ELSEVIER

Thermochimica Acta 389 (2002) 49–58

thermochimica acta

www.elsevier.com/locate/tca

Effect of substituents and alkoxy-chain length on the phase behavior of 4-substituted phenyl-4-alkoxybenzoates

Refaat I. Nessim

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

Received 20 September 2001; received in revised form 23 January 2002; accepted 26 January 2002

Abstract

Four series of 4-substituted phenyl-4-alkoxybenzoates were prepared 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 (X) alternatively changed from CH_3O, CH_3, Cl, CN, and NO_2. Compounds prepared were characterized by infrared spectroscopy and their mesophase stabilities investigated by differential scanning calorimetry and polarized-light microscopy. The results were discussed in terms of mesomeric, polarity, and polarizability effects. In all four series, the mesophase–isotropic transition temperatures (T_c) were successfully related to the polarizability anisotropy of bonds to the small compact substituent, X. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Unsymmetrical di-substituted phenyl benzoates; Mesophase stability; Polarizability anisotropy

1. Introduction

Interests in liquid crystalline materials have expanded greatly in recent years because of their important role in new and emerging electro-optical techniques and their richness in physical phenomena. Liquid crystals form a state of matter intermediate between crystalline solids and true isotropic liquids. Such mesophases behave mechanically as liquids, but differ from normal liquids in that molecules in them are oriented, having lost 2 d.f. Organic compounds that form mesophases upon melting (thermotropic) are those having either linear or disk-like molecules. Linear thermotropic liquid crystals are characterized by being long, narrow, and rod-shaped molecules. Both permanent dipoles and polarizable moieties are required. The thermal stability of the mesophase formed depends, in large measures, on subtle structural, steric, and electronic effects within the central and terminal groups. Attempts to correlate the mesophase stability with molecular structures, in liquid-crystalline compounds, are based on considerations of the nature and magnitude of intermolecular forces that favor the lateral association of their rod-shaped molecules. However, recent works [1–9] has led to the conclusion that intermolecular forces due to dipole–dipole interaction are not the only factors important in determining mesophase stability. Linking units containing multiple bonds that maintain the rigidity and linearity of the molecules are satisfactory in promoting mesophase stability. The ester linkage, in the phenyl benzoate system, contains no multiple bonds in the chain of atoms linking the two benzene rings, however, conjugative interactions within the ester moiety and the rings do lead to some double bond character. Hence, the mesophase becomes more

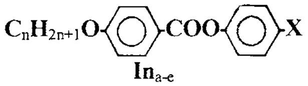
---

E-mail address: magdi@chem-sci.cairo.eun.eg (R.I. Nessim).

PII: S0040-6031(02)00057-6

persistent when the phase stability effect of the mutual conjugation between the substituent and the ester carbonyl or oxygen is increased. A decrease in the degree of conjugation will lead to a decrease in the polarizability, and consequently in the thermal stability of the mesophase, i.e. to a decrease in the mesophase–isotropic transition temperature, T_c. To realize this dependence, van der Veen [10] has deduced an equation that relates the mesophase–isotropic transition temperatures (T_c) to the polarizability anisotropy ($\Delta\alpha_X$) of bonds (C_{Ar}–X) to small compact substituents.

The 4-hexadecyloxyphenyl esters of 4-substituted benzoic acids and their corresponding isomers, 4-substituted phenyl esters of 4-hexadecyloxybenzoic acid were studied [2] to investigate the effect of substituent and inversion of the ester group on the mesophase behavior of pure components as well as their binary [3,4], ternary [8,9], and quaternary [7] mixtures. In these investigations, the alkoxy group were chosen to be $C_{16}H_{33}O$ because homologues with chain length of 16 carbons exhibit the smectic A phase as the only anisotropic phase. In the latter series of compounds, direct conjugation occurs between the hexadecyloxy oxygen and the ester carbonyl group via the intervening phenylene ring on one side of the molecule, while extreme interaction takes place between the *para*-substituent, X, and the ester oxygen on the other side, dependent on the electronic nature of the substituent. Accordingly, the 4-substituted phenyl-4-alkoxybenzoate series seemed suitable for investigating structural effects on mesophase stability, since the substituent, X, and the alkoxy-chain length can be easily modified. Thus, a number of compounds of this type was planned to be prepared and their ability to form mesophases be studied.



$\mathbf{In}_{a\text{-}e}$

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

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

These esters were chosen because in a single series the difference between its members lies in the electronic nature of the terminal substituent, X, while the difference between the corresponding homologues within the four series is the length (n) of the alkoxy group.

The purpose of the present study is to investigate, first, the effect of polarity of the terminal substituent (X) as well as the length of the alkoxy chain on the phase stability of the compound. Secondly, it is to test the applicability of the relation derived by van der Veen [10], and modified later by Naoum et al. [3,7–9], to the four investigated series of compounds. Substituents (X) were chosen to cover a wide range of electronic nature, which represent extremes in the conjugative interactions with the ester oxygen via the intervening benzene rings.

2. Experimental

Chemicals were purchased from the following companies: Aldrich, WI, USA; E. Merck, Darmstadt, Germany; and Fluka, Buchs, Switzerland.

2.1. Preparation of materials

2.1.1. 4-n-Alkoxybenzoic acids

Ethyl-4-*n*-alkoxybenzoates were first prepared from ethyl-4-hydroxy benzoate and the appropriate 1-bromo-*n*-alkane; the esters were then saponified to the corresponding acids using alcoholic potassium hydroxide, by the method described in our previous work [2]. The resulting acids were TLC pure and exhibited phase transition temperatures agreed with those reported in the literature [11].

2.1.2. 4-n-Alkoxybenzoyl chlorides

These were prepared from the acids by heating with excess thionyl chloride under reflux for 5 h. The unused thionyl chloride was removed under vacuum to give the acid chloride as residue.

2.1.3. 4-Substituted phenyl-4′-n-alkoxybenzoates

One molar equivalent of the 4-*n*-alkoxy benzoyl chloride in dry pyridine was added drop-wise to a solution of the substituted phenol in dry pyridine over a period of 1 h and the resulting mixture was heated overnight with stirring at 60 °C. The cold reaction mixture was poured over cold dilute hydrochloric acid, the solid separated filtered and column purified over silica gel using dichloro methane as the eluent, and finally crystallized from ethanol. The products have melting points that agreed with those reported in the literature [2,12–14]. The new chloro derivative (**I**14_c) was analyzed to give: Anal. Calc. (found) for $C_{27}H_{37}O_3Cl$: C 72.79 (73.12); H 8.31 (8.27); Cl 7.98 (8.13).

2.2. Physical characterization

Infrared spectra were measured (4000–400 cm^{-1}) with a Perkin-Elmer B25 spectrophotometer, and ^1H NMR-spectra with Varian EM 350 l.

Calorimetric investigations were made using Polymer Laboratories differential scanning calorimeter, PL-DSC (UK), with nitrogen as a purge gas. The instrument was calibrated from the melting points of ultra-pure metals, and a value of 28.45 J g^{-1} was used for the enthalpy of fusion of indium. Typical heating rates were 10 K min^{-1}, and sample mass was 2–3 mg. Transition temperatures were identified with a standard polarized-light microscope (C. Zeiss, Germany), attached to a FB 52 hot-stage equipped with a FB 80 central processor (Mettler, Switzerland).

Thin layer chromatography was performed with TLC-sheets coated with silica gel (E. Merck); spots were detected by UV-illumination. Silica gel (no. 6634, E. Merck) was used for column chromatography.

3. Results

Since identical infrared absorption frequencies were observed for all corresponding members in the four series (**I6**–**I16**), the absorption frequencies for

Table 1
Characteristic infrared absorption frequencies (cm^{-1}) and polarizability anisotropy ($\Delta\alpha_X$) of the C_{Ar}–X bonds (cm^3) for compounds **I**$6_{a–e}$ in KBr

Compounds	X	$\nu_{C=O}$	$\nu_{C–O}$	ν_{NO_2}	$\nu_{C\equiv N}$	$\Delta\alpha_X$ ($\times 10^{24}$)
I6_a	CH_3O	1728	1247	–	–	3.86
I6_b	CH_3	1725	1260	–	–	2.12
I6_c	Cl	1728	1247	–	–	3.11
I6_d	CN	1742	1248	–	2224	5.12
I6_e	NO_2	1740	1247	1510	–	4.58

Table 2
Transition temperatures (°C) for compounds 4-$C_nH_{2n+1}O$–C_6H_4–COO–C_6H_4–X-4

Compounds	n	X	$T_{C–A}$	$T_{C–N}$	$T_{C–I}$	$T_{A–N}$	$T_{A–I}$	$T_{N–I}$
I6_a	6	CH_3O	–	–	95.0	–	–	(71.2)
I6_b	6	CH_3	–	–	66.7	–	–	(50.0)
I6_c	6	Cl	–	–	89.9	–	–	(53.0)
I6_d	6	CN	72.0	–	–	–	–	82.2
I6_e	6	NO_2	–	–	68.0	–	–	(58.5)
I8_a	8	CH_3O	–	–	85.0	–	–	(76.2)
I8_b	8	CH_3	–	–	61.8	–	–	(55.2)
I8_c	8	Cl	–	–	79.4	–	(65.0)	–
I8_d	8	CN	–	78.0	–	–	–	84.1
I8_e	8	NO_2	53.1	–	–	62.6	–	69.2
I14_a	14	CH_3O	–	–	96.3	–	(75.0)	–
I14_b	14	CH_3	–	–	71.1	–	(53.0)	–
I14_c	14	Cl	–	–	79.8	–	(71.0)	–
I14_d	14	CN	78.0	–	–	–	94.8	–
I14_e	14	NO_2	74.6	–	–	–	87.9	–
I16_a	16	CH_3O	–	–	96.1	–	(80.0)	–
I16_b	16	CH_3	–	–	77.7	–	(54.5)	–
I16_c	16	Cl	–	–	84.7	–	(71.0)	–
I16_d	16	CN	85.9	–	–	–	96.9	–
I16_e	16	NO_2	79.4	–	–	–	88.7	–

compounds of series **I**6, with their assignments, were given as representative examples in Table 1.

Transition temperatures, as measured by DSC and identified by polarized-light microscopy, for all compounds investigated are summarized in Table 2. In the table the subscripts (C, A, N, and I) given to specify transition temperatures, denote the solid, smectic A, nematic, and isotropic, respectively.

Infrared spectra and elemental analyses for compounds investigated were consistent with the structures assigned. NMR data showed expected integrated aliphatic to aromatic proton ratios.

4. Discussion

4.1. Infrared absorption spectra

The identical infrared spectra observed for similarly substituted members in the four series of compounds revealed that the mesomeric shift of the ester carbonyl group attached to the alkoxy group is not significantly affected by the length of the alkoxy chain. Further, it can be noted from Table 1 that compounds bearing the nitro or cyano substituents have their ester carbonyls that absorb at $\approx$1740 cm^{-1}. This may be attributed to the mesomeric interactions affected by the two terminal groups on both ends of the molecule, that is between the alkoxy oxygen and the ester carbonyl, at one side, and between the cyano (or nitro) group and the ester oxygen, on the other side. Thus, while the conjugative interactions in the former increase the single bond character of the C=O, hence lower its force constant and consequently, its absorption frequency, the latter raise the C=O stretching frequency and a value of $\approx$1740 cm^{-1} is observed. Conversely, in derivatives bearing the electron releasing ($-$E) substituents, opposite interactions on both sides of the molecule would result in compounds that absorb at lower frequency ($\approx$1725 cm^{-1}) as is observed.

4.2. DSC analyses

In order to look at the effect of terminal substituents and alkoxy-chain length on the liquid crystalline properties of compounds of type **I**, the number of carbons in the terminal alkoxy group, has kept subsequently at 6, 8, 14, or 16 carbons, while the substituent X was alternatively varied between the CH_3O, CH_3, Cl, CN, and NO_2 groups. Table 2 compares the transition temperatures of these four groups of compounds from which it can be seen that the mesogenic group polarizability, which differs according to the electronic nature of the substituent as well as the length of the alkoxy chain, have led to a significant variation in the mesophase behavior of the individual components. Generally, for a given substituent X in the substituted phenyl 4-alkoxybenzoate homologous series, the methoxy and ethoxy analogues have extensive aromatic-aromatic interactions in their solid crystals, which are responsible for their high melting points (T_m). In the butoxy compound, the alkyl residue is of such a length that the weaker aromatic–aliphatic interactions occur, as a steric necessity in the crystal, and the melting point is reduced. If the melting of the crystals occurs at a lower temperature than does the breakdown of molecular association in the liquid phase, there will be sufficient molecular anisotropy and mobility to cause the formation of a nematic phase. There is a progressive decline in the melting points (T_m) for the first eight homologues and this is taken to indicate that a similar end-to-end packing of the molecules occurs in all cases, while aliphatic-aromatic interactions becoming steadily more dominant. Beyond this point there is an abrupt change to a new type of crystal structure where it was assumed that aliphatic-aliphatic interactions would be predominant and an increase in melting point takes place. This can be shown from Table 2 where the melting point (T_m) of the compound decreases from C_6 to C_8 and then rises again to C_{16}. For example, the melting point of the methyl substituted homologues, $\mathbf{I}_b$, decreases from 66.7 °C in $\mathbf{I}6_b$ to 61.8 °C in $\mathbf{I}8_b$ and then increases again to 71.1 and 77.7 °C in $\mathbf{I}14_b$ and $\mathbf{I}16_b$, respectively. Similar trends were observed in other homologous series.

On the other hand, the stability of the liquid crystalline phase should be greater, the stronger the anisotropic forces between molecules. Strong anisotropic forces should be reflected in a high mesophase–isotropic transition temperature (T_c). In a homologous series, as the alkoxy chain in a compound is lengthened, the stability of the mesophase should be affected in at least four different ways [15]. First, the alkoxy group will act as a diluent increasing the mean separation between molecules, which reduces the anisotropy of the intermolecular forces, and so make the mesophase less stable. Secondly, the increase in the size of the terminal alkoxy group will like-wise reduce the attractions between these groups. Thirdly, the increase in the length of the molecule will lead to an increase in its geometrical anisotropy. Fourthly, the overall polarizability of the molecule should increase with increasing molecular size. The first two factors would lead to a decrease in the mesophase stability, i.e. T_c, with increasing size of the alkoxy group, and the latter two to an increase. In our case, the last two factors seem to be relatively more pronounced; this explains why, irrespective of the substituent present and within our range of chain length, the mesophase–isotropic transition temperatures (T_c) increase with increasing the alkoxy-chain length. For example, the smectic A–isotropic liquid transition temperature of the cyano-substituted homologues, $\mathbf{I}_d$, increases from 82.2 °C in $\mathbf{I}6_d$ to 96.9 °C in $\mathbf{I}16_d$. That is, the stability of the mesophase is greater, the greater the lateral adhesion of the rod-shaped molecules in question. In a homologous series, irrespective of the substituent X, the small alkoxy group (methyl or ethyl) furnishes poor insulation against strong terminal attractions that preclude a smectic phase. As the size of the alkoxy group increases, terminal attractions decrease while lateral intermolecular attraction is added and a smectic phase appears; this increasing lateral attraction restricts the movement of the molecules from one layer to another thus favoring a smectic structure [15].

Now we extend our studies to analogous compounds in which the terminal alkoxy group is held, at a time, at 6, 8, 14, or 16 carbons, while the other terminal polar substituent varies between the electron donating methoxy and methyl groups, through the chloro, and finally the electron withdrawing cyano and nitro groups. The last two analogues in the four series, i.e. the cyano and nitro substituted homologues, form their mesophases enantiotropically, while the other three show their mesophases monotropically. A monotropic transition simply means that the mesophase is not stable above the melting point of the compound and, therefore, observed only if the phase can be super-cooled sufficiently. This phenomenon is observed for compounds having either high crystal stability, i.e. of high T_m, e.g. $\mathbf{I}6_a$ and $\mathbf{I}8_a$, or low mesophase stability, i.e. of low T_c, e.g. $\mathbf{I}6_b$ and $\mathbf{I}8_b$. In such cases, the virtual mesophase–isotropic transition temperatures (on heating) were determined by extrapolation [16] from their binary phase diagrams with the corresponding enantiotrope. The extrapolated values were included (in parentheses) in Table 2.

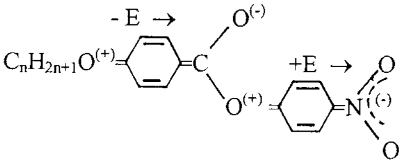
If one considers the crystal–mesophase transition temperatures (T_m) as a direct measure of the net attractive forces acting among the molecules in the crystals immediately below the melting point, the following stability order is found in almost all the four series irrespective of the length of the alkoxy group.

$CH_3O > Cl > CN > NO_2 > CH_3$

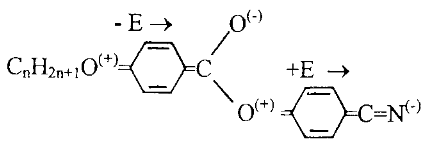
This order suggests a picture of the crystal–mesophase transition in which there are two opposing factors at work. One factor seems to be intermolecular attractions caused by substantial polarity order and/or the presence of lone pairs of electrons on the substituent; these lone pairs may interact with electron deficient parts of adjacent molecules. The other factor appears to be the destabilizing effect of the dipole–dipole or lone-pair repulsions of neighboring molecules.

Since the mesophase stability of a liquid crystalline compound is mainly dependent upon the intermolecular attractions, in which molecular polarity plays a significant role, it has been shown [2] that, in a series of compounds, the dipole moment of any compound is dependent upon the nature of the substituent. A change in the extent of conjugation alters the polarizability and the resultant dipole moment of the molecule. It has also been shown [6] that the dipole moments of all members of a homologous series are virtually the same irrespective of the alkoxy-chain length. This result is in accordance with the fact that the alkoxy groups are of the same polarity regardless of the length and, at the same time, do not affect the extent of conjugative interactions between the alkoxy oxygen and the ester carbonyl group through the intervening phenylene group, as is observed from infrared measurements.

With regard to the nitro derivative, its apparent dipole moment ($\mu \approx 5.73$ D) is found [2,6] to be close to that of its cyano analogue ($\mu \approx 5.84$ D). This is expected since the two groups are of comparable electronic characteristics and the same conjugative interactions (+E) between the cyano (or nitro) group and the ester oxygen atom, on one side of the molecule, which is augmented by that occurring between the alkoxy oxygen and the ester carbonyl (−E), on the other side of the molecule, has led to these high dipole moment values.



I_e, $\mu \approx 5.73$ D

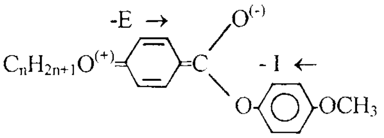


I_d, $\mu \approx 5.84$ D

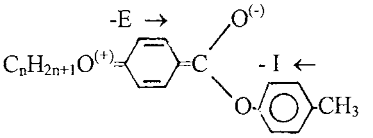
In view of the highly polar cyano or nitro groups, one might expect that the dipole–dipole interactions would favor liquid crystallinity; this is found to be true since most of these derivatives are enantiotropic. Conversely, it might be noted that although the dipole moments of these derivatives are greater than those of the corresponding methoxy analogues ($\mu \approx 2.69$ D), their melting points (T_m) are lower. This is explicable in terms of repulsive forces. This again indicates that the dipole moment is not the only factor that determines the stability of the liquid crystalline phase. In the case of the lower cyano (**I6**$_d$) and nitro (**I6**$_e$) homologues, repulsive contribution predominates and thereby lowers their T_m and T_c values. As the alkoxy-chain length increases, which acts as diluent, lateral attraction between molecules increases while repulsive forces decrease resulting in a decrease in both T_m and T_c, as is observed in Table 2.

It might be further noticed that the crystalline or mesophases of the nitro compounds are less stable, in both, than the corresponding cyano derivatives. Such a behavior is ascribed to the difference in the steric effects between the nitro and cyano groups. The large terminal nitro group forces the long axes of the molecules apart thereby weakening intermolecular bonding, therefore lessening the molecular order of the mesophase. In addition, the electron lone pairs on the two oxygen atoms of the nitro group are also considered; a less stable phase is favored in which the nitro groups force neighboring molecules further apart due to repulsive electron pair interactions. The intermolecular bonding loss is greater than loss of positional order, which leads to an enhanced dipole–dipole and/or lone-pair repulsion than that in the case of the cyano analogue, resulting in a decrease in both T_m and T_c. Such a behavior is more pronounced in the lower homologues.

In the case of the methoxy (**I**$_a$, $\mu \approx 2.69$ D), and methyl (**I**$_b$, $\mu \approx 2.79$ D) analogues, the situation is quite different; there are opposing inductive and conjugative effects of the two terminal groups, on both sides of the molecules, consequently, there will be no reinforcement of the dipolar character of the compound. The mesomeric interaction affected by the alkoxy group on one side of the molecule is partially counteracted by the opposing inductive effect of the other substituent (methoxy or methyl group) on the other side of the molecule, resulting in a molecule of low dipole moment value.



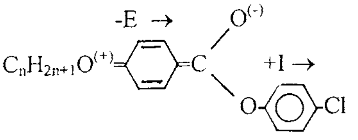
I_a, $\mu \approx 2.69$ D



I_b, $\mu \approx 2.79$ D

The effect of the methoxy group in **I**$_a$ seems explicable [17] in terms of a shielding effect on the lone pairs by the methyl group. The repulsive forces involving oxygen lone pairs are thereby substantially reduced and consequently a decrease in the repulsive forces allows a close approach of neighboring molecules, thus increasing bonding forces. Such strong forces are associated with high melting point in such a way that no mesophase is detected on heating.

As for the chloro derivatives, two augmenting effects, but of different nature, occur on both sides of the molecule. On one side, there is a conjugative interaction between the alkoxy lone pair and the ester carbonyl, while on the other side of the molecule, the inductive effect (+I) of the chlorine atom increases the total polarity of the molecule that gives a dipole moment value ($\mu \approx 3.87$ D) intermediate between the methoxy and methyl (−I) analogues, from one hand, and the nitro and cyano (+E) derivatives, on the other hand. Such relatively high dipole moment would lead to increased dipole–dipole interactions resulting in high melting points.



I$_d$, $\mu \approx 3.87$ D

It can also be noted from Table 2 that the mesophase–isotropic transition temperature for homologues, with a given substituent, increases with increasing alkoxy group length suggesting that lateral adhesion becomes dominant over polarity variation in the centers of the molecules [2]. This reflects the increasing thermal stability of the mesophase with decreasing molecular rigidity (increasing *n*-alkane character).

In terms of transition temperatures, T_c, chlorine substituted compounds always have higher values than the analogous methyl terminated compounds. This may be taken as evidence that strong dipole acting out of the molecule is advantageous in promoting terminal associations. However, the low enthalpy change of the nitro and cyano compounds in the first two series (**I**6 and **I**8) is in opposition of the idea of strong attractions due to terminal dipoles. The entropies seem to roughly parallel the enthalpies of the mesophase–isotropic transitions implying that the ordering of the molecules in the mesophase is intimately related to the strength of the intermolecular association.

Table 3 gives the clearing points, T_c, on cooling, of the compounds investigated along with the enthalpy, ΔH_c, and entropy, ΔS_c, for this transition. It is readily seen from Table 3 that the enthalpies of transition do not correlate well with either the polarity of the substituent or with T_c. The most probable explanation may be found in that in the liquid crystal phases repulsive forces are operative in determining mesophase properties. Thus, the very low ΔH_c for the nitro compound **I**6$_e$ can be seen [18] as arising from the repulsion between the nitro groups themselves and with other strongly negative ends of dipoles. In the case of the cyano (**I**6$_d$), and nitro (**I**6$_e$) compounds, repulsive contribution dominates and thereby lowers both ΔH_c and ΔS_c. As the chain length of the alkoxy group is increased in series **I**6–**I**16, the repulsive forces are gradually reduced by the shielding effect of the long chain alkyl group. The lack of strong repulsive forces could simply allow a close approach of the neighboring molecules, thus increasing attractive forces and consequently ΔH_c and ΔS_c values.

Table 3
Thermodynamic properties for investigated compounds, on cooling

Compounds	X	T_c (°C)	ΔH_c (kJ mol^{-1})	ΔS_c (J mol^{-1})
I6$_a$	CH_3O	74.9	0.52	1.49
I6$_b$	CH_3	48.0	–	–
I6$_c$	Cl	55.0	–	–
I6$_d$	CN	80.5	0.38	1.07
I6$_e$	NO_2	56.1	0.19	0.58
I8$_a$	CH_3O	76.8	0.61	1.74
I8$_b$	CH_3	55.4	0.94	2.86
I8$_c$	Cl	75.9	3.62	10.37
I8$_d$	CN	82.6	0.79	2.22
I8$_e$	NO_2	67.7	0.37	1.08
I14$_a$	CH_3O	72.0	–	–
I14$_b$	CH_3	61.4	1.24	3.71
I14$_c$	Cl	76.8	3.85	11.00
I14$_d$	CN	93.7	3.42	9.32
I14$_e$	NO_2	86.3	2.84	7.90
I16$_a$	CH_3O	75.0	2.10	6.03
I16$_b$	CH_3	61.6	4.01	11.98
I16$_c$	Cl	73.4	4.90	14.14
I16$_d$	CN	95.2	4.63	12.57
I16$_e$	NO_2	87.0	3.70	10.27

4.3. *Clearing temperatures and polarizability anisotropy of C_{Ar}–X bonds*

The relationship between the stability of the mesophase in a liquid crystalline compound was studied by van der Veen [10], which is expressed as the clearing temperature, T_c, and the anisotropy of polarizability ($\Delta\alpha_X$) of bonds to small compact terminal substituent (C_{Ar}–X). The relation had the following form:

$$T_c \propto (\Delta\alpha_M^2 + 2\Delta\alpha_M\Delta\alpha_X + \Delta\alpha_X^2) \qquad (1)$$

where T_c is measured in Kelvin. The term $\Delta\alpha_M$ is the anisotropy of polarizability for all the molecular structure except the terminal substituent, X. Eq. (1) can be put in the following form:

$$\sqrt{T_c} \propto (\Delta\alpha_M + \Delta\alpha_X) = a\,\Delta\alpha_M + a\,\Delta\alpha_X \qquad (2)$$

where "a" is the proportionality constant. The polarizability anisotropy, $\Delta\alpha_X$, of the various C_{Ar}–X bonds was calculated using the data of LeFevre and coworkers [19–21] and the values are included in Table 1. Thus, if $\sqrt{T_c}$ is plotted against $\Delta\alpha_X$ for any series of liquid crystalline compounds, a straight line is expected, the slope of which equals "a" and intercept equals "$a\Delta\alpha_M$". Consequently, the anisotropy of polarizability, $\Delta\alpha_M$, for all the molecular structure except the terminal substituent, X, is given by:

$$\Delta\alpha_M = \frac{\text{intercept}}{\text{slope}}$$

In this manner, $\Delta\alpha_M$ can be evaluated for the four series to investigate the effect of alkoxy-chain length on the anisotropy of polarizability of the group containing it. The $\sqrt{T_c}$ values were plotted as a function of $\Delta\alpha_X$ and the plots were depicted in Fig. 1.

As shown in Fig. 1, linear plots were obtained; the slopes and intercepts were calculated for each regression line by the method of least squares, from which $\Delta\alpha_M$ could be calculated for the four series of compounds. The results of computation are given in Table 4. It can also be seen from Fig. 1 that the nitro derivatives in the first two series (**I6**$_e$ and **I8**$_e$) have lower T_c values than those expected from the linear plot. This is again in accordance with the enhanced repulsive forces due to the bulkiness of the nitro group; its effect decreases as the alkoxy-chain length increases in the higher two series (**I14**$_e$ and **I16**$_e$). The calculated $\Delta\alpha_M$ values were again plotted, in Fig. 2, as a function of the number of carbons in the alkoxy-chain length. Fig. 2 reveals that the anisotropy of polarizability of the molecule, $\Delta\alpha_M$, except for the polar substituent, X, increases linearly as the alkoxy chain is lengthened. This again reflects the increased lateral aliphatic–aliphatic adhesion of the rod-shaped molecules, which is added to the dipole–dipole interactions, as a result of increasing the n-alkane character.

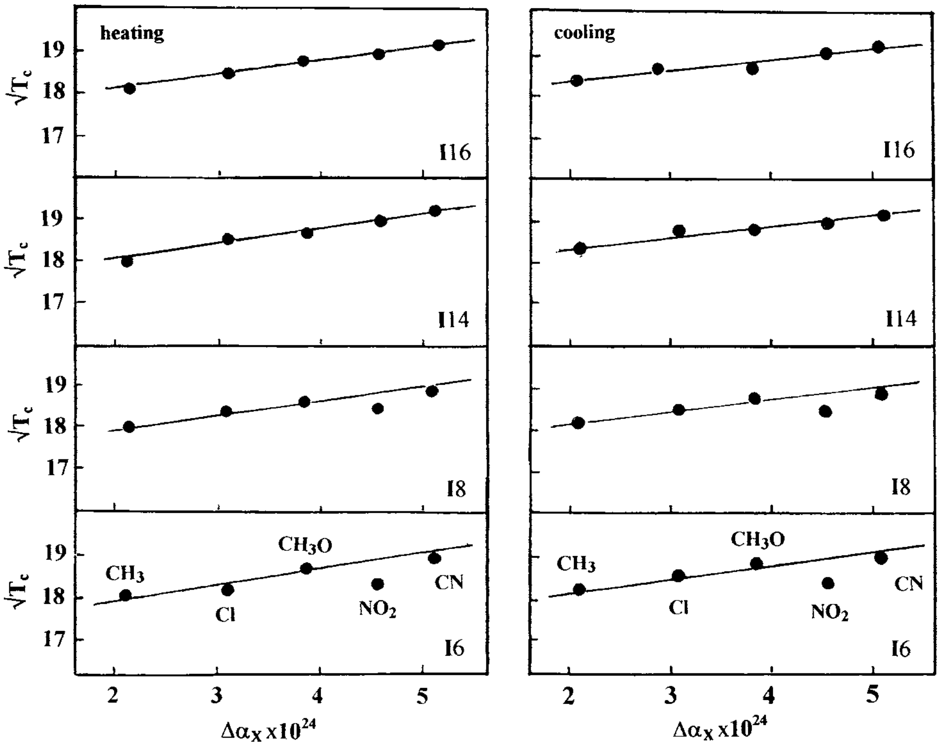


Fig. 1. Dependence of $\sqrt{T_c}$ on the anisotropy of polarizability ($\Delta\alpha_X$) for series I6, I8, I14 and I16.

Table 4
Slopes and intercepts of regression lines as well as the $\Delta\alpha_M$ on heating and on cooling for the four series investigated

Series	n	Condition	Slope ($\times 10^{-23}$)	Intercept	$\Delta\alpha_M$ ($\times 10^{23}$)
I6	6	Heating	4.23	17.01	4.02
		Cooling	3.26	17.30	5.30
I8	8	Heating	3.89	17.20	4.42
		Cooling	3.18	17.51	5.51
I14	14	Heating	3.48	17.41	5.01
		Cooling	2.94	17.71	6.05
I16	16	Heating	3.35	17.50	5.22
		Cooling	2.84	17.75	6.25

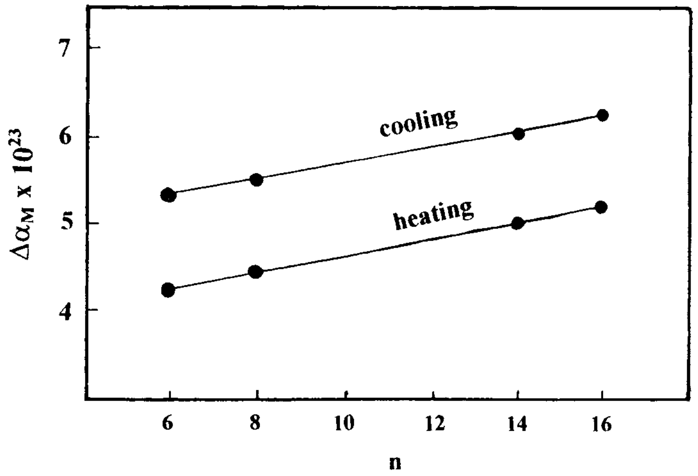


Fig. 2. Dependence of the anisotropy of polarizability ($\Delta\alpha_M$) on the number of carbon atoms (n) in the alkoxy group.

5. Conclusion

The 4-substituted phenyl-4′-alkoxy benzoates were prepared and thermally characterized for their phase transition temperatures. Two types of substituents were used, viz. an alkoxy group of varying chain length and a small compact polar group, X. The conjugation between the alkoxy and the ester carbonyl groups, on one side of the molecule, increases the polarity of the carbonyl oxygen and so stabilizes the mesophase. On the other side of the molecule, the varying electronic nature of the substituent X resulted in extremes in the electronic interactions between the substituent and the ester oxygen atom. Such differences would lead to a significant variation in the mesophase behavior of the compound. The infrared spectra were consistent with these inferences. In the nitro and cyano analogues, the polarity of the molecule is augmented by the conjugative effect of the substituent, which helps to stabilize both the solid and mesophases. Conversely, the opposing effects on both sides of a molecule of the methyl and methoxy derivatives resulted in compounds that showed their mesophases monotropically.

Furthermore, the identical infrared spectra and dipole moments, observed for similarly substituted homologues, indicate that the length of the attached alkoxy chain does not affect the polarization of the ester carbonyl group, while extension of the terminal n-alkoxy chain gave rise to an increase in the mesophase–isotropic transition temperatures suggesting that its effect becomes dominant over polarity variation.

Finally, It was found that $\sqrt{T_c}$ is linearly related to the polarizability anisotropy, of the C_{Ar}–X for all series investigated.

References

[1] M.M. Naoum, G.W. Hoehne, H. Seliger, E. Happ, Liquid Cryst. 23 (1997) 653.

[2] M.M. Naoum, G.R. Saad, R.I. Nessim, T.A. Abdel Aziz, H. Seliger, Liquid Cryst. 23 (1997) 789.

[3] M.M. Naoum, R.I. Nessim, G.R. Saad, T.A. Abdel Aziz, Liquid Cryst. 25 (1998) 73.

[4] M.M. Naoum, G.R. Saad, R.I. Nessim, T.A. Abdel Aziz, Liquid Cryst. 25 (1998) 165.

[5] M.M. Naoum, R.I. Nessim, G.R. Saad, Liquid Cryst. 25 (1998) 655.

[6] G.R. Saad, R.I. Nessim, Liquid Cryst. 26 (1999) 629.

[7] M.M. Naoum, A.A. Mansour, A.A. Bayoumy, Liquid Cryst. 27 (2000) 177.

[8] M.M. Naoum, A.A. Mansour, A.A. Bayoumy, Liquid Cryst. 27 (2000) 243.

[9] M.M. Naoum, R.I. Nessim, T.Y. Labeeb, Liquid Cryst. 27 (2000) 889.

[10] J. van der Veen, J. Physique, Colloque C1 36 (1975) 375.

[11] G.W. Gray, B. Jones, J. Chem. Soc. (1953) 4179.

[12] A.C. Griffin, R.F. Fisher, S.J. Havens, J. Am. Chem. Soc. 100 (1978) 6329.

[13] A. Goeblwunsch, G. Hepke, R. Hopf, Z. Naturforsch. 36a (1981) 213.

[14] M.M. Naoum, E. Happ, H. Seliger, Liquid Cryst. 23 (1997) 247.

[15] G.W. Gray, Mol. Cryst. Liquid Cryst. 1 (1966) 33.

[16] A. Bogavlenski, N.Z. Winogradow, Z. Phys. Chem. 64 (1908) 228.

[17] G.W. Gray, Mol. Cryst. Liquid Cryst. 7 (1969) 127.

[18] M.J.S. Dewar, A.C. Griffin, J. Chem. Soc., Perkin II (1976) 713.

[19] R.J.W. LeFevre, B.P. Rao, J. Chem. Soc. B (1958) 1465.

[20] M.J. Aroney, K.J.E. Kalderbank, R.J.W. LeFevre, R.K. Pierens, J. Chem. Soc. B (1969) 159.

[21] M.J. Aroney, R.J.W. LeFevre, M.G.M. Pierens, J. Chem. Soc. B (1969) 666.