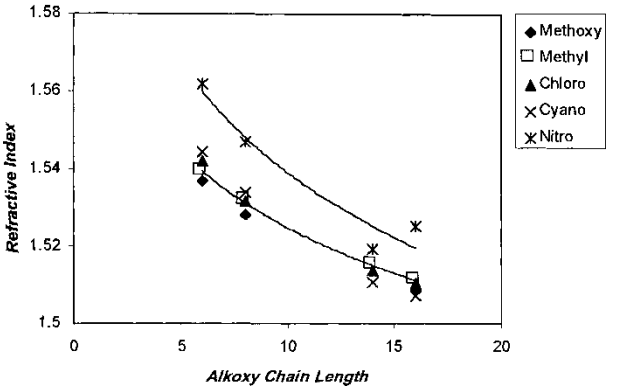


Figure 3. Dependence of the refractive index of compounds **I***n*a–e on the alkoxy chain length in the isotropic phase.

3. Results and discussion

3.1. *Refractive index and molecular polarizability*

The ordinary refractive index $\boldsymbol{n_o}$ of the pure compounds of the homologous series **I***n*a–e ($n = 6$, 8, 14 or 16) with different substituents X (a = CH_3O, b = CH_3, c = Cl, d = CN, e = NO_2), was measured as a function of temperature during cooling from the isotropic phase to the mesophase. Examples of the data are presented in figure 2; all the graphs show the expected trend for $\boldsymbol{n_o}$ with temperature for liquid crystals (see figure 1). In order to investigate the effect of the substituents and the chain length on the phase behaviour, the results are analysed for the two regions: the isotropic phase and the liquid crystalline phase.

In the isotropic phase (see figure 3), irrespective of the side group X and at a temperature just above the clearing temperature T_c of each compound, the refractive index $\boldsymbol{n}$ decreases as the chain length of the alkoxy group increases. This suggests that, although the increase in the number of carbon atoms increases the molecular polarizability, it also leads to a decrease in the number of molecules occupying a unit volume. This will, in turn, decrease the density and consequently the refractive index. For the nitro side group curve, and irrespective of the alkoxy chain length, $\boldsymbol{n}$ has higher values relative to the other compounds which have more or less the same values. This may be attributed to the high molecular polarizability of the nitro group which, on average, will increase $\boldsymbol{n}$.

In the mesophase the ordinary refractive index $\boldsymbol{n_o}$, or correspondingly the transverse molecular polarizability $\alpha_\perp$, shows, in general, a decrease as the chain length of the alkoxy group increases. This will lead to a more ordered mesophase and hence, increasing the alkoxy group chain length will increase the linear molecular polarizability $\alpha_\parallel$ [1] and decrease $\alpha_\perp$ (see figure 4). Thus, the polarizability anisotropy ($\Delta\alpha = \alpha_\parallel - \alpha_\perp$) of the mesophase may increase leading to a structurally more stable mesophase. This is clearly evident from the enthalpy values, ΔH_c, of the mesophase–isotropic transitions (see the table). For example, ΔH_c values for cyano derivatives increase from 0.38 kJ mol^{-1} for **I** 6d to 4.63 kJ mol^{-1} for **I** 16d.

At long chain lengths ($n = 14$ or 16) the $\boldsymbol{n_o}$ values tend to approach a single value. In this range of chain

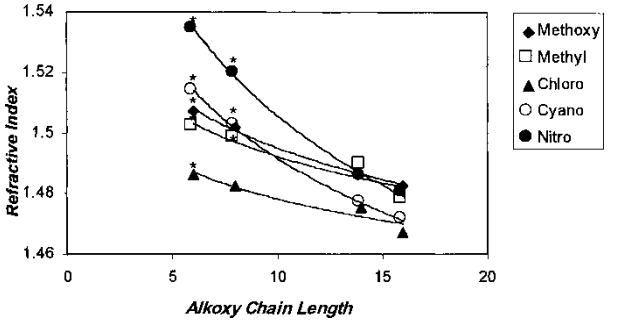


Figure 4. Dependence of the refractive index of compounds **I***n*a–e on the alkoxy chain length in the mesophase. The points indicated by an asterisk refer to a nematic–isotropic transition, others are smectic–isotropic transitions.

lengths $\alpha_{\perp}$ will no longer have a large effect on the mesophase behaviour. Instead, $\alpha_{\parallel}$ dominates and plays a role in aligning the molecules within the mesophase favouring a bilayer structure. For shorter alkoxy chain lengths, chlorine-substituted compounds were observed to have lower n_o values while the nitro-substituted materials exhibited higher values than those of the analogous alkoxy-terminated compounds. This may clarify why the mesophases of the chloro derivatives are more ordered and those of the nitro derivatives less ordered than those of the remaining compounds. This is highlighted by comparing the corresponding heats of transitions, ΔH_c.

3.2. *Identification of phases and transition temperatures*

Polarizing microscopy was used to identify the mesophases of the liquid crystalline compounds under test,

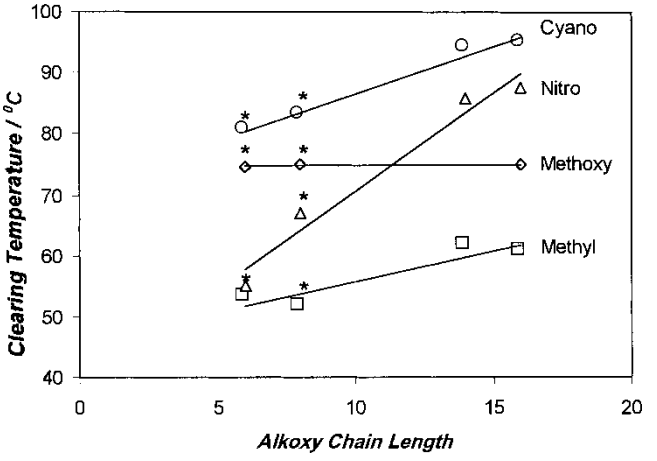


Figure 5. Variation of clearing temperature T_c for compounds **I**a–e with the number of carbon atoms in the alkoxy chain. The points indicated by an asterisk refer to nematic–isotropic transitions, others are smectic–isotropic transitions.

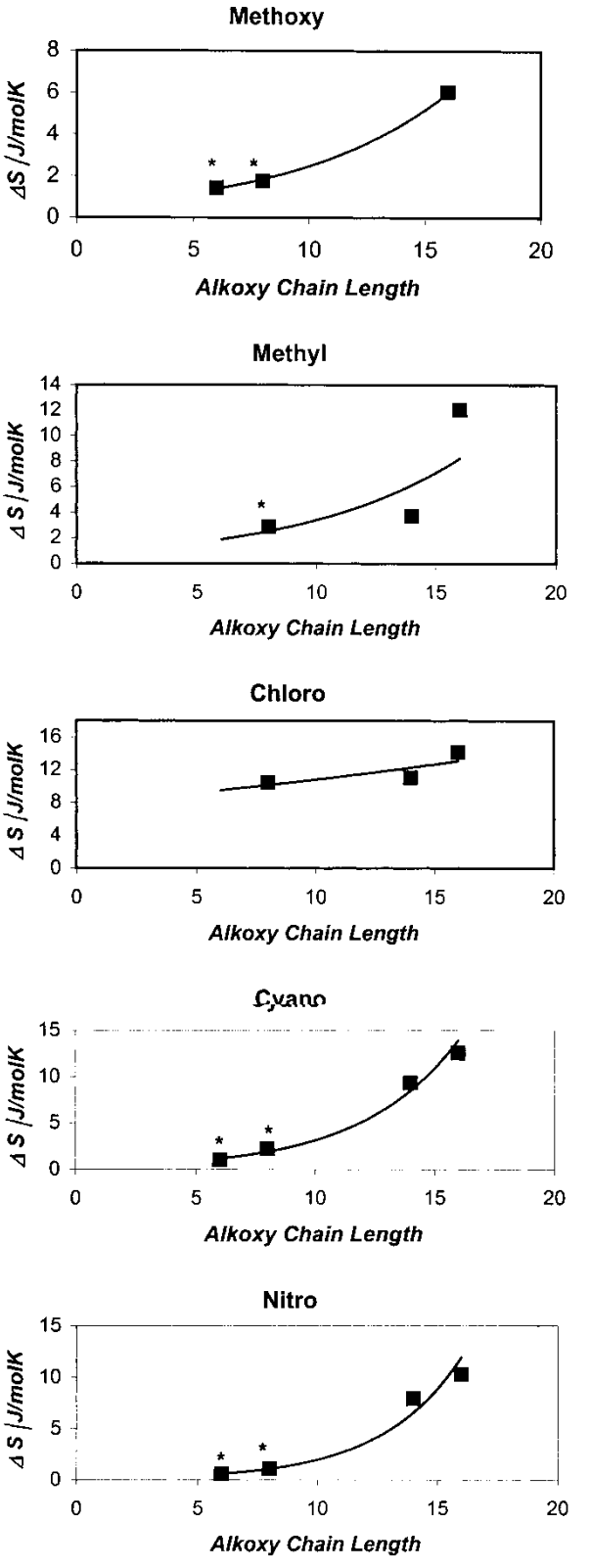


Figure 6. Dependence of the entropy change ΔS_c for mesophase–isotropic transition on the alkoxy chain length. The points indicated by an asterisk refer to nematic–isotropic transitions, others are smectic–isotropic transitions.

as well as to measure their transition temperatures. The textures observed for the twenty compounds investigated allowed the assignment of the mesophases shown in the table. The clearing temperatures T_c are in good agreement with those obtained from either refractive index or DSC measurements to within $\pm 1^{\circ}$C. Figure 5 shows the dependence of T_c on the chain length of the alkoxy group, showing an approximately linear dependence over the range of chain length investigated. The calculated slopes (or in other words, the increment in T_c for each methylene group added) were found to increase according to the order **I**a < **I**b < **I**d < **I**e.

From the average values of T_c, and with the aid of the heats of transition ΔH_c, the mesophase–isotropic transition entropy ΔS_c was calculated and plotted as a function of chain length (see figure 6). The trend shows in general an increase in ΔS_c with increasing alkyl chain length. The calculated ΔS_c values are in good agreement with those of typical nematic and smectic A phases [2].

4. Conclusion

From measurements of the ordinary refractive index of some 4-substituted-phenyl 4-alkoxybenzoates (**I***n*a–e) in their mesophases, increasing the chain length has been found to decrease the transversal electronic polarizability of the molecules irrespective of the group *X*, leading to a more ordered mesophase. The clearing temperatures of the compounds, detected from refractive index measurements and using the polarizing microscope, were in good agreement with those obtained from DSC. The calculated mesophase–isotropic transition entropy ΔS_c was found to increase smoothly with increasing chain length and values were in good agreement with those previously reported for typical nematic or smectic phases. The mesophases indicated from ΔS_c values were verified using polarizing optical microscopy.

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