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Mesomorphic behaviour of di[(4-substituted phenyl)esters] of aromatic dicarboxylic acids

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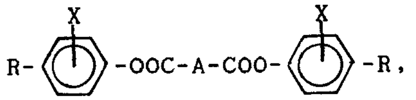
Some di(4-alkyloxyphenyl ester)s of aromatic dicarboxylic acids which presumably exert significant steric hindrance to molecular packing, such as di(2- and/or 3-methyl or -chloro-4-alkyloxyphenyl) 2,5-pyridinedicarboxylates, di(2- and/or 3-methyl-4-alkyloxyphenyl) 2,6-naphthalenedicarboxylates, and di(4-alkylxyphenyl) 3,5-pyrazoledicarboxylates, are shown to indicate nematic liquid-crystalline behaviour.

1. Introduction

Since the discovery of nematogen liquid crystal compounds, it has been the common understanding that rod-like molecules with appropriate lateral interactions are required to form the nematic molecular array [1–4]. The presence of a polar lateral substituent at the core 1,4-benzene ring such as OH and Cl has been favoured for some purpose [5–7] whilst the 1,2- and 1,3-disubstituted core benzene rings have seldom provided the nematic phase [1, 8, 9].

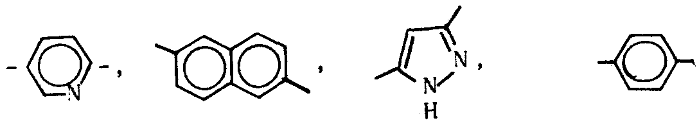
In this paper, we report the results obtained either by introducing lateral substituents such as methyl and chloro groups into the 4-substituted phenyl portion of 2,5-pyridinedicarboxylates or by using an unprecedented aromatic core unit for arenedicarboxylates such as 2,6-naphthalene and 3,5-pyrazole, in order to see whether the molecular structure thus obtained is compatible with the mesophase formed.

The compounds synthesized and investigated were as follows:



(I)

where *A*:



X: H, Me, Cl

R: $n-C_mH_{2m+1}O-, n-C_mH_{2m+1}OOC-$ $m=4$–10.

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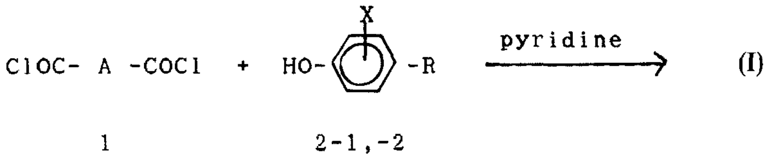
2. Results and discussion

Compounds (I) were prepared by the esterification reaction of the dichloride of arenedicarboxylic acid (1) either with 2- and/or 3-substituted hydroquinone mono(*n*-alkyl)ether (2-1) or *n*-alkyl 3-chloro-4-hydroxybenzoate (2-2) in pyridine, as described in a previous paper [10], as follows



(1)

where 2–1: $X = 2$- and/or 3-Me, –Cl; $R = n\text{-}C_mH_{2m+1}O$–

2–2: $X = 3\text{-Cl}$; $R = n\text{-}C_mH_{2m+l}OOC$–.

Table 1 lists compounds (I) thus prepared.

It is recognized from this table, that yields are not high partly because compounds (I) were subjected to repetitive SiO_2 column chromatography for purification so as to afford a single spot by TLC, and that use of a high molecular weight 2–1 tends to decrease the yield.

Mass (M^+) and analytical results in the experimental section such as those of IR, ^1H NMR, and elemental analyses (CHN) were all satisfactory.

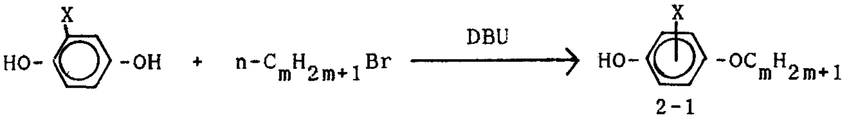
Table 1. Arenedicarboxylates I prepared according to equation (1).

A	*X*	*R*	M^+†	Yield/%
2,5-pyridine	2- and/or 3-Me	$n\text{-}C_4H_9O$	491	47
2,5-pyridine	2- and/or 3-Me	$n\text{-}C_6H_{13}O$	547	27
2,5-pyridine	2- and/or 3-Me	$n\text{-}C_8H_{17}O$	603	22
2,5-pyridine	2- and/or 3-Me	$n\text{-}C_{10}H_{21}O$	659	16
2,5-pyridine	2- and/or 3-Cl	$n\text{-}C_4H_9O$	532	30
2,5-pyridine	2- and/or 3-Cl	$n\text{-}C_6H_{13}O$	588	30
2,5-pyridine	2- and/or 3-Cl	$n\text{-}C_8H_{17}O$	644	26
2,5-pyridine	2- and/or 3-Cl	$n\text{-}C_{10}H_{21}O$	700	21
2,5-pyridine	2-Cl	$n\text{-}C_4H_9OOC$	588	55
2,5-pyridine	2-Cl	$n\text{-}C_6H_{13}OOC$	644	38
2,5-pyridine	2-Cl	$n\text{-}C_8H_{17}OOC$	—‡	43
2,5-pyridine	2-Cl	$n\text{-}C_{10}H_{21}OOC$	—‡	47
3,5-pyrazole	H	$n\text{-}C_4H_9O$	452	26
3,5-pyrazole	H	$n\text{-}C_6H_{13}O$	508	11
3,5-pyrazole	H	$n\text{-}C_8H_{17}O$	564	22
3,5-pyrazole	H	$n\text{-}C_{10}H_{21}O$	620	14
2,6-naphthalene	2- and/or 3-Me	$n\text{-}C_6H_{13}O$	604	42
2,6-napthalene	2- and/or 3Cl	$n\text{-}C_6H_{13}O$	637	36
2,6-naphthalene	2-Cl	$n\text{-}C_6H_{13}OOC$	693	51
1,4-benzene	2- and/or 3-Me	$n\text{-}C_8H_{17}O$	602	28
1,4-benzene	2- and/or 3-Me	$n\text{-}C_{10}H_{21}O$	658	31
1,4-benzene	2-Cl	$n\text{-}C_6H_{13}OOC$	643	50

† All M^+ coincide with molecular weights.
‡ Undetermined.

The monoether 2–1 was synthesized, in its turn, by the reaction of methyl- or chlorohydroquinone with *n*-alkyl bromide in DMF in the presence of an equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a proton acceptor under nitrogen to avoid alkaline air oxidation of the hydroquinone, as shown in equation (2).

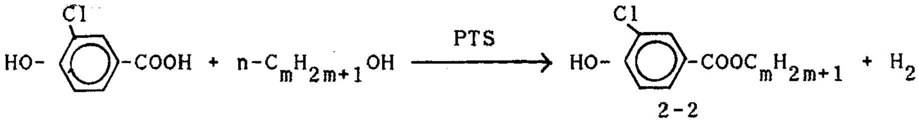
Yields after SiO_2 column chromatography to remove the by-product diethers ranged from 16 to 70 per cent



(2)

Trials to separate 2- and 3-*X* isomers failed due to their similar physical properties.

The benzoate 2–2 was synthesized by the esterification reaction of 3-chloro-4-hydroxybenzoic acid and an *n*-alkyl alcohol in toluene with p-toluenesulphonic acid (PTS) as acid catalyst using a Dean–Stark trap (see equation (3)). Yields were high (70–94 per cent).



(3)

Table 2 summarizes the transition temperatures determined for 2,5-pyridinedicarboxylate (A = 2,5-pyridine; R = alkyloxy) as compared with those for A = 1,4-benzene.

It is known within the scope of the present study that, for A = 2,5-pyridine, the nematic to isotropic transition temperature decreases in the order: $X = \mathrm{H} > \mathrm{Cl} > \mathrm{Me}$ and that, in the case of X = Me, the order is A = 1,4-benzene > 2,5-pyridine. The former result clearly indicates the effect of substituents directed laterally to the longer axis of the rod-like molecule [11]. The fact that the non-polar Me affords significantly lower nematic to isotropic transition temperatures as compared to the polar Cl, in spite of both having similar van der Waals dimensions, may indicate that the latter causes larger lateral interactions than the former.

With 2,6-pyridine as A might cause a lower nematic to isotropic transition temperature than 1,4-benzene due to the loss of molecular symmetry [10]. It is also recognized that a lower nematic to isotropic transition temperature is generally accompanied by a narrower nematic range. Table 3 also summarizes the transition temperatures determined for another 2,5-pyridinedicarboxylate (A = 2,5-pyridine; R = alkyloxycarbonyl; X = 2-Cl). It is known that all compounds with lateral Cl atoms shown in this table do not exhibit any mesophases, whereas those without substituents, including the case of A = 1,4-benzene, exhibit the nematic phase [10], thereby demonstrating that the lateral Cl atom hinders the nematic molecular array.

In table 4, the results for arenedicarboxylates with an unprecedented A such as 2,6-naphthalene and 3,5-pyrazole are further summarized. It should be noted that III16 and IIIP4 among the compounds listed in this table exhibit the nematic phase in spite of the possible presence of significant steric hindrances to the molecular array. This fact may indicate that a rod-like molecular array is also not incompatible even with these molecular structures, as recently reported in similar cases [9, 12].

As for the crystal to nematic and nematic to isotropic transition data listed in tables 2, 3, and 4 some unusual differences between the values with increasing temperature and those with decreasing temperature are seen, although the results obtained for the

Table 2. The effect of the lateral substituent (X) on the transition temperatures of the 2,5-pyridinedicarboxylate (R = alkyloxy).

Compound	R	X	Transition temperature
I14	n-C_4H_9O	2- and/or 3-Me	C 88°C N 106°C I
I24	n-C_4H_9O	2- and/or 3-Cl	$C \underset{88^\circ C}{\overset{115^\circ C}{\rightleftharpoons}} N \underset{134^\circ C}{\overset{135^\circ C}{\rightleftharpoons}} I$
I04†	n-C_4H_9O	None	C 165°C N 208°C I
I16	n-$C_6H_{13}O$	2- and/or 3-Me	$C \underset{94^\circ C}{\overset{91^\circ C}{\rightleftharpoons}} N \underset{134^\circ C}{\overset{112^\circ C}{\rightleftharpoons}} I$
I26	n-$C_6H_{13}O$	2- and/or 3-Cl	$C \underset{94^\circ C}{\overset{105^\circ C}{\rightleftharpoons}} N \underset{146^\circ C}{\overset{138^\circ C}{\rightleftharpoons}} I$
I06†	n-$C_6H_{13}O$	None	$C \underset{130^\circ C}{\overset{135^\circ C}{\rightleftharpoons}} N \underset{200^\circ C}{\overset{200^\circ C}{\rightleftharpoons}} I$
	[n-$C_6H_{13}O$	None	C 164°C N 200°C I‡
I18	n-$C_8H_{17}O$	2- and/or 3-Me	$C \underset{83^\circ C}{\overset{80^\circ C}{\rightleftharpoons}} N \underset{110^\circ C}{\overset{94^\circ C}{\rightleftharpoons}} I$
	[n-$C_8H_{17}O$	2- and/or 3-Me	$C \underset{100^\circ C}{\overset{97^\circ C}{\rightleftharpoons}} N \underset{132^\circ C}{\overset{127^\circ C}{\rightleftharpoons}} I$‡
I28	n-$C_8H_{17}O$	2- and/or 3-Cl	$C \underset{89^\circ C}{\overset{103^\circ C}{\rightleftharpoons}} N \underset{150^\circ C}{\overset{138^\circ C}{\rightleftharpoons}} I$
I08†	n-$C_8H_{17}O$	None	$C \underset{170^\circ C}{\overset{172^\circ C}{\rightleftharpoons}} N \underset{180^\circ C}{\overset{180^\circ C}{\rightleftharpoons}} I$
I20	n-$C_{10}H_{21}O$	2- and/or 3-Me	$C \underset{77^\circ C}{\overset{75^\circ C}{\rightleftharpoons}} N \underset{117^\circ C}{\overset{103^\circ C}{\rightleftharpoons}} I$
	[n-$C_{10}H_{21}O$	2- and/or 3-Me	$C \underset{89^\circ C}{\overset{92^\circ C}{\rightleftharpoons}} N \underset{125^\circ C}{\overset{116^\circ C}{\rightleftharpoons}} I$‡
I30	n-$C_{10}H_{21}O$	2- and/or 3-Cl	$C \underset{93^\circ C}{\overset{103^\circ C}{\rightleftharpoons}} N \underset{145^\circ C}{\overset{141^\circ C}{\rightleftharpoons}} I$
I10†	n-$C_{10}H_{21}O$	None	$C \underset{112^\circ C}{\overset{115^\circ C}{\rightleftharpoons}} N \underset{175^\circ C}{\overset{175^\circ C}{\rightleftharpoons}} I$

† See [10].

‡ Contains a benzene instead of a pyridine ring.

analogous compounds without lateral substituents were usual [10]. Satisfactory explanations of these data are not possible at the present time.

In conclusion, it can be said with certainty that the molecular structure made up either by introducing lateral substituents such as Me and Cl into the 4-alkyloxyphenyl portion of 2,5-pyridinedicarboxylate or by employing unprecedented groups such as 2,6-naphthalene or 3,5-pyrazole as the core unit A of arenedicarboxylates, bring about some steric hindrance to the rod-like molecular array, which is not incompatible with the nematic phase.

Table 3. The effect of a lateral substituent (X) on the transition temperatures of 2,5-pyridinedicarboxylate (R = alkylcarbonyl).

Compound	R	X	Transition temperature
II24	n-C_4H_9OOC	2-Cl	$C \xrightleftharpoons[75^\circ C]{141^\circ C} I$
II04†	n-C_4H_9OOC	None	$\begin{array}{ccc} C & \xrightarrow{110^\circ C} & I \\ \nwarrow & N & \swarrow \\ 92^\circ C & & 108^\circ C \end{array}$
	[n-C_4H_9OOC	None	$C \xrightleftharpoons[105^\circ C]{116^\circ C} N \xrightleftharpoons[121^\circ C]{121^\circ C} I$‡
II26	n-$C_6H_{13}OOC$	2-Cl	$C \xrightleftharpoons[87^\circ C]{95^\circ C} I$
	[n-$C_6H_{13}OOC$	2-Cl	$C \xrightleftharpoons[98^\circ C]{90^\circ C} I$‡
II06†	n-$C_6H_{13}OOC$	None	$C \xrightleftharpoons[110^\circ C]{127^\circ C} N \xrightleftharpoons[137^\circ C]{137^\circ C} I$
II28	n-$C_8H_{17}OOC$	2-Cl	$C \xrightleftharpoons[85^\circ C]{75^\circ C} I$
II08†	n-$C_8H_{17}OOC$	None	$C \xrightleftharpoons[117^\circ C]{130^\circ C} N \xrightleftharpoons[155^\circ C]{155^\circ C} I$
II30	n-$C_{10}H_{21}OOC$	2-Cl	$C \xrightleftharpoons[90^\circ C]{83^\circ C} I$
II10†	n-$C_{10}H_{21}OOC$	None	$C \xrightleftharpoons[94^\circ C]{105^\circ C} I$

† See [10].

‡ Contains a benzene instead of a pyridine ring.

3. Experimental

IR, ^1H NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX60 spectrometer, and a Hitachi M-808 spectrometer, respectively, under standard conditions. Elemental analyses were carried out with a Perkin–Elmer 250 instrument. Mesomorphic ranges were determined by means of a Mitamurariken micro melting point apparatus, equipped with crossed polarizers.

3.1. *2- And/or 3-methyl or -chlorohydroquinone mono(n-alkyl)ether(2–1)*

The same procedure as in a previous paper [10] was applied to methyl or chlorohydroquinone to afford a liquid. Yield (X = Me): 16 per cent for $R = C_4$, 19 per cent for C_6, 21 per cent for C_8, 21 per cent for C_{10}. (X = Cl): 70 per cent for C_4, 37 per cent for C_6, 19 per cent for C_8, 56 per cent for C_{10}. IR ($CHCl_3$): 3200–3400 (OH), 1200 (ether) cm^{-1} ^1H NMR ($CDCl_3$): δ 3·9–4·0 (t, CH_2O). Elemental analysis results (CHN) were satisfactory.

Table 4. The effect of the aromatic core unit (A) on the transition temperatures of the arenedicarboxylates.

Compound	R	X	A	Transition temperature
III16	n-$C_6H_{13}O$	2- and/or 3-Me	2,6-naphthalene	$C \underset{162°C}{\overset{153°C}{\rightleftharpoons}} N \underset{202°C}{\overset{198°C}{\rightleftharpoons}} I$
III26	n-$C_6H_{13}O$	2- and/or 3-Cl	2,6-naphthalene	C 182°C I
IIIT	n-$C_6H_{13}OOC$	2-Cl	2,6-naphthalene	$C \underset{153°C}{\overset{151°C}{\rightleftharpoons}} I$
IIIP4	n-C_4H_9O	None	3,5-pyrazole	$C \underset{160°C}{\overset{161°C}{\rightleftharpoons}} N \underset{173°C}{\overset{169°C}{\rightleftharpoons}} I$
IIIP6	n-$C_6H_{13}O$	None	3,5-pyrazole	$C \underset{182°C}{\overset{179°C}{\rightleftharpoons}} I$
IIIP8	n-$C_8H_{17}O$	None	3,5-pyrazole	$C \underset{182°C}{\overset{180°C}{\rightleftharpoons}} I$
IIIP10	n-$C_{10}H_{21}O$	None	3,5-pyrazole	$C \underset{182°C}{\overset{178°C}{\rightleftharpoons}} I$

3.2. *n-Alkyl 3-chloro-4-hydroxybenzoate* (*2–2*)

The same acid esterification procedure as in a previous paper [10] was applied to 3-chloro-4-hydroxybenzoic acid and n-alkyl alcohol, with a Dean–Stark trap, to afford a colourless solid. Yield: 70 per cent for $R = C_4$, 83 per cent for C_6, 73 per cent for C_8, 94 per cent for C_{10}. IR (KBr): 3200–3400 (OH), 1700 cm^{-1} (COO). ^1H NMR ($CDCl_3$): δ 4·35 (t, CH_2O). Elemental analysis results (CHN) were satisfactory.

3.3. *Di[4-(n-alkyloxy or n-alkyloxycarbonyl)phenyl] arenedicarboxylate* (*I*)

The same procedure as in a previous paper [10] was applied to arenedicarboxylic acid dichloride (1) and 2–1, –2 to afford colourless or slightly coloured crystalline powder (single spot by TLC). IR (KBr): 1720–1740 (COO), 1200–1250 cm^{-1} (ether, ester). ^1H NMR ($CDCl_3$): δ 3·9–4·4 (t, CH_2O). Elemental analyses results (CHN) were satisfactory.

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