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Magdi M. Naoum; H. Seliger; E. Happ

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Effect of structural changes on mesophase stability of some model compounds based on the aryl benzoate group

by MAGDI M. NAOUM*
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

H. SELIGER and E. HAPP
University of Ulm, Sktion Polymere, D 89069 Ulm, Germany

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Compounds based on 4,4′-substituted phenylbenzoate [RO–C_6H_4COO–C_6H_4–X] (**I**), where X is a cyano group and R is a terminal alkyl chain ranging from 12 to 30 carbon atoms, and alternatively where R is held at 16 carbons and X is CN, COOH, OH, $COOCH_2C_6H_4$, $OCH_2C_6H_4$ and $OC_{16}H_{33}$, were prepared and their mesophase stabilities characterized. Similarly, compounds based on symmetric dimers of terminally alkoxy-substituted phenyl esters [$C_{16}H_{33}O$–C_6H_5COO–A–OOCC_6H_5–$OC_{16}H_{33}$] (**II**), the central linkage A being 1,2-, 1,3- and 1,4-phenylene, and 4,4′-biphenyl, were synthesized and studied. A partial success was achieved in the synthesis of compounds similar to series **II**, but where the ester groups were reversed (series **III**), in order to assess the influence of this structure variation on the liquid crystallinity.

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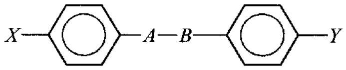
1. Introduction

It is well known [1] that the great majority of liquid crystalline materials are aromatic in nature and of the general formula



where X and Y represent a range of terminal substituents such as alkyl, alkoxy, carboxy, nitro, and cyano groups; and A-B represents a linkage unit in the core structure, for example, CH=N, N=CH, N=N, N=NO, COO, OOC [2–5], etc.

It was also realized that a substituent, X or Y, that increases the length-to-breadth ratio of the molecule is superior to a H atom at the end of the molecule, and that groups such as cyano or alkoxy are more favourable than others in promoting high temperature mesophase–isotropic transitions.

The nature of the central linkage is also of great importance. Linking units containing multiple bonds that maintain the rigidity and linearity of the molecules are most satisfactory in promoting mesophase stability. The ester linkage contains no multiple bonds in the chain of atoms actually linking the benzene rings; however, conjugative interactions within the ester moiety and the rings do lead to some double bond character and to a stiffer structure than might be expected. Esters are, in fact, fairly planar systems and quite strongly nematogenic.

Furthermore, in accordance with the general requirements of an elongated and fairly rigid molecular structure, substitution of any of the lateral H atoms of the rings by a bulkier substituent strongly depresses the transition temperatures, the effect being proportional to substituent size.

Extension of a terminal n-alkyl chain substituent gives rise to a gradient in the liquid crystal transition temperatures [6, 7]. In the lower homologues of a series a nematic mesophase appears, and if the terminal chain length increases there is a tendency for a smectic A phase to appear.

The goal of the present study is to prepare first, a series of model compounds **I**, where $X = $ CN and R changes from n-dodecyl to n-triacontanyl, in an attempt to determine the effect of terminal chain length on the liquid crystalline phase stability and the limit beyond which the compounds are no longer liquid crystalline. Secondly, to prepare a series of model compounds **I**, where R is the n-$C_{16}C_{33}$ group and X being OH and COOH together with their benzylether and ester derivatives, respectively, in order to study the effect of these groups on the LC behaviour of the compounds. Finally, to synthesize two series of model compounds, **II** and **III**, which differ only in the orientation of the two ester groups, using two different central units, namely, the

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*Author for correspondence.

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three isomeric dihydroxybenzenes and three isomeric benzene dicarboxylic acids, respectively. The 4,4′-dihydroxybiphenyl and the 1,3,5-trihydroxybenzene derivatives of *p*-*n*-hexadecyloxybenzoic acid were prepared for comparison.

2. Experimental

2.1. *Materials and analysis*

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

Thin layer chromatography was performed with TLC sheets coated with silica gel (E. Merck); spots were detected by UV irradiation. Silica gel (No. 7734, E. Merck) was used for column chromatography. Infrared spectra were measured with a Perkin–Elmer 325 Spectrophotometer, ^{1}H NMR spectra with a Varian EM 350L (60 MHz), and mass spectra with a Varian MAT 71. Calorimetric investigations were performed with a differential scanning calorimeter, Perkin–Elmer DSC-7. Typical heating and cooling rates were 10 K min^{-1}. Melting temperatures were determined with a standard WL polarizing microscope (C. Zeiss, Germany) attached to a FB82 hot-stage equipped with a FB80 central processor (Mettler, Switzerland).

The synthetic routes to the compounds under investigation are shown in schemes 1–3, and are described below.

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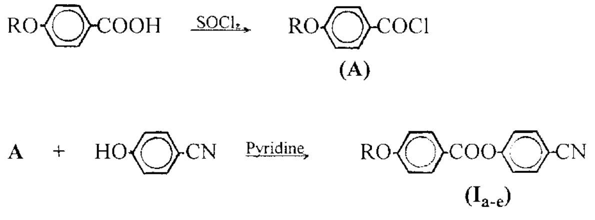

(A)

(I_{a-e})

2.2. *Preparation of the 4-n-alkoxybenzoic acids*

The 4-*n*-alkoxybenzoic acids were prepared by alkylation of ethyl 4-hydroxybenzoate [8] with the corresponding alkyl halides, and were recrystallized twice from glacial acetic acid.

2.3. *Preparation of the 4-n-alkoxybenzoyl chlorides*

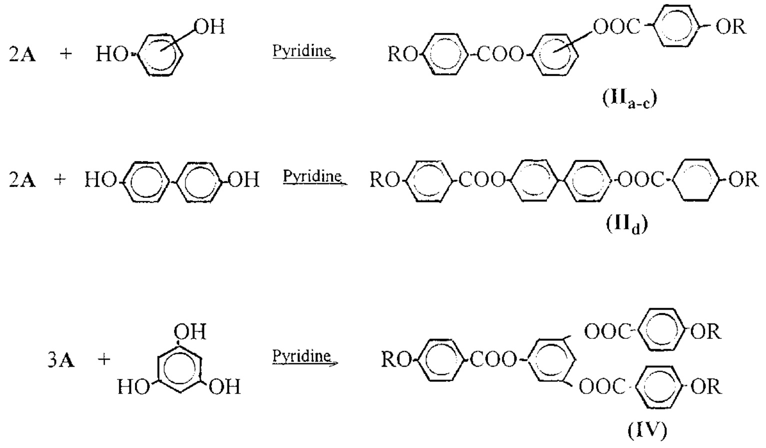
The 4-*n*-alkoxybenzoyl chlorides were prepared from the corresponding acids by heating them with an excess of thionyl chloride at reflux for 5 h. The excess thionyl chloride was removed using a rotatory evaporator to give, as a residue, the acid chloride.

2.4. *Preparation of the 4-cyanophenyl esters of the 4-n-alkoxybenzoic acids (**Ia–e**)*

Typically, a solution of 4-cyanophenol (0·03 mol) in 50 ml dry pyridine was added dropwise to a solution of 4-*n*-alkoxybenzoyl chloride (0·03 mol) in 50 ml dry pyridine over 2 h. The mixture was stirred at room temperature for 24 h and then acidified with cold dilute hydrochloric acid. The precipitate was filtered, washed with water, and shaken for 2 h in 200 ml of 5 per cent aqueous sodium bicarbonate solution. The solid, separated by filtration, was recrystallized twice from ethanol. The still impure products were further purified by column chromatography over silica gel using dichloromethane as the eluent.

2.5. *Preparation of the 4-n-hexadecyloxybenzoic esters of dihydroxyphenol (**IIa–d**)*

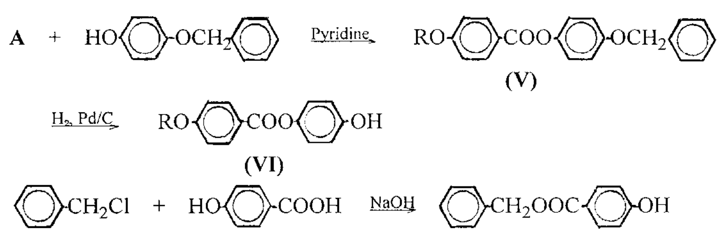
Typically a solution of 0·03 mol of the dihydroxyphenol, namely, pyrocatechol, resorcinol, hydroquinone and 4,4′-dihydroxybiphenyl, in 50 ml dry pyridine was added slowly with stirring to a solution of 4-*n*-hexadecyloxybenzoyl chloride (0·06 mol) in 50 ml pyridine. The mixture was further stirred for at least 24 h at room


(II_{a-c})

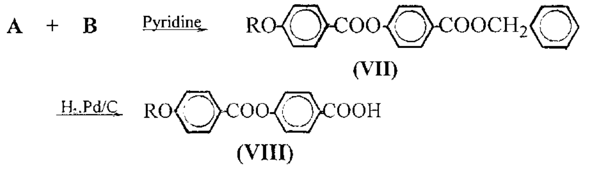
(II_d)

(IV)

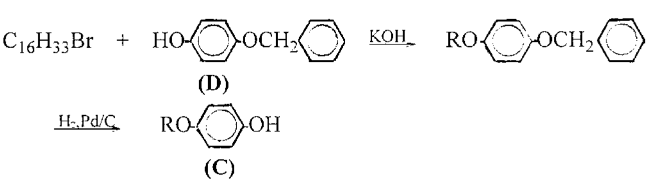
R = C_nH_{2n+1}, n = 12,14,16,20,30.


(V)

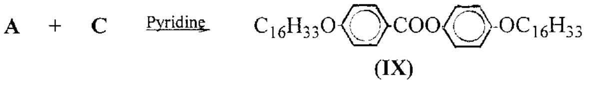
(VI)


(VII)

(VIII)


(D)

(C)

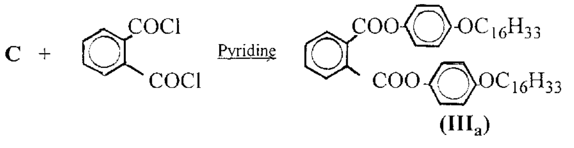

(IX)

R = $C_{16}H_{33}$

temperature. The products were treated and purified as for compounds **Ia–d**.

2.6. *Preparation of the 4-n-hexadecyloxybenzoic esters of phloroglucinol (**IV**)*

These were similarly prepared, but using 0·09 mol of the acid chloride.


(III_a)

2.7. *Preparation of 4-n-hexadecyloxyphenol*

The method of Klarman *et al.* [9], was used. The 4-hexadecyloxyphenol benzylether, prepared by alkylation of hydroquinone monobenzylether with 1-bromohexadecane and recrystallized twice from ethanol, was dissolved in chloroform, and hydrogen allowed to react overnight, in the presence of Pd/C, at room temperature under atmospheric pressure. The product was recrystallized from ethanol to give TLC pure crystals that melted at 88·3°C.

2.8. *Preparation of benzyloxyphenyl ester of 4-n-hexadecyloxybenzoic acid (**V**)*

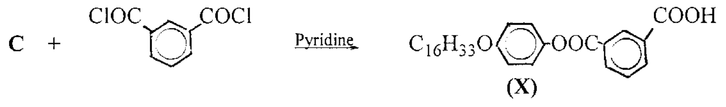
A typical condensation reaction of 4-*n*-hexadecyloxybenzoyl chloride (0·03 mol) with hydroquinone monobenzyl ether (0·03 mol) in dry pyridine was applied. The product after crystallization from ethanol was TLC pure.

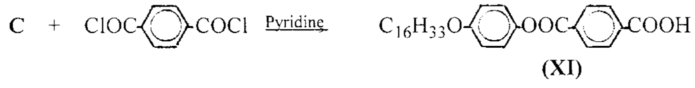
2.9. *Preparation of the 4-hydroxyphenyl esters of 4-n-hexadecyloxybenzoic acid (**VI**)*

Compound **VI** was obtained from **V** by selective cleavage of the benzyl ether linkage. 0·01 mol of **V** was dissolved in 50 ml of dry chloroform, 0·05 g of Pd/C added, and hydrogen allowed to react until no more hydrogen was consumed. The catalyst was filtered, chloroform evaporated, and the residue separated on a silicagel column (50 cm) using 1 per cent methanol/dichloromethane as the eluent.

2.10. *Preparation of benzyl 4-hydroxybenzoate*

It was prepared [10] by the reaction of benzyl chloride (0·06 mol) with 4-hydroxybenzoic acid (0·06 mol) in aqueous sodium hydroxide at reflux with stirring. The product was shaken for 2 h in aqueous sodium bicarbonate, then extracted from ether in aqueous sodium hydroxide and acidified. The precipitated solid was


(X)


(XI)

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recrystallized twice from ethanol to give a TLC pure product that melted at 107·7°C.

2.11. *Condensation of 4-n-hexadecyloxybenzoyl chloride with benzyl 4-hydroxybenzoate (**VII**)*

The condensation was typically performed in dry pyridine using 0·03 mol of each starting material. The product was purified by double crystallization from ethanol to give a TLC pure compound.

2.12. *Preparation of 4-carboxyphenyl ester of 4-n-hexadecyloxybenzoic acid (**VIII**)*

Compound **VIII** was prepared from **VII** by the catalytic cleavage of the benzyl ester using hydrogen over Pd/C. The procedure was the same as that described for the benzyl ether cleavage of compound **VI**. The solid obtained after double crystallization from ethanol was TLC pure.

2.13. *Preparation of 4-n-hexadecyloxyphenyl ester of 4-n-hexadecyloxybenzoic acid (**IX**)*

In a similar manner, the condensation was performed in dry pyridine between 4-*n*-hexadecyloxybenzoyl chloride and 4-*n*-hexadecyloxyphenol. A TLC pure product was obtained after recrystallization from ethanol.

2.14. *Condensation of 4-n-hexadecyloxyphenol with the three isomeric phthaloyl chlorides*

Typically a solution of 4-*n*-hexadecyloxyphenol (0·06 mol) in dry pyridine was added to the appropriate phthaloyl chloride (0·03 mol) in dry pyridine with stirring. The mixture was further stirred for at least 24 h at room temperature and the products were treated as before. Only the *o*-derivative gave the diesterified product (**IIIa**), while the *m*- and *p*-benzenedicarboxylic acid chlorides gave the mono esters (**X** and **XI**), as detected from their mass spectra.

3. Results

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

All transition temperatures of the prepared 4-*n*-alkoxybenzoic acids agreed with those cited in the literature [8]. For the C_{20}-alkoxybenzoic acid, there was a crystal to smectic transition at 104°C and to the isotropic phase at 129°C. With respect to the C_{30}-alkoxybenzoic acid, the corresponding transition temperatures were 110·5°C and 117·7°C, respectively.

The thermal properties of 4-cyanophenyl, 4-*n*-alkoxybenzoate (**Ia–e**) are given in table 1, and those of the 4-*n*-hexadecyloxybenzoic esters of di- and trihydroxyphenols (**IIa–d** and **IV**) in table 2 and are discussed below.

The transition temperatures of 4-substituted phenyl esters of 4-*n*-hexadecyloxybenzoic acids (**Ic** and **V–IX**) are given in table 2, and those of 4-*n*-hexadecyloxyphenyl esters of benzene dicarboxylic acids (**IIIc**, **X** and **XI**) in table 4.

4. Discussion

The 4-substituted phenyl esters of the 4-alkoxybenzoic acids (**I**) provide an excellent system for studying the effects of structural changes on liquid crystalline behaviour. Such systems can be used to study the roles of both terminal groups on mesophase stability. The homologous series of 4-cyanophenyl-4′-*n*-alkoxybenzoate (**Ia–e**) exhibits a pattern in which the mesophase to isotropic phase transition (T_c) rises with increasing chain length [11]. The lower homologues exhibit an even–odd effect, which diminishes as the number of carbons in the alkoxy group (n) approaches 12. The homologues with $n=6$–8 exhibit a nematic mesophase only. Homologues with $n=9$–11 exhibit both smectic and nematic mesophases, while those with $n\geqslant 12$ possess only a smectic A mesophase which transforms directly to the isotropic phase [11]. In this series of compounds a high degree of polymorphism was not detected. In table 1 the transition temperatures of the homologues for $n=12$–30 are given. It is clear from this table that both the solid–mesophase and mesophase–isotropic transition temperatures increase, but at different rates, which results in a narrowing of the mesophase width and becomes zero when the number of carbon approaches 30. Increase in the transition temperatures in such series were attributed by Gray [12] to the fact that the lateral attractions grow stronger as the alkoxy group is lengthened while the terminal attractions grow relatively weaker or remain unchanged. The net result is a rising curve for the mesophase–isotropic transition curve, which levels off as the series reaches 16 carbon atoms. On the other hand, the alkyl group will act as a dilutent, increasing the average distance between the molecules; this in turn reduces the anisotropy of the intermolecular forces and makes the mesophase less stable. In a similar study, the mesogenic properties of the 4-*n*-alkoxybenzoic acids were investigated by Jones *et al.* [8, 13], who found that the liquid crystalline properties change with alkyl chain length. They suggested that, from extrapolation of the available data, the crystal-to-mesophase transition temperature approaches that of the mesophase-to-isotropic transition when there are about 30 carbons in the chain. The 4-*n*-triacontanyloxybenzoic acid, which we prepared as intermediate in preparing compound **Ie**, proved to possess a weak mesophase stability of 7·2°C ($\Delta T=$ 117·7–110·5°C).

In order to look at the substituent effect on the liquid crystalline properties of compounds of type **I**, the number

Table 1. Yields, characterization and thermal properties of the 4-cyanophenyl-4′-*n*-alkoxybenzoates (**Ia–e**).

Compound	Alkoxy group	Yield/per cent	T_m/°C	T_c/°C	Phase width	Analyses found (calc) % C	% H	% N
Ia	$C_{12}H_{25}O$	64·5	73·0	89·5	16·5		Ref. [11]	
Ib	$C_{14}H_{29}O$	62·9	73·9	89·4	15·5	77·42 (77·20)	8·74 (8·56)	3·16 (3·21)
Ic	$C_{16}H_{33}O$	70·3	83·2	96·3	12·6	77·82 (77·71)	8·95 (8·91)	3·09 (3·02)
Id	$C_{20}H_{41}O$	43·7	84·0	93·0	9·0	78·60 (78·57)	9·83 (9·50)	2·73 (2·69)
Ie	$C_{30}H_{61}O$	64·5	—	99·9	—	79·24 (80·07)	10·33 (10·54)	2·14 (2·12)

T_m = Solid–mesophase transition; T_c = Mesophase–isotropic or solid–isotropic transition.

of carbons in the terminal alkoxy group were kept constant at 16, while the CN group (in **Ic**) was alternatively replaced by $OCH_2C_6H_5$ (**V**), OH (**VI**), $COOCH_2C_6H_5$ (**VII**), COOH (**VIII**), and $OC_{16}H_{33}$ (**IX**). Table 2 compares the transition temperatures of these compounds from which it can be seen that only compound **VIII**, with *p*-COOH, gave a smectic mesophase at 119·9°C, while compound **IX**, with two terminal $OC_{16}H_{33}$ groups, exhibited a mesophase only on cooling at 78·3°C. Gnilomedova *et al.* [14], found that compounds of type **IX**, namely the 4-methoxyphenyl-4-alkoxybenzoates, are monotropic. Examination of the mesogenic behaviour of the homologous series of the type **IX**, as reported in the literature [15, 16], reveals that increasing the terminal alkoxy chain length leads to the appearance of a smectic mesophase. Our compound **IX**, with 16 carbon atoms in the terminal alkoxy chain, showed only one smectic mesophase, as shown in table 2. Recalling the transition temperatures of compound **Ic**, with a *p*-CN substituent and a mesophase stability of 12·6°C, and comparison with compound **VIII** revealed that *para*-substitution with a carboxy group greatly increases the stability of the mesophase compared to any other substituent due to dimer formation [17].

Comparing the effect of the *p*-CN group in **Ic** with the other substituents in compounds **V–VII** and **IX** on the mesophase stability of these compounds, there is a strong tendency in the cyano compounds to loose molecular pairing [18], so that an antiparallel distribution of the cyano dipoles occurs. Each cyano group in a pair is located close to the opposite end of its neighbour, and the effective molecular length is therefore enhanced. This may explain the strong promotion of the mesophase stability by the terminal cyano group.

With respect to the *p*-OH substituent, and as is expected [19], compound **VI** displayed no liquid crystalline behaviour, supporting Gray's statement [20] that phenolic compounds are unable to display a mesophase because of intermolecular hydrogen bonding. As for the non-linear $OCH_2C_6H_5$ (in **V**) and $COOCH_2C_6H_5$ (in **VII**) groups, there are neither possibilities of antiparallel alignment of molecules resulting in molecular pairing, nor dimer formation enhancing molecular length. This could explain the lack of mesogenicity associated with these compounds.

Also of considerable interest are compounds of type **II** which were prepared to create model compounds in which the two mesogens are separated by a well-defined distance and angle to see how the transition temperatures

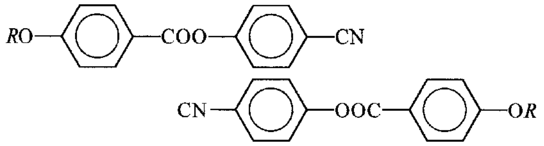

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Table 2. Yields, characterization and thermal properties of 4-substituted phenyl esters of 4-*n*-hexadecyloxybenzoic acid.

Compound	Substituent	Yield/per cent	T_m/°C	T_c/°C	Phase range	Analyses found (calc) % C	% H
Ic	CN	70·8	83·7	96·3	12·6		
V	$OCH_2C_6H_5$	68·2	—	105·6	—	79·46 (79·37)	9·05 (8·81)
VI	OH	43·2	—	114·8	—	76·66 (76·61)	9·53 (9·31)
VII	$COOCH_2C_6H_5$	60·4	—	72·5	—	77·64 (77·59)	8·89 (8·45)
VIII	COOH	58·5	119·8	212·4	92·6	74·57 (74·65)	8·72 (8·77)
IX	$OC_{16}H_{33}$	62·6	(78·3)[a]	85·6	7·3	77·43 (78·15)	9·75 (9·84)

[a] On cooling.

T_m = Solid–mesophase transition; T_c = Mesophase–isotropic or solid–isotropic transition.

Table 3. Yields, characterization, and thermal properties of the 4-*n*-hexadecyloxybenzoic acid esters of the di- and tri- hydroxy phenolic compounds.

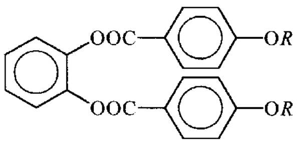
Compound	Phenol used	Yield/per cent	T_m/°C	T_c/°C	Phase width	Analyses found (calc.) % C	Analyses found (calc.) % H
IIa	Pyrocatechol	62·0	—	68·5	—	78·17 (78·15)	10·52 (9·84)
IIb	Resorcinol	64·3	—	75·6	—	78·18 (78·15)	9·84 (9·84)
IIc	Hydroquinone	61·5	108·2	156·5	48·3	Ref. [15]	
IId	Dihydroxybiphenyl	64·3	121·0	228·0	107·0	79·58 (79·59)	9·99 (9·44)
IV	Phloroglucinol	65·1	—	65·5	—	77·57 (77·72)	9·85 (9·89)

T_m = Solid–mesophase transition; T_c = Mesophase–isotropic or solid–isotropic transition.

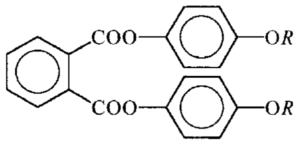
are influenced by structural variations. It is evident from table 3 that only compounds **IIc** [15] and **IId** possess a smectic mesophase, while the variations do not. This is to be expected since compounds **IIc** and **IId** are linear. Also, it is clear from table 3 that increasing the branching in the molecule leads to a decrease in its melting point. Thus, the 1,3-phenylene ester (**IIb**) melts at 75·6°C, while the 1,3,5-trisubstituted benzene (**IV**) has a melting point of 65·5°C.

It is well known [15, 19] that the addition of more phenyl rings into a mesogenic compound increases the range of the liquid crystalline phase and the transition temperatures. This was found to be the case. Replacement of the central phenylene group in **IIc** by the biphenyl group in **IId** raised the crystal-to-mesophase transition from 108·2 to 121°C, and the mesophase-to-isotropic transition from 156·5 to 228°C; the mesophase stability was nearly doubled. For compounds of these types, Dewar and Schroeder [19] claimed that increasing the alkyl chain length reduces the rigidity of rod-shaped molecules, and thus their ability to fit readily into a parallel molecular arrangement of the mesophase. The result would be a decrease in the mesophase stability and a lowering of the transition temperatures. They also added that the disturbing effect of the alkyl substituent does not appear to increase with length beyond *n*-hexyl when the central group is phenylene. On the contrary, our product **IIc**, with its *n*-hexadecyloxy substituent, proved to have transition temperatures of 108·2 and 156·5°C (see table 3) which are still lower than those of the decyloxy analogue, 122 and 178°C, respectively [15, 21]. However, it was found that the effect of the alkyl chain length is much more pronounced when the central aromatic group is biphenyl, because the more rigid biphenyl moiety produces a higher degree of stability and consequently higher transition temperatures. Under these circumstances, even very long alkyl chains (such as the hexadecyloxy group in **IId**) would be relatively mobile and their disturbing effect would continue to increase with chain length beyond 16 carbons (compare our results, i.e. 121–228°C for **IId** with those of the hexyl [19], and heptyl [19, 22] analogues, which are 153–181–330°C and 150–211–316°C, respectively).

Trials were made to prepare the di-4-*n*-hexadecyloxyphenyl esters of the three isomeric benzene dicarboxylic acids. Only the diester of the *o*-isomer (**IIIa**) was obtained; while the other isomers, isophthalic and terephthalic acids, gave the mono-esterification products (**X** and **XI**), respectively. As expected, with a non-linear compound, **IIIa** exhibits no mesophase (see table 4). On the other hand, it possesses a higher melting point compared to that of its isomeric compound **IIa**, indicating a stronger dipole–dipole interaction between individual molecules. In the *o*-phenylene- *p*-*n*-alkoxybenzoate



IIa



IIIa

$R = C_{16}H_{33}$

Table 4. Yields, characterization and thermal properties of 4-*n*-hexadecyloxy esters of benzene dicarboxylic acids.

Compound	Acid used	Ester formed	Yield/per cent	T_m/°C	T_c/°C	Analyses found (calc.) % C	Analyses found (calc.) % H
IIIa	Phthalic	Diester	50·5	—	78·8	78·12 (78·15)	9·91 (9·84)
X	Isophthalic	Mono	43·5	—	143·0	74·68 (74·65)	8·76 (8·77)
XI	Terephthalic	Mono	45·7	133·8	197·5	74·46 (74·65)	8·97 (8·77)

T_m = Solid–mesophase transition; T_c = Mesophase–isotropic or solid–isotropic transition.

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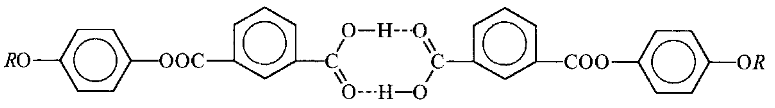
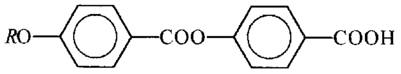
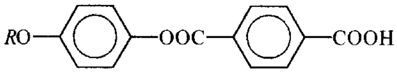


X, $R = C_{16}H_{33}$





VIII $R = C_{16}H_{33}$ **XI**

(**IIa**) there is a mutual conjugation between the alkoxy and carboxy groups; this should increase the polarity of the carbonyl oxygen, thus leading to an increased intramolecular dipole–dipole interaction [21].

This might, in turn, lead to greater molecular deformation, and consequently lower intermolecular interaction. In the 4-*n*-alkoxyphenyl phthalate (**IIIa**) such mutual conjugation is lacking; this could explain why, in such a pair of isomers, **IIIa** has the higher melting point.

The mono 4-*n*-hexadecyloxyphenyl isophthalate (**X**) melts at 143°C without displaying a mesophase. This relatively high melting point may be attributed to dimer formation, but since these dimeric molecules are nonlinear, they were not expected to be liquid crystalline.

Finally, the mono 4-*n*-hexadecyloxyphenyl ester of terephthalic acid (**XI**) exhibited a mesophase range of 63·7°C ($\Delta T = 197{\cdot}5$–$133{\cdot}8$°C) due to the formation of linear dimeric molecules. This, when compared with its isomeric compound (**VIII**) with its mesophase stability ($\Delta T = 212{\cdot}4$–$119{\cdot}8 = 92{\cdot}6$°C), indicates greater lateral adhesion of the rod-shaped molecules in **VIII**, which in turn should be greater the larger the polarity and or polarizability of the central parts of the molecules. In **VIII**, the mutual conjugation between the alkoxy and carboxy groups increases the polarity of the carbonyl oxygen and so helps to stabilize the mesophase. The two isomers **VIII** and **XI** will be studied in detail in a subsequent paper.

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