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Effect of molecular structure on the phase behavior of some liquid crystalline compounds and their mixtures

X. Unsymmetrical 1,4-phenylene-bis-(4-substituted benzoates)☆

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Abstract

Four series of unsymmetrical 1,4-phenylene-bis-(4-substituted benzoates) were prepared in which one substituent is a terminal alkoxy group with a number of carbon atoms kept constant (at $n = 6$, 8, 14, and 16) while the other substituent (X) alternatively changed from CH_3O, CH_3, Cl, NO_2, CN, and $C_nH_{2n+1}O$. Compounds prepared were characterized by infrared spectroscopy and their mesophase stabilities investigated by differential scanning calorimeter (DSC) and polarized-light microscope. The results were discussed in terms of mesomeric and polarizability effects. In all the four series, the mesophase–isotropic transition temperatures (T_c) were successfully related to the polarizability anisotropy of bonds to the small compact substituent, X.

Keywords: Dibenzoates; Mesophase stability; Polarizability anisotropy

1. Introduction

Trends in the mesophase–isotropic liquid transition temperatures of liquid crystalline compounds were rationalized in terms of molecular structure even for subtle differences as in homologous series. Two types of terminal substituents may be distinguished: the homologous series and the small compact type. Generally, the stability of a mesophase should be greater, the greater the lateral adhesion of the rod-shaped molecules, which in turn, would be augmented by the increase of polarity or polarizability of the central part of the molecule. Of course, the terminal substituents can affect the polarizability of the aromatic rings to which they are attached, in addition, they may interact with the lateral portion of an adjacent molecule. As the polarity of the group decreases, the clearing point (T_c) seems to be lowered also. This is attributed [2] to increased intermolecular attractions as the polarity and polarizability of the substituent are increased.

van der Veen [3] 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 goal of the present study is to prepare series of model compounds, **I**, where R is an alkoxy group with carbon atoms varying between 6, 8, 14, and 16, and X = CH_3O, CH_3, Cl, NO_2, CN, and $C_nH_{2n+1}O$, in an attempt to investigate, first, the effect of polarity of

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☆ Part IX, see [1].

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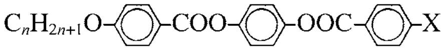
terminal substituent as well as the length of the alkoxy chain on the stability of the liquid crystalline phase. Secondly, it is to test the applicability of the relation derived by van der Veen [3], and modified later by Naoum et al. [4], to the four investigated series of compounds. Substituents, X, were chosen to cover a wide range of electronic nature, which represent extremes in the conjugative interactions with the ester C=O group via the intervening benzene rings.



I$_{a\text{-}f}$

I6, $n = 6$; **I**8, $n = 8$; **I**14, $n = 14$; **I**16, $n = 16$

a, X = CH_3O; b, X = CH_3; c, X = Cl; d = NO_2; e, X = CN; f, X = $C_nH_{2n+1}O$

2. Experimental

Chemicals were purchased from the following companies: Aldrich, WI, USA; 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-hydroxybenzoate and the appropriate 1-bromo-*n*-alkane, and the esters were then saponified to the corresponding acids using alcoholic potassium hydroxide, by the method described in our previous work [5]. The resulting acids were TLC pure and exhibited phase transition temperatures in agreement with those reported in [6].

2.1.2. 4-n-Alkoxy benzoyl 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-Hydroxyphenyl-4′-n-alkoxybenzoates

One molar equivalent of the 4-*n*-alkoxy benzoyl chloride in dry pyridine was added dropwise to a solution of hydroquinone in dry pyridine over a period of 1 h, and the resulting mixture was heated overnight with stirring at 60 °C. The products were fractionally crystallized from ethanol to separate the mono (more soluble) from the diesters (**I**$_f$, less soluble). Both products were column purified over silica gel using

Table 1

Yield and elemental analyses of newly prepared compounds 4-$C_nH_{2n+1}O{-}C_6H_4{-}COO{-}C_6H_4{-}OOC{-}C_6H_4{-}X$-4

Compound	n	X	Yield (%)	Analyses calculated (found)			
				C	H	N	Cl
I6$_b$	6	CH_3	68	74.98 (74.75)	6.52 (6.45)	–	–
I6$_c$	6	Cl	64	68.95 (68.94)	5.56 (5.36)	–	–
I14$_a$	14	CH_3O	65	74.94 (74.72)	7.91 (7.68)	–	–
I14$_b$	14	CH_3	70	77.17 (76.93)	8.14 (8.32)	–	–
I14$_c$	14	Cl	69	72.26 (72.45)	7.31 (7.12)	–	6.27 (6.45)
I14$_d$	14	NO_2	72	70.94 (70.85)	7.18 (7.03)	2.43 (2.54)	–
I14$_e$	14	CN	71	75.65 (75.61)	7.44 (7.35)	2.52 (2.60)	–
I14$_f$	14	$C_{14}H_{29}O$	33	77.59 (77.68)	9.50 (9.43)	–	–
I16$_a$	16	CH_3O	65	75.48 (75.29)	8.21 (8.41)	–	–
I16$_b$	16	CH_3	67	77.59 (77.90)	8.44 (8.56)	–	–
I16$_c$	16	Cl	66	73.02 (73.42)	7.66 (7.98)	–	6.27 (6.43)
I16$_d$	16	NO_2	70	71.62 (71.81)	7.51 (7.69)	2.32 (2.12)	–
I16$_e$	16	CN	71	76.13 (76.04)	7.76 (7.54)	2.40 (2.34)	–

Table 2
Characteristic infrared absorption bands (cm^{-1}) for compounds **I6**$_{a\text{–}f}$ in KBr

Compound	X	$\nu_{C=O}$[a]	$\nu_{C=O}$[b]	$\nu_{C–O}$[a]	$\nu_{C–O}$[b]	ν_{NO_2}	$\nu_{C\equiv N}$
I6$_a$	CH_3O	1729.9	–	1254.4	1164.8	–	–
I6$_b$	CH_3	1731.2	–	1268.0	1166.4	–	–
I6$_c$	Cl	1729.3	–	1254.0	1191.2	–	–
I6$_d$	NO_2	1736.0	1719.5	1261.5	1192.9	1527.2	–
I6$_e$	CN	1736.8	1721.5	1254.5	1192.8	–	2228.7
I6$_f$	$C_6H_{13}O$	1731.5	–	1257.1	1163.2	–	–

[a] For ester group attached to ring bearing the substituent X.

[b] For ester groups attached to ring bearing the alkoxy group.

dichloro methane as the eluent, and finally crystallized from ethanol. The products have melting points in agreement with those reported in [5,7].

2.1.4. *1,4-Phenylene-bis-(4-substituted benzoates)*

One molar equivalent of the 4-substituted benzoyl chloride in dry pyridine was added dropwise with stirring to a solution of 4-hydroxyphenyl-4′-*n*-alkoxy benzoate in dry pyridine, and the reaction was continued as described in the previous section. The products, after being crystallized twice from acetic acid, were TLC pure, and the elemental analyses of new derivatives are given in Table 1. The new symmetrical diester, viz. 1,4-bis-4-tetradecyloxybenzoate, **I14**$_f$, prepared as by-products in the previous section, was included in the same table.

Table 3
Transition temperatures[a] (°C) for compounds 4-$C_nH_{2n+1}O–C_6H_4–COO–C_6H_4–OOC–C_6H_4–X$-4

Compound	*n*	X	$T_{C–A}$[b]	$T_{C–N}$	$T_{A–N}$	$T_{A–I}$	$T_{N–I}$	Reference
I6$_a$	6	CH_3O	–	129.9	–	–	244.6	[7]
I6$_b$	6	CH_3	–	119.9	–	–	218.9	–
I6$_c$	6	Cl	–	165.4	–	–	231.7	–
I6$_d$	6	NO_2	165.4	–	219.0	–	256.7	[8]
I6$_e$	6	CN	146.7	–	161.1	–	268.6	[9]
I6$_f$	6	$C_6H_{13}O$	–	127.3	–	–	212.7	[10–12]
I8$_a$	8	CH_3O	–	126.3	–	–	227.7	[7]
I8$_b$	8	CH_3	–	107.2	–	–	203.3	[13]
I8$_c$	8	Cl	–	165.2	–	–	218.0	[13]
I8$_d$	8	NO_2	168.2	–	241.0	–	246.7	[13]
I8$_e$	8	CN	145.2	–	193.0	–	253.9	[9]
I8$_f$	8	$C_8H_{17}O$	121.5*	–	125.4	–	195.0	[12]
I14$_a$	14	CH_3O	–	125.6	–	–	193.2	–
I14$_b$	14	CH_3	–	105.0	–	–	172.5	–
I14$_c$	14	Cl	157.4	–	180.9	–	190.2	–
I14$_d$	14	NO_2	160.0	–	–	235.1	–	–
I14$_e$	14	CN	138.6	–	–	230.2	–	–
I14$_f$	14	$C_{14}H_{29}O$	108.6*	–	–	162.8	–	–
I16$_a$	16	CH_3O	–	115.5	–	–	178.1	–
I16$_b$	16	CH_3	–	109.1	–	–	166.5	–
I16$_c$	16	Cl	157.2	–	182.1	–	184.6	–
I16$_d$	16	NO_2	159.4	–	–	222.2	–	–
I16$_e$	16	CN	136.5	–	–	229.7	–	–
I16$_f$	16	$C_{16}H_{33}O$	108.2*	–	–	156.5	–	[5]

[a] $T_{C–A}$: crystal–smectic A; $T_{C–N}$: crystal–nematic; $T_{A–N}$: smectic A–nematic; $T_{A–I}$: smectic A–isotropic; $T_{N–I}$: nematic–isotropic.

[b] The asterisk (∗) symbol denotes the formation of smectic C instead of smectic A.

2.2. Physical characterization

Infrared spectra were measured with a Perkin-Elmer B25 spectrophotometer, ^{1}H NMR spectra with Varian EM 350 L.

Calorimetric investigations were made using Polymer Laboratories (UK) differential scanning calorimeter (PL-DSC) 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 the sample mass was 2–3 mg. Transition temperatures were identified with a standard polarized-light microscope (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 (Merck); spots were detected by UV irradiation. Silica gel (No. 6634, Merck) was used for column chromatography.

3. Results

Since identical infrared absorption spectra were observed for all corresponding members in the four series, the absorption bands for compounds of series **I**6, with their assignments, are given as representative examples in Table 2.

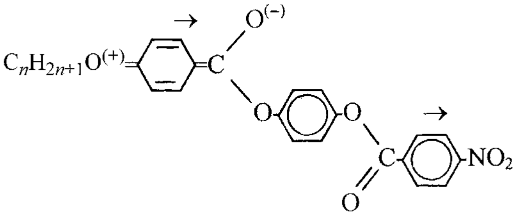
Transition temperatures, as measured by DSC and identified by polarized-light microscopy, for all compounds investigated are summarized in Table 3.

Infrared spectra and elemental analyses for compounds investigated were consistent with the structures assigned. ^{1}H NMR data showed the expected integrated aliphatic to aromatic proton ratios in all compounds investigated.

4. Discussion

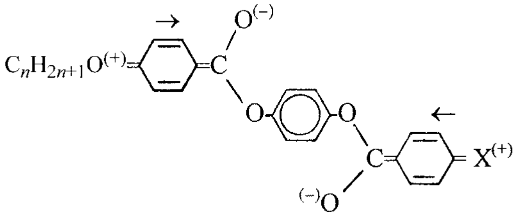
4.1. Infrared absorption spectra

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 2 that compounds bearing the nitro or cyano substituents have their two ester C=O groups that absorb at two separate frequencies, while those of the remaining derivatives both absorb at one and the same frequency, that is intermediate between the two frequencies in the former case. This may be attributed, in the case of the nitro and cyano derivatives, to extremes in the mesomeric interactions affected by the two terminal substituents of the molecule, that is between the nitro (or cyano) substituent and its attached ester carbonyl at one side, and between the alkoxy group and the second ester carbonyl at the other side of the molecule.



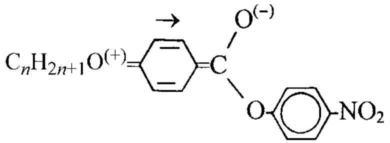
Thus, the electron-withdrawing (NO_2 or CN) group raises the C=O stretching absorption ($v = 1736$ cm^{-1}), while the conjugative interaction between the lone pair of the alkoxy oxygen and the other ester carbonyl group increases the single bond character of the C=O bond, hence, lowers its force constant and, consequently, its absorption ($v = 1720$ cm^{-1}).

In contrast, in derivatives bearing electron-releasing (−E) substituents, opposite conjugative interactions on both sides of the molecule would result in compounds that absorb at one intermediate band ($v = 1730$ cm^{-1}) as is observed from Table 2.

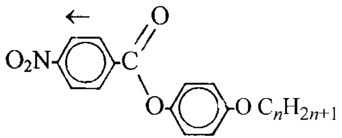


Similar conclusions were arrived at [14] for the two isomeric derivatives, 4-nitrophenyl-4′-hexadecyloxybenzoate and 4-hexadecyloxyphenyl-4′-substituted benzoate, where the carbonyl absorptions occur at

1742 and 1722 cm^{-1}, respectively.



$\tilde{\nu} = 1722\ cm^{-1}$



$\tilde{\nu} = 1742\ cm^{-1}$

That is, mesomerism in the first compound leads to lower absorption frequency, while in the later electron-withdrawing substitution leads to higher frequency.

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, were kept constant at 6, 8, 14, or 16 carbons, while the substituent X was alternatively varied between the CH_3O, CH_3, Cl, NO_2, CN, and $C_nH_{2n+1}O$. Table 3 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, has led to a significant variation in the mesophase behavior of the individual components. The stability of a mesophase would be augmented by the increase in the polarity of the central part of the molecule. In the nitro (or cyano) analogues, as shown above, the mutual conjugation between the alkoxy oxygen and the ester C=O group in one side which is augmented by the inductive withdrawing effect of the nitro (or cyano) group, on the other side of the molecule, should increase the polarity of the mesogenic portion as a whole; this helps to stabilize both the solid and mesophase. This inference is in harmony with the observation that the nitro and cyano analogues have the highest melting (T_m) and clearing (T_c) points.

In the case of the methoxy, chloro, and alkoxy analogues, the situation is quite different; there are opposing conjugative effects on both sides of the molecules. Consequently, there will be no reinforcement of the dipolar character of the compound. This is born out experimentally, as given in Table 3, in which these derivatives have their T_m and T_c values lower than those of the nitro and cyano analogues. Similar arguments can be said with respect to the methyl-substituted derivatives. The mesomeric interaction affected by the alkoxy group on one side of the molecule is partially counteracted by the opposing inductive effect of the methyl group on the other side resulting in a molecule of low intermolecular forces of association and, consequently, of low T_m and T_c, as is observed from Table 3.

It can also be noted from Table 3 that the mesophase–isotropic transition temperature for compounds with a given substituent decreases with increasing alkoxy group length suggesting that its effect becomes dominant over polarity variation in the centers of the molecules [2]. This reflects the decreasing thermal stability of the mesophase with decreasing molecular rigidity and polarity (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 extremely advantageous in promoting terminal associations. However, the low enthalpy of the nitro and cyano compounds in the first three series (**I**1, **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.

Included in Table 4 are the clearing points, T_c, of the compounds investigated along with the enthalpy, ΔH_c, and entropy, ΔS_c, for this transition, together with those of the methoxy analogues ($\mathbf{I}1_{a\text{–}e}$, R = CH_3O) as collected from [15]. It is readily seen from Table 4 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

Table 4
Thermodynamic properties for investigated compounds

Compound	X	T_c (°C)	ΔH_c (kJ mol^{-1})	ΔS_c (J mol^{-1} K^{-1})
I1$_a$	CH_3O	297.0	1.707	2.975
I1$_b$	CH_3	269.1	1.619	2.983
I1$_c$	Cl	277.8	1.180	2.138
I1$_d$	NO_2	300.2	0.803	1.397
I1$_e$	CN	321.4	0.954	1.602
I6$_a$	CH_3O	244.6	1.858	3.589
I6$_b$	CH_3	218.9	1.737	3.536
I6$_c$	Cl	231.7	0.929	1.840
I6$_d$	NO_2	256.7	0.679	1.281
I6$_e$	CN	268.6	1.447	2.671
I8$_a$	CH_3O	227.7	1.656	3.306
I8$_b$	CH_3	203.3	1.429	2.999
I8$_c$	Cl	218.0	1.007	2.050
I8$_d$	NO_2	246.7	1.481	2.849
I8$_e$	CN	253.9	1.578	2.994
I14$_a$	CH_3O	193.2	1.645	3.527
I14$_b$	CH_3	172.5	1.459	3.274
I14$_c$	Cl	190.2	0.922	2.031
I14$_d$	NO_2	235.1	5.853	11.517
I14$_e$	CN	230.2	4.791	9.518
I16$_a$	CH_3O	178.1	1.848	4.095
I16$_b$	CH_3	166.5	1.174	2.670
I16$_c$	Cl	184.6	2.673	5.673
I16$_d$	NO_2	222.2	7.728	15.601
I16$_e$	CN	229.7	5.665	11.265

low ΔH_c for the nitro compound **I1**$_d$ can be seen [15] as arising from the repulsion between the nitro groups themselves and with other strongly negative ends of dipoles. It is believed that the forces constituting the mesophase energetics are actually a combination of attractive and repulsive forces. The attractive forces consist primarily of polar carbonyl units and terminal dipoles interacting with appropriately charged polar groups of the other molecules in the mesophase; the repulsive forces being constituted primarily of interactions between protruding negative ends of the molecule. In the case of the nitro (**I1**$_d$), and cyano (**I1**$_e$) and to lesser extents the chloro (**I1**$_c$) 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 **I6**–**I16**, 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.

The effect of the methoxy group in **I1**$_a$ seems explicable in terms of a shielding effect on the oxygen lone pairs by an insulator [2], the methyl group. Increasing the alkoxy chain length in series **I6**–**I16** does not affect greatly the shielding effect on the oxygen lone pairs and consequently ΔH_c values do not change significantly.

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

van der Veen [3] studied the relationship between the stability of the mesophase in a liquid crystalline compound, expressed as the clearance temperature, T_c (K), and the anisotropy of polarizability ($\Delta\alpha_X$) of bonds to small compact terminal substituent (C_{ar}–X). The relation had the form

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

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 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. Thus, if $\sqrt{T_c}$ is plotted against $\Delta\alpha_X$ for any series of liquid crystalline compounds, a straight line is expected with slope a and intercept $a\,\Delta\alpha_M$. 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 $\Delta\alpha_X$, as calculated before [4], and the plots are depicted in Fig. 1. T_c values for series **I1**, where the alkoxy substituent is CH_3O, were collected from [15] and their plot is included in Fig. 1 for sake of comparison.

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 five series of compounds. The results of computation are given in Table 5. $\Delta\alpha_M$ values were again plotted, in Fig. 2, as a function

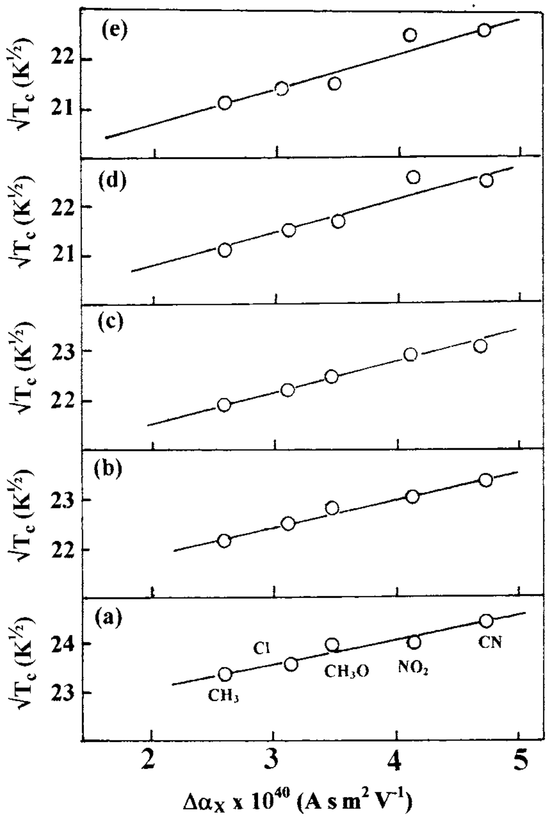


Fig. 1. Dependence of $\sqrt{T_c}$ on the anisotropy of polarizability of the C_{ar}–X bond, $\Delta\alpha_X$, for series (a) **I**1, (b) **I**6, (c) **I**8, (d) **I**14, and (e) **I**16.

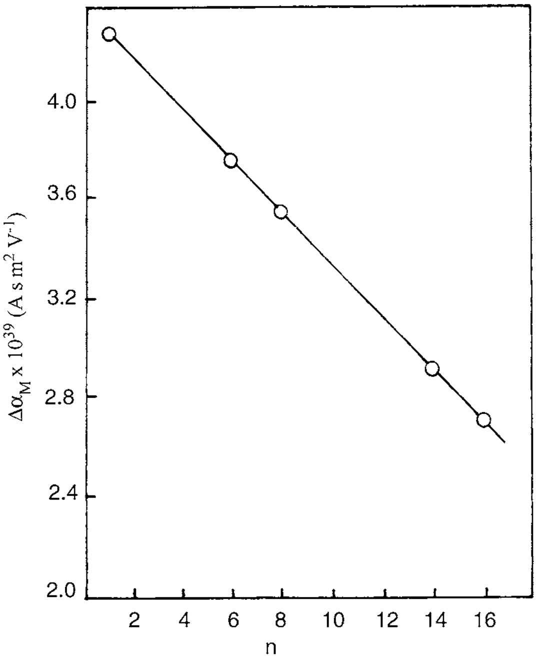


Fig. 2. Dependence of the anisotropy of polarizability, $\Delta\alpha_M$, on the number of carbon atoms (n) in the alkoxy group.

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, decreases linearly as the alkoxy chain is lengthened. This again reflects the decrease in the molecular rigidity and polarity of the molecule as a result of increasing *n*-alkane character.

The values of slopes and intercepts (Table 5) were used, in an inverse way, to calculate the polarizability anisotropy ($\Delta\alpha_X$) for the $C_nH_{2n+1}O$-benzene bonds as a function of its chain length. Thus, making use of Eq. (2), the experimentally determined T_c values (Table 3) for the symmetrically di-substituted alkoxy derivatives (**I**1_f–**I**16_f) were used to calculate $\Delta\alpha_X$ for the alkoxy-benzene bonds in the five series. The results of computation are included in Table 5. These results show that the polarizability anisotropy of the alkoxy-benzene bond decreases as the chain length of the alkoxy group is increased up to six carbon atoms

Table 5

Slopes and intercepts of regression lines as well as the $\Delta\alpha_M$ and $\Delta\alpha_X$ for the $C_nH_{2n+1}O$-benzene bonds in the five series investigated

Series	*n*	Slope × 10^{-39} ($K^{1/2}$ V A^{-1} s^{-1} m^{-2})	Intercept ($K^{1/2}$)	$\Delta\alpha_M \times 10^{39}$ (A s m^2 V^{-1})	$\Delta\alpha_X \times 10^{40}$ (A s m^2 V^{-1})
I1	1	5.14	21.95	4.27	3.75
I6	6	5.50	20.73	3.76	2.40
I8	8	5.71	20.27	3.55	2.39
I14	14	6.61	19.30	2.92	2.39
I16	16	7.02	19.05	2.72	2.39

and thereafter remains constant at about 2.39×10^{40} A s m^2 V^{-1}. This inference, together with that deduced from Fig. 2, reveals that increasing the alkoxy chain length beyond six carbon atoms, although has no effect on the alkoxy-benzene bond, still affects the polarizability anisotropy of the central linkage that plays a main role in the mesophase stability.

5. Conclusion

Unsymmetrical 1,4-phenylene-bis-(4-substituted benzoates) were prepared and thermally characterized for their phase transition temperatures. Two types of substituents were used, viz. an alkoxy group of varying length and a small compact polar group, X. All compounds investigated were found to possess high transition temperatures indicating strong intermolecular association either in the solid or mesophases. The conjugation between the alkoxy and the first 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 second ester carbonyl group. Such differences would lead to a significant variation in the mesophase behavior of the compound. The infrared spectra were consistent with these inferences. Thus, the nitro- and cyano-substituted compounds have their two ester carbonyl groups absorb at two separate frequencies, while the spectra of the remaining derivatives, each showed one carbonyl absorption only. In the nitro and cyano analogues, the polarity of the molecule is augmented by the inductive withdrawing 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 other derivatives resulted in less polar compounds that have relatively lower T_m and T_c values.

Furthermore, the identical infrared spectra, observed for similarly substituted derivatives, indicate that the length of the attached alkoxy chain does not affect the polarization of the first ester carbonyl group, while extension of the terminal *n*-alkoxy chain gave rise to a drop 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.

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References

[1] M.M. Naoum, R.I. Nessim, T.Y. Labeeb, Liq. Cryst. 27 (2000) 889.
[2] J.P. Schroeder, D.W. Bristol, J. Org. Chem. 38 (1973) 3160; J.P. Schroeder, D.W. Bristol, J. Org. Chem. 35 (1970) 2711.
[3] J. van der Veen, J. Phys., Colloque C1 36 (1975) 375.
[4] M.M. Naoum, G.R. Saad, R.I. Nessim, T.A. Abdel Aziz, Liq. Cryst. 25 (1998) 73.
[5] M.M. Naoum, H. Seliger, E. Happ, Liq. Cryst. 23 (1997) 247.
[6] G.W. Gray, B. Jones, J. Chem. Soc. (1953) 4179.
[7] S.A. Haut, D.C. Schroeder, J.P. Schroeder, J. Org. Chem. 37 (1972) 1425.
[8] Y. Sakurai, S. Takenaka, S. Kusabayashi, Y. Nishihata, H. Teranchi, T. Takagi, Mol. Cryst. Liq. Cryst. 201 (1991) 95.
[9] H.T. Nguyen, C. Destrade, Nouv. J. Chim. 5 (1981) 337.
[10] J.P. Schroeder, Mol. Cryst. Liq. Cryst. 61 (1980) 229.
[11] M.J.S. Dewar, J.P. Schroeder, J. Org. Chem. 30 (1965) 2296.
[12] M.J.S. Dewar, R.S. Goldberg, J. Am. Chem. Soc. 92 (1970) 1582.
[13] S. Takenaka, Y. Sakurai, H. Takeda, T. Ikemoto, H. Miyaka, S. Kusabayashi, T. Takagi, Mol. Cryst. Liq. Cryst. 178 (1990) 103.
[14] M.M. Naoum, G.R. Saad, R.I. Nessim, T.A. Abdel Aziz, H. Seliger, Liq. Cryst. 23 (1997) 789.
[15] M.J.S. Dewar, A.C. Griffin, J. Chem. Soc., Perkin Trans. II (1976) 713.