Polar smectogens: polymorphism of some cyanoalkoxybiphenylalkoxybenzoates and related compounds

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Polar smectogens: polymorphism of some cyanoalkoxybiphenylalkoxybenzoates and related compounds

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A series of new cyanoalkoxybiphenylalkoxybenzoates containing a highly dipolar end group electrically and mechanically decoupled from the rigid moiety has been synthesized. The thermal behaviour of these compounds and their precursors (cyanoalkoxyhydroxybiphenyls) has been investigated by means of differential scanning calorimetry and optical polarizing microscopy. It has been found that such compounds often exhibit double melting behaviour through isotropic or smectic phases. A rather rich polymorphism (N, S_A, S_B and S_E phases) is observed at high temperature (100–200°C).

1. Introduction

Some aspects of the liquid-crystalline polymorphism of a series of 4-cyanoalkoxybenzylidene-4'-*n*-alkylanilines were recently reported [1–3]. For this new series of Schiff's bases, the cyano end group is electrically and mechanically decoupled from the rigid aromatic core through an aliphatic chain containing three, four or six carbons. Interesting effects due to the presence of the –C≡N group are evidenced. Compared with the corresponding non-cyano compounds (the classical *n*O.*m*'s) [4–5], the cyano Schiff's bases exhibit an enhanced trend to form smectic phases without displaying any nematic phase at all. Highly ordered S_B phases are observed but the thermal range of the mesophase is narrower than for the corresponding *n*O.*m*'s. The interactions with the highly dipolar cyano groups lead to a rapid crystallization in the solid state. A bimolecular layering is found to occur for some compounds of the series [1–2]. Moreover, a transition from a monomolecular smectic arrangement to a bimolecular one (S_{A_1}–S_{A_2}) is observed in a pure mesogen. This transition can be interpreted in terms of a two dimensional phase separation [3] of the molecular end groups (cyano and methyl respectively). These results have to be contrasted with those obtained for cyanomesogens where the –C≡N is rigidly attached to the aromatic core [6–9]. In such dissymmetric compounds, a sesquimolar smectic arrangement of molecules, incompletely associated head to head, is often observed. In contrast, the polymorphism of cyano mesogens with a decoupled polar end group reveals either monomolecular or bimolecular smectic arrangements. The point of difference between the two structures is simply connected with the specific location of the cyano end groups with respect to the molecular layers. Located at the surface of the monolayers, the polar groups are either equally distributed on both faces of each monolayer leading to the formation of S_{A_1} phases, or else significantly accumulated on only one face, including an antiparallel stacking of the monolayers and giving rise to S_{A_2} phases.
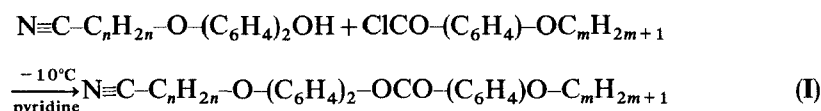
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These results make it worthwhile to investigate further the polymorphism of cyano mesogens with decoupled polar end groups. We report in this paper the thermotropic behaviour of a set of cyanoalkoxybiphenylalkoxybenzoates. These molecules are symmetrical and are formed of a central aromatic core with three phenyl rings and two terminal aliphatic chains. The cyano end group is not carried directly by the aromatic core but instead is attached to the free end of one of the aliphatic chains ($n = 1, 3, 4$ or 6 carbons). It is thus (except for $n = 1$) mechanically and electrically decoupled from the aromatic moiety.

2. Materials
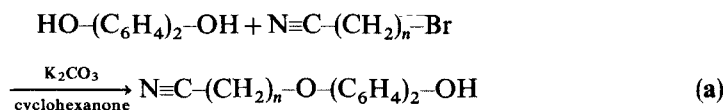
2.1. Synthesis of cyanoalkoxybiphenylalkoxybenzoates

The cyanoalkoxybiphenylalkoxybenzoates under investigation here were prepared according to the reaction [10]:

$$N{\equiv}C\text{-}C_nH_{2n}\text{-}O\text{-}(C_6H_4)_2OH + ClCO\text{-}(C_6H_4)\text{-}OC_mH_{2m+1}$$

$$\xrightarrow[\text{pyridine}]{-10^\circ C} N{\equiv}C\text{-}C_nH_{2n}\text{-}O\text{-}(C_6H_4)_2\text{-}OCO\text{-}(C_6H_4)O\text{-}C_mH_{2m+1} \qquad \textbf{(I)}$$

The mixture was stirred at $-10^\circ C$ for 15 min and then warmed to room temperature. The benzoate was washed in cold ethanol and purified by chromatography with $CHCl_3$–2 per cent NO_2CH_3 as eluent. Finally it was recrystallized from an ethanol–nitromethane mixture and dried under vacuum.

2.2. Synthesis of p-cyanoalkoxyhydroxydiphenyls

These compounds were obtained from the reaction of an α-bromo-ω-cyano-n-alkane with 4,4'-dihydroxybiphenyl in the presence of potassium carbonate within an inert medium [11].

$$HO\text{-}(C_6H_4)_2\text{-}OH + N{\equiv}C\text{-}(CH_2)_n\text{-}Br$$

$$\xrightarrow[\text{cyclohexanone}]{K_2CO_3} N{\equiv}C\text{-}(CH_2)_n\text{-}O\text{-}(C_6H_4)_2\text{-}OH \qquad \textbf{(a)}$$

The formation of the monoether was favoured by using an excess of dihydroxybiphenyl. However the formation of the 4,4'-dicyanoalkoxybiphenyl

$$N{\equiv}C\text{-}(CH_2)_n\text{-}O\text{-}(C_6H_4)_2\text{-}O\text{-}(CH_2)_n\text{-}C{\equiv}N \qquad \textbf{(b)}$$

could not be avoided. A rough separation of the ethers and of the unreacted dihydroxybiphenyl was performed using the differences of solubilities of these compounds in chloroform. Afterwards they were thoroughly separated by means of column chromatography with $CHCl_3$–2 to 10 per cent CH_3NO_2 as eluent. They were recrystallized from an ethanol–water mixture for (a) and pure methanol (or ethanol) for (b). For such compounds, polar solvents are hardly removed, so they are dried for several hours in their crystalline state under vacuum.

2.3. Physicochemical characterizations

All of the chemical species were characterized by microanalysis. The expected elementary composition is found with a good accuracy and table 1 summarizes data for some of the compounds ($n = 3, 6$; $m = 7$). These new compounds were examined by IR

spectroscopy with a Fourier transform NICOLET apparatus. The vibrations phenyl rings ($3050\,cm^{-1}$), aliphatic chains (2980–$2990\,cm^{-1}$), OH group ($3280\,cm^{-1}$) and COO group ($1725\,cm^{-1}$) were unambiguously identified. The C≡N band was identified at $2245\,cm^{-1}$ for the diethers (b) and at $2260\,cm^{-1}$ for the monoethers (a). The C≡N band for the benzoates was observed at $2250\,cm^{-1}$. For $n=1$, the C≡N band was not observed; this is because the close neighbouring of a C≡N and an oxygen in the same molecule strongly reduces the intensity of the IR C≡N line [12–13] and makes it disappear when the –C≡N group and the oxygen atom are bound to the same carbon atom. Finally, NMR experiments (^1H and ^{13}C–300 MHz in $CDCl_3$) were performed (for $n=3$) to ascertain the chemical structure of (a) and (b) and to exclude the possibility of having grafted the polar chain onto an undesirable site.

The thermotropic behaviour of compounds (a), (b) and (I) was analysed by differential scanning calorimetry performed with Mettler FP 85 equipment and by optical polarizing microscopy (Leitz microscope equipped with a Mettler FP 82 hot stage). The nature of the mesophases was identified from the observed texture and DSC.

3. Thermal behaviour of dicyanoalkoxybiphenyls

The essential characteristic of these compounds lies in the fact that the molecules are highly symmetrical from the standpoint of their global chemical architecture and of the dipolar end groups. For $n=3$, 4 and 6 the symmetrical –C≡N end groups are mechanically and electrically decoupled from the aromatic core. With $n=1$, they are more rigidly attached, the molecule being considered to be a rigid one. The $n=3$, 4 and 6 compounds exhibit the usual behaviour, melting from crystal to an isotropic liquid with enthalpies of transition of about $35\,kJ\,mol^{-1}$ (see table 2). Upon decreasing the temperature from the melt, the supercooled liquid abruptly crystallizes; a very sharp and intense exothermic peak is observed from DSC thermograms. No intermediate

Table 1. Elemental analysis.

Compound		C%	H%	N%	O%	Total
(a)	$n=3$	75·85	6·04	5·45	12·73	100·07
		(75·89)	(5·93)	(5·53)	(12·65)	
(a)	$n=6$	76·88	7·12	4·60	10·93	99·53
		(77·28)	(7·12)	(4·75)	(10·85)	
(b)	$n=3$	74·95	6·30	8·68	10·04	99·97
		(75)	(6·25)	(8·75)	(10·00)	
(b)	$n=6$	77·00	8·01	6·85	7·98	99·84
		(77·23)	(7·92)	(6·93)	(7·92)	
(I)	$n=3$ $m=7$	76·44	7·14	2·83	13·77	100·18
		(76·43)	(7·01)	(2·97)	(13·59)	
(I)	$n=6$ $m=7$	77·29	7·72	2·58	12·51	100·10
		(77·19)	(7·60)	(2·73)	(12·48)	

(a) cyanoalkoxyhydroxybiphenyls; (b) dicyanoalkoxybiphenyls; (I) cyanoalkoxybiphenyl-alkoxybenzoates. Percentages given in parentheses are the calculated values.

Table 2.   Melting point and enthalpies of transition of the dicyanoalkoxybiphenyls.

$$NC-(CH_2)_n-O-(C_6H_4)_2-O-(CH_2)_n-CN$$

n	Transition temperature/°C
	Enthalpy of transition/kJ mol^{-1}
1	$C_2 \xleftarrow{\dfrac{c.\ 55}{3}} C_1 \xrightleftharpoons[20]{103} I$ $\qquad \dfrac{115}{23}$
3	$C \xrightarrow{\dfrac{155}{34\cdot3}} I$
4	$C \xrightarrow{\dfrac{156}{35\cdot8}} I$
6	$C \xrightarrow{\dfrac{121\cdot5}{37\cdot5}} I$

Table 3.   Crystallization temperature (°C) of the dicyanoalkoxybiphenyls as a function of the cooling rate (from DSC).

Chain length	Cooling rate/K min^{-1}		
n	10	3	0·1
1	90·5	94·5	98·0
3	138·0	140·5	143·5
4	147·0	151·0	152·5
6	115·0	116·0	117·0

mesophase was observed. For such symmetrical molecules, the relatively strong interactions between the $-C\equiv N$ groups stabilize the crystalline state. The temperature range of existence of the supercooled liquid is not very large (about 10°C) and depends slightly on the cooling rate (see table 3).

The $n = 1$ compound exhibits a double melting behaviour [14] observable either by optical microscopy or DSC. Thus the crystal has two solid polymorphs C_1 and C_2 [15]. When the virgin crystal (recrystallized from ethanol) is heated from room temperature, the crystal melts into an isotropic liquid at 115°C (melting point of C_2). Upon cooling from the melt, the compound crystallizes into the C_1 form for usual or even slow cooling rates (0·1 to 40 K/min) with an intense and very sharp exothermic peak. C_1 melts at 103°C. The crystallization into the C_2 form at $103°C < T < 115°C$ is not observed in the absence of C_2 seeds and the DSC thermograms do not exhibit classical double melting behaviour [15]. From the melt, the C_1 metastable phase tranforms slowly into the C_2 form. From optical microscopy, complete irreversible transformation $C_1 \rightarrow C_2$ needs very slow cooling rates ($< 0·1$ K min^{-1}). In such conditions the $C_1 \rightarrow C_2$ transition is hardly observed from the DSC thermograms. A moderate cooling rate (10 K min^{-1}) of the C_1 form allows us to obtain it stable at room temperature. On heating the $C_1 \rightarrow C_2$ transition is observable either from microscopy observations or
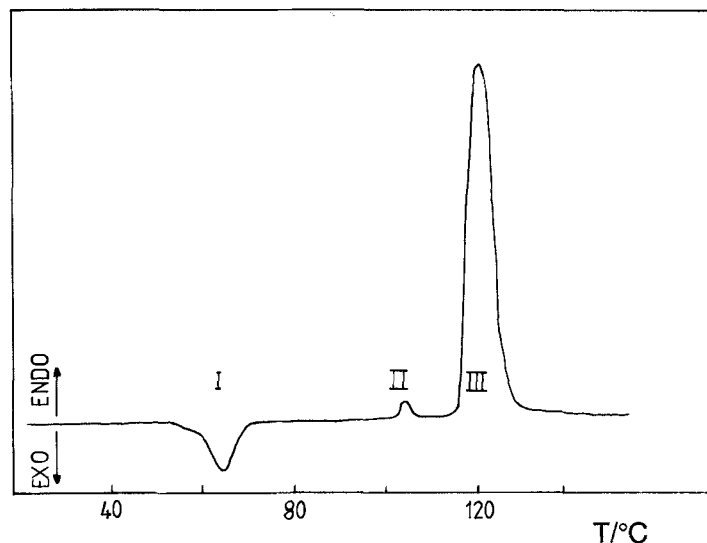
Figure 1. DSC of $NC-CH_2-O-(C_6H_4)-O-CH_2-CN$ peak I: transition from the C_1 (metastable) crystalline form to the C_2 (stable) form; peak II: melting of residual C_1; peak III: melting of C_2.

from DSC experiments. The exothermic enthalpy change (about $3\,kJ\,mol^{-1}$) is in good agreement with the transition enthalpies measured for the $C_1 \to I$ transition [16] $(20\,kJ\,mol^{-1})$ and $C_2 \to I$ transition $(23\,kJ\,mol^{-1})$. From DSC thermograms we can define a temperature ($c.$ 55°C) below which the irreversible transformation does not take place rapidly. If the heating rate is fast enough ($10\,K\,min^{-1}$) the C_1 form does not transform entirely into the C_2 crystalline state and can be superheated up to its melting point (103°C). The DSC thermograms (see figure 1) exhibit an exothermic peak at $c.$ 55°C ($C_1 \to C_2$) followed by a residual peak at 103°C ($C_1 \to I$) and the major melting peak at 115°C ($C_2 \to I$). When the compound is cooled very rapidly from the melt to 77 K and then heated the crystal transforms into the C_2 form at 55°C with a transition enthalpy of $3\,kJ\,mol^{-1}$, which means that even by very fast cooling the C_1 form is always obtained. In such conditions it seems difficult to obtain a third phase with a degree of organization lower than it is in the C_1 (or C_2) phase; the polar end groups induce a very fast and energetic recrystallization. The $n = 3$, 4 and 6 compounds give similar results. Cooling from the melt to 77 K and then heating, no exothermic peak is observed indicating that the crystalline organization is rather independent of the cooling rate (in these cases only one form is observed) and is governed primarily by strong dipolar CN–CN interactions.

4. Double melting behaviour of cyanoalkoxyhydroxybiphenyls

Such compounds are dissymmetric molecules, the OH group being rigidly attached to the aromatic moiety, the cyano end group being attached to the free end of the aliphatic chain. Table 4 gives the thermal properties (transition temperatures and enthalpies) of the (a) series. The thermal behaviour of such cyanophenols is dominated by phenomena related to the double melting process [15], these compounds exhibiting liquid and solid metastable phases. Except for the compound with $n = 4$, the
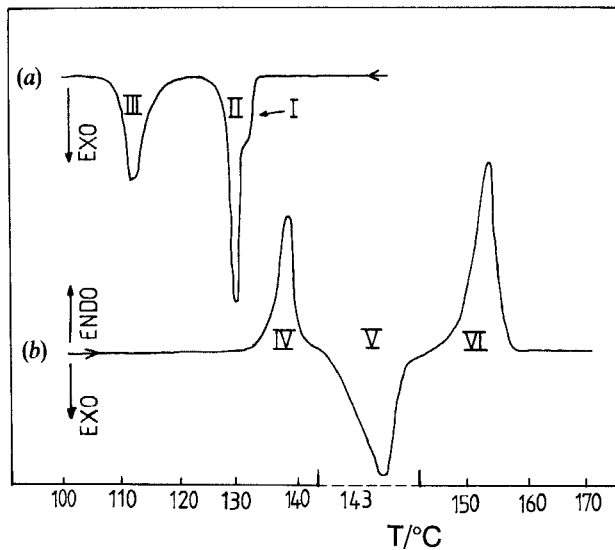
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Figure 2.   DSC of NC–(CH$_2$)$_3$–O–(C$_6$H$_4$)$_2$–OH (a) cooling from the melt showing the sequence
I→S$_A$ (peak I), S$_A$→C$_1$ (peak II), C$_1$→C$_2$ (peak III); (b) heating from the metastable C$_1$
form showing the sequence C$_1$→I (peak IV), I→C$_2$ (peak V), C$_2$→I (peak VI).

Table 4.   Polymorphism, phase transition temperatures and enthalpy changes of
cyanoalkoxyhydroxybiphenyls.

| Compound	Transition temperature/°C Enthalpy of transition/kJ mol^{-1}		

(1) Very slow cooling ($<$0·5 K min^{-1}). (2) Medium cooling (3–20 K min^{-1}).

Table 5. Polymorphism of cyanoalkoxyhydroxybiphenyl ($n=3$) as a function of the cooling rate.

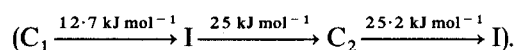| Cooling rate/K min^{-1}	Transition temperature/°C
40	$I \xrightarrow{134} S \xrightarrow{132} C_1$
20	$I \xrightarrow{134} S \xrightarrow{132} C_1 \xrightarrow{104} C_2$
3	$I \xrightarrow{134} \bullet S \xrightarrow{133} C_1 \xrightarrow{120} C_2$
1	$I \xrightarrow{134 \cdot 5} C_1 \xrightarrow{124} C_2$
$\leqslant 0\cdot5$	$I \xrightarrow{135 \cdot 4} C_2$

monocyanoethers (a) have two solid polymorphs denoted C_1 and C_2 in table 4. We take T_{M1} and T_{M2} to be the melting points of respectively C_1 and C_2; they are labelled in such a way that $T_{M1} < T_{M2}$. The case $n=3$ typically illustrates the thermal behaviour of this series of cyanophenols. Numerical data concerning this product (polymorphism versus cooling rate) are listed in table 5 while figure 2 presents two typical thermograms. The virgin crystal (recrystallized from ethanol and dried under vacuum) is obtained under the C_2 form and melts into an isotropic liquid at T_{M2}. Upon cooling from the melt with a slow cooling rate ($<0\cdot5$ K min^{-1}) crystallization occurs at a temperature $T_{M1} < T < T_{M2}$ and leads back to the C_2 form. By increasing the cooling rate (c. 1 K min^{-1}) the isotropic liquid recrystallizes into the C_1 form which rapidly transforms into the C_2 state. DSC thermograms show two recrystallization exotherms corresponding to the C_1 and C_2 forms. On increasing the cooling rate more (c. 5 K min^{-1}) the transition from the melt to the solid occurs via a very unstable monotropic lamellar phase whose texture corresponds to an S_A (or S_B) phase. This mesophase is readily observable by optical microscopy. The DSC thermograms (see figure 2(a)) show no more than a shoulder (labelled I) in the exothermic peak (II) corresponding to crystallization into the C_1 phase. The $C_1 \rightarrow C_2$ transition is responsible for the exotherm III. From the C_1 phase (the whole crystal is in the C_1 form when following the routine [16]) the crystal can be heated according to the cycle illustrated in figure 2(b). First C_1 is brought to its melting point T_{M1} of 134·5°C (peak IV), then the isotropic liquid recrystallizes into the C_2 form (V) which melts again at T_{M2} of 150·1°C (VI).

The melting points of the two forms are rather different. The enthalpy change of the C_2 to isotropic liquid transition is much higher than that of the melting of the metastable C_1 form. The enthalpies of crystallization

$$(I \xrightarrow{12 \cdot 7 \text{ kJ mol}^{-1}} C_1 \xrightarrow{12 \cdot 3 \text{ kJ mol}^{-1}} C_2)$$
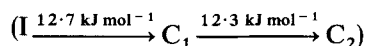
are in agreement with those measured during the double melting process

$$(C_1 \xrightarrow{12 \cdot 7 \text{ kJ mol}^{-1}} I \xrightarrow{25 \text{ kJ mol}^{-1}} C_2 \xrightarrow{25 \cdot 2 \text{ kJ mol}^{-1}} I).$$

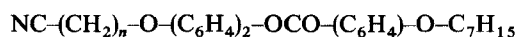226   F. Barbarin *et al.*

With rapid cooling rates (see table 5) the C_1 crystalline state is obtained in a stable form at room temperature. When heated it transforms rapidly into the C_2 form. As for the $n = 1$ dicyanoalkoxybiphenyl we can define the temperature (c. 60°C) below which the irreversible transformations ($C_1 \rightarrow C_2$) do not take place. An exothermic $C_1 \rightarrow C_2$ peak is observed by DSC. The enthalpy change (about 7 kJ mol^{-1}), a little lower than that measured from recrystallization or double melting process could indicate that in such experiments, the sample has partially transformed into the C_2 form during the cooling. These situations are summarized in table 5. A very slow cooling rate leads to the most stable C_2 form while irreversible transformations $S \rightarrow C_1 \rightarrow C_2$ are observed with a moderate cooling rate. A very fast cooling rate can also induce a solid state retaining the smectic arrangement.

The $n = 1$ compound gives similar results. The pristine sample crystallizes into the stable C_2 form which melts at 159°C with a transition enthalpy of $23 \cdot 5 \text{ kJ mol}^{-1}$. Similar to the $n = 3$ case, two irreversible transitions occur on fast cooling. They correspond to a smectic A (or B) phase followed by the crystal–crystal $C_1 \rightarrow C_2$ transition. The DSC recrystallization peak is an unresolved doublet ($C_1 \rightarrow C_2$) with a shoulder corresponding to the $S \rightarrow C_1$ transition. The different enthalpies of transition cannot be calculated from this recrstallization peak. They are obtained by heating the C_1 form [16] which leads to the double melting behaviour. In a way similar to the $n = 3$ case, the enthalpy of the $C_2 \rightarrow I$ transition is larger than that of the $C_1 \rightarrow I$ transition and the two melting points are rather different ($\Delta T = 32°C$).

The $n = 1$ and $n = 3$ cyanophenols exhibit very similar double melting behaviours. Liquid–solid and solid–solid irreversible transformations are observed. In a general manner the crystallization in the C_1 form corresponds to a sharp DSC peak ($I \rightarrow S \rightarrow C_1$) followed by a larger $C_1 \rightarrow C_2$ peak. The melting points of C_1 and C_2 are rather different

Table 6. Polymorphic scheme of some cyanoalkoxybiphenylalkoxybenzoates. Influence of the decoupling of the polar end group.

$$NC-(CH_2)_n-O-(C_6H_4)_2-OCO-(C_6H_4)-O-C_7H_{15}$$

n	Transition temperature/°C
	Enthalpy of transition/kJ mol^{-1}

(†) See table 8.

Figure 3. Infrared spectra of the two polymorphs C_1 and C_2 of $NC-(CH_2)_3-O-(C_6H_4)_2-OH$: single -OH line for C_1, doublet for C_2.

as are the corresponding enthalpies of transition. We notice that the S and C_1 metastable forms are slightly more stable for $n = 3$ than for $n = 1$. However, it is worth noting that the stability of any of the metastable phases depends strongly on the purity of the compound. The purer the product the less stable are the metastable forms. Moreover it should be noted that the crystalline metastable C_1 form (for both $n = 1$ and $n = 3$) is less stable than that of the $n = 1$ cyanoalkoxybiphenyl. In the latter case the presence of the two polar $-C\equiv N$ end groups induces a very fast recrystallization into the metastable C_1 form which can be easily stabilized at room temperature.

For $n = 1$ and $n = 3$ cyanophenols, the two polymorphs C_1 and C_2 have characteristic infrared spectra (see figure 3). C_1 shows a narrow single band (at $3391 \, cm^{-1}$) assigned to the OH group while C_2 gives a distinctive spectrum (a doublet at $3347 \, cm^{-1}$ and $3435 \, cm^{-1}$) indicating that for such a crystalline arrangement there are two inequivalent OH sites. No shift of the $C\equiv N$ band was observed. For the symmetrical bipolar cyanoalkoxybiphenyl $(n = 1)$ the C_1 and C_2 IR spectra do not exhibit any difference or significant shift of the lines.

For $n = 6$, a somewhat similar behaviour is observed. The pristine sample recrystallized from ethanol (coloured parallelograms) melts at $137 \cdot 6°C$ recrystallizes into the C_2 form (from optical microscopy) and melts again at $141 \cdot 5°C$. By cooling at usual cooling rates, the compound crystallizes into the C_2 form and the $C_1 \rightarrow I$ transition at $137 \cdot 6°C$ is no longer observed. Contrary to what occurs for $n = 1$ and $n = 3$ the two melting points are very close to one another and the classical double melting behaviour [15] is not observed from DSC thermograms. For $n = 4$, only one melting point was observed.

It would be of interest to compare these results concerning the cyanoalkoxyhydroxybiphenyls to those of the preceding section dealing with dicyanoalkoxybiphenyls. In the latter case we observe the effects of the presence of two polar (CN) groups
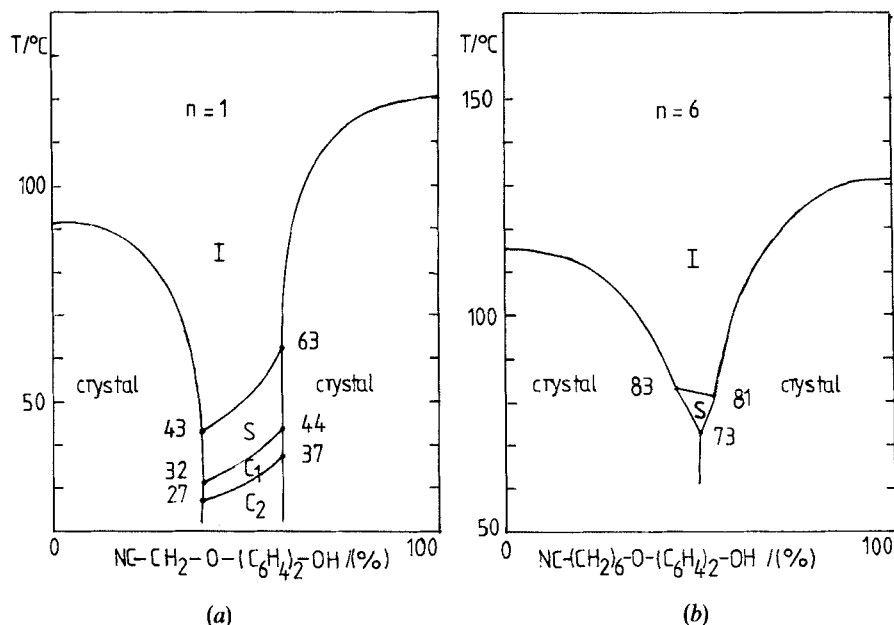
Figure 4. Phase diagrams (obtained by cooling) showing induced phases in binary mixtures of dicyanoalkoxybiphenyls $NC-(CH_2)_n-O-(C_6H_4)_2-O-(CH_2)-CN$ and cyanoalkoxyhydroxybiphenyls $NC-(CH_2)_n-O-(C_6H_4)_2-OH$. (a) $n=1$ for both compounds; (b) $n=6$ for both compounds.

electrically and mechanically decoupled from a rigid aromatic core. The interactions between these polar end groups are strong enough to lead to the abrupt crystallization of the system and prevent the occurrence of any mesophase. With the cyanoalkoxyhydroxybiphenyls, we also consider rod-like molecules with two polar end groups. The situation, however, is different since one of these groups (CN) is decoupled from the central aromatic core while the other (OH) is rigidly bound to this core. This architecture results into a complex melting behaviour closely related to mesomorphism [15] if not to mesomorphism itself. From these two antagonist tendencies (brutal crystallization versus multiple melting) it is very tempting to analyse binary mixtures of dicyanodiethers and monocyanoalkoxyphenols. We have prepared some of these mixtures by the contact method of Kofler [17] which allows us to obtain an indicative shape of the phase diagram. Figure 4 shows typical examples of such binary mixtures: $n = 1$ and $n = 6$. The two types of binary mixtures are capable of giving rise to induced smectic mesophases.

5. Polymorphism of cyanoalkoxybiphenylalkoxybenzoates

The thermotropic liquid-crystalline behaviour of these compounds was first studied by optical microscopy and by DSC. They all present a rather rich polymorphism and exist as liquid crystals over a temperature range of about 100°C. All have a high clearing temperature (roughly 200°C). Upon cooling, the isotropic melts transform into a nematic phase (short aliphatic chain) and then into smectic phases. A fan-shaped focal-conic texture characterizes a smectic A phase. In most samples wide homeotropic zones were observed. Decreasing the temperature, transient striations are indicative for

Table 7. Polymorphic scheme of some cyanoalkoxybiphenylalkoxybenzoates. Influence of the aliphatic chain length.

$$NC-(CH_2)_n-O-(C_6H_4)_2-OCO-(C_6H_4)-O-C_mH_{2m+1}$$
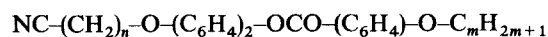
n	m	Transition temperature/°C
		Enthalpy of transition/kJ mol^{-1}

4	12	$C \xrightarrow[30 \cdot 0]{112 \cdot 6} S_E \xleftarrow[2 \cdot 2]{122 \cdot 7} S_B \xleftarrow[2 \cdot 0]{139 \cdot 6} S_A \xleftarrow[5 \cdot 0]{195 \cdot 7} I$

| 4 | 16 | $C \xrightarrow[36 \cdot 5]{114 \cdot 8} S_E \xleftarrow[2 \cdot 3]{121 \cdot 7} S_B \xleftarrow[2 \cdot 0]{138 \cdot 4} S_A \xleftarrow[6 \cdot 0]{196 \cdot 1} I$ |

6 12 $C \xrightarrow[30 \cdot 5]{105 \cdot 9} S_B \xleftarrow[2 \cdot 2]{129 \cdot 4} S_A \xleftarrow[5 \cdot 0]{182 \cdot 2} I$; $S_E \xleftarrow[1 \cdot 6]{90 \cdot 0}$

| 6 | 16 | $C \xrightarrow[38 \cdot 5]{110 \cdot 5} S_B \xleftarrow[2 \cdot 3]{130 \cdot 2} S_A \xleftarrow[6 \cdot 5]{181 \cdot 3} I$ |

Table 8. Double melting behaviour of cyanoalkoxybiphenyloxybenzoate, the CN is decoupled from the rigid part ($n=4$, $m=7$) or not ($n=1$, $m=7$).

$$NC-(CH_2)_n-O-(C_6H_4)_2-OCO-(C_6H_4)-O-C_7H_{15}$$

n	Transition temperature/°C
	Enthalpy of transition/kJ mol^{-1}

1   $C_1 \xrightarrow[6]{c.\ 63} C_2 \xrightarrow{127} \cdots$; $c.\ 70\uparrow 6 \xleftarrow{25}$; $C_1' \quad C_1'' \xleftarrow{} S_A \xleftrightarrow{}$; $86, 5/93 \xrightarrow{} S_A \xrightarrow{} C_2 \xrightarrow{}$

4   $C_2 \xrightarrow{115}{19} \cdots$; $c.\ 100 \xrightarrow{(2)} \xrightarrow{107} S_E \xleftrightarrow{}$; $C_1 \xleftarrow{}$; $\xrightarrow{} S_E \xrightarrow{(1)} C_2 \xrightarrow{}$

(1) Slow heating rate ($c.$ 0·5 K min^{-1}). (2) Rapid heating rate ($c.$ 10 K min^{-1}).

a smectic A to smectic B phase transition while persistent concentric arcs in the texture reveal the occurrence of an S_E phase. DSC experiments show [18] that the S_B–S_A and S_E–S_B phase transitions are first order, the transition enthalpies lying in the range 2–3 kJ mol^{-1}. The results in table 6 show the influence of the cyano chain length on the mesomorphic behaviour. For a given cyano chain length, the influence of the alkyl chain length is given in table 7.

5.1. *Influence of the chain lengths*

For a relatively short alkyl chain (i.e. largely shorter than the aromatic part of the molecule) the high temperature mesophase is nematic. The nematic to isotropic transitional enthalpy is low (less than or equal to 1 kJ mol^{-1}). This nematic phase exists over a temperature range of about 20 to 30°C. At lower temperatures an S_A phase is observed, the S_A–N transitional enthalpy being less than 1 kJ mol^{-1}. This S_A phase extends over a relatively wide range of temperature (*c.* 50°C). The (almost) rigid cyano chain for $n = 1$ leads to a situation such that the cooling of the S_A phase leads to the crystalline state. In contrast, for longer cyano chains S_B and S_E phases are observed.

A lengthening of the alkyl chain ($m = 12$ or 16 instead of $m = 7$) causes the stability of the lamellar phases to increase. The liquid crystal does not display a nematic phase but transforms directly into an S_A phase with an enthalpy change of 5 to 7 kJ mol^{-1}. The thermal stability range of the S_B and S_E phases is noticeably increased.

These results should be compared with those obtained for compounds similar in architecture to the cyanoalkoxybiphenylalkoxybenzoates but without the polar CN end group [19]. Of interest is the comparison with cyanomesogens the polar group of which is rigidly bound to the central aromatic core [6–7]. The compounds investigated here seem to exhibit a somewhat richer polymorphism, even though the clearing temperatures and stability range of the mesophases are almost identical. A possible explanation could be that the occurrence of ordered mesophases is largely governed by the interactions between the aromatic cores in their own register and by the alkyl chain length but those ordered phases are stabilized by the CN–CN interactions at the interface. The cyanomesogens can give rise to two possible smectic arrangements, either a monomolecular layering (CH_3 and CN groups equiprobably distributed at the interfaces between the layers) or a bimolecular layering (a largely CH_3 interface alternating with a largely CN interface). In both cases, molecules belonging to two different layers or sublayers can dimerize by setting their CN groups side-by-side in an antiparallel fashion. These interactions can in turn result (or not) in a stabilization of the lamellar mesophase.

In the dicyanodiethers, these interactions were strong enough to mediate an abrupt crystallization. Here they are modulated by the strong thermal agitation of the chain ends of which one-half are non-polar. This modulation prevents a strong crystallization and allows the existence of a domain over which ordered lamellar phases can exist.

Preliminary X-ray investigations of the liquid-crystalline phases [20] confirm the identification of the S_A, S_B and S_E phases. The determination of the structure and lamellar periodicity is in progress and will be published in a forthcoming paper.

5.2. *Crystalline state*

Most of the compounds behave classically and exhibit only one crystalline phase C_2 which can be obtained either by recrystallization from a convenient solvent or by cooling the melt at any cooling rate (up to 50 K min^{-1}). For an extremely fast cooling (tempering at liquid nitrogen temperature) a phase C is formed which transforms on

heating into the C_2 phase. An exothermic enthalpy change of about $10 \, kJ \, mol^{-1}$ at temperatures of 30–50°C is evidenced from DSC. The benzoates ($n=1$, $m=7$; $n=4$, $m=7$), however behave in a more complex way which has something to do with the double melting behaviour of cyanoalkoxyhydroxybiphenyls and dicyano-alkoxybiphenyls.

5.3. n = 1, m = 7 benzoate

This compound exhibits a rather more complex melting behaviour occurring from the possibility of obtaining different crystalline states. The virgin crystal, grown from an appropriate solvent is obtained from a C_1 form which transforms into the C_2 form at 62·8°C via an endothermic peak (about $7 \, kJ \, mol^{-1}$). The $C_2 \rightarrow S_A$ transition occurs at 127°C with an enthalpy change of $26·5 \, kJ \, mol^{-1}$ (see figure 5(a)). From a sample with an homeotropic alignment in the S_A phase, usual cooling rates lead to a crystallization into the C_2 form, stable at room temperature (a sharp DSC exothermic recrystallization peak of about $25 \, kJ \, mol^{-1}$ is observed). Upon heating, this C_2 phase melts at 127°C without any other transformation (see figure 5(b)). A recrystallization at constant temperature [16] (about 75°C) gives needles (noted C_1') and large dark plages (noted C_1'') which grow very slowly from the S_A phase. Fast heating rates allow us to determine the $C_1'' \rightarrow S_A$ transition at 86·5°C and the $C_1' \rightarrow S_A$ transformation at 93°C (figure 5(c)). The C_1' and C_1'' phases stable at room temperature (after cooling) transform very rapidly into the C_2 form at 68·7°C (endothermic transition). Since the transformation C_1', $C_1'' \rightarrow C_2$ occurs rapidly, the DSC thermograms only exhibit residual melting peaks at 86·5°C and 93°C. Without such a process, the enthalpies of the C_1', $C_1'' \rightarrow S_A$ transitions could not have been measured. The endothermic transformation C_1',
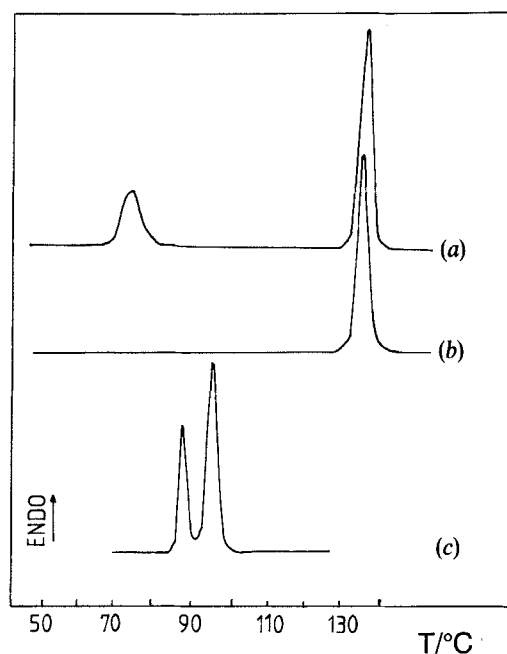

Figure 5. DSC of the cyanomethoxybiphenylheptyloxybenzoate $NC-CH_2-O-(C_6H_4)_2-$ $OCO-(C_6H_4)-OC_7H_{15}$ (a) pristine material; (b) heating from the C_2 form; (c) heating from the (C_1', C_1'') metastable form(s).

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$C''_1 \rightarrow C_2$ occurs at a temperature slightly different from the $C_1 \rightarrow C_2$ one (respectively 68·7°C and 62·8°C from DSC for a given heating rate). The enthalpies of the C'_1, $C''_1 \rightarrow C_2$ transitions do have not reproducible values. Probably a partial transformation into C_2 occurs during the cooling process.

5.4. n = 4, m = 7 *benzoate*

This compound (DSC thermograms of which are given in figure 6) exhibits a classical double melting behaviour [15]. A virgin C_2 crystal melts at 114·5°C to give an S_E phase. On slow cooling (cooling rate < 10 K min^{-1}) the melt crystallizes into a C_1 form, which in contrast to the preceding case is stable; C_1 can be heated (see figures 6 (a) and (b)) to melt at 107°C (peak I). The C_1–C_2 solid transformation is very slow; at 100°C it needs about one hour to undergo. Thus the C_1–C_2 transition temperature cannot be measured with accuracy. The enthalpy change at the C_1–S_E transition can then be measured and is not very different from the C_2–S_E enthalpy change (respectively 17 and 19 kJ mol^{-1}). The smectic E phase obtained by the melting of C_1 crystallizes into C_2 (peak II) when heated (the transformation S_E phase (peak III).

A fast (or very fast) cooling of the sample leads to a freezing into a less ordered phase denoted C which transforms into C_1 on heating (see figure 6 (c)). The transformation of the frozen phase into C_1 is easily observed in the DSC thermograms (transition temperature between 40 and 60°C, peak IV). The enthalpy change ΔH is about 10 kJ mol^{-1} for very fast cooling (> 500 K min^{-1}) and $\Delta H = 3$ kJ mol^{-1} for a moderate cooling rate (20 K min^{-1}) indicating that the transformation into the C phase is not complete.
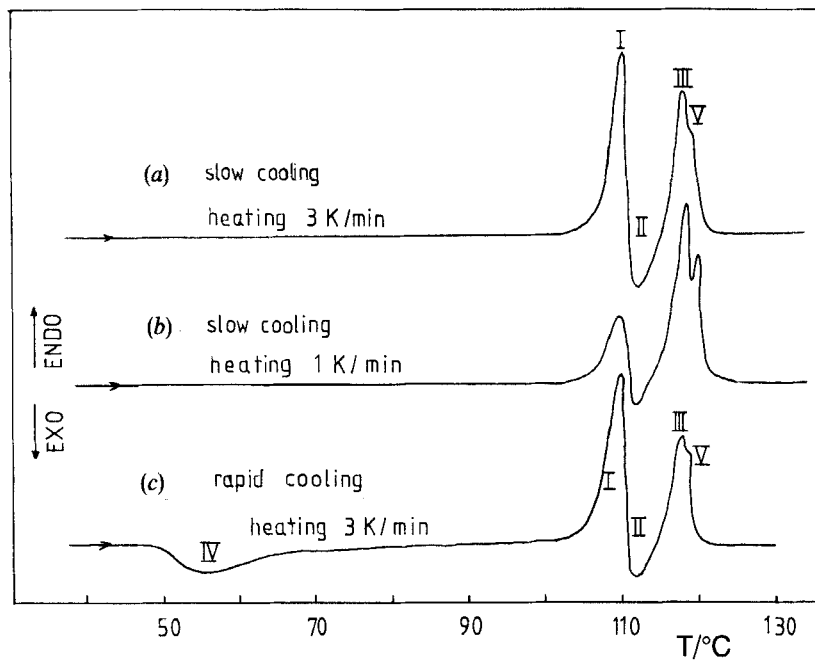

Figure 6. DSC of the cyanobutoxybiphenylheptyloxybenzoate NC–(CH$_2$)$_4$–O–(C$_6$H$_4$)$_2$–OCO–(C$_6$H$_4$)–O–C$_7$H$_{15}$ for different heating rates. Peak I: $C_1 \rightarrow S_E$–peak II: $S_E \rightarrow C_2$–III: $C_2 \rightarrow S_E$–IV: from the C less ordered solid phase to C_1–V: $S_E \rightarrow S_B$.

The ($n = 1, m = 7$) and ($n = 4, m = 7$) compounds show similar behaviour according to the unusual double melting scheme defined by Ohta and his co-workers [15]. In the first case the transformation C_1-C_2 is obtained via an S_A phase while for ($n = 4, m = 7$) the transformation occurs via a much more ordered phase (S_E). On the one hand the C_1 phase is not stable ($n = 1, m = 7$) and the C_1-C_2 solid transition can be observed at low temperature (70°C), on the other hand the C_1 phase is always obtained on cooling for the ($n = 4, m = 7$) compound and is stable from room temperature up to its melting point. The transformation C_1-C_2 occurs via a fluid phase at $T > T_{M1}$ while the C_1-C_2 solid-solid transition occurs very slowly.

6. Conclusion

As a conclusion it is worth pointing out that the present work emphasizes the effects of the presence and location of polar end groups in some mesogens and related compounds derived from biphenyl. The main feature of the dicyanodiethers is their trend to an extremely rapid crystallization into their most symmetrical (C_1) solid phase. A very slow transformation of this C_1 phase into a C_2 polymorph occurs for $n = 1$ (that is to say for the CN's not entirely decoupled from the rigid aromatic core). This latter transformation is not observed for $n = 3$, 4 or 6 (CN's electrically and mechanically decoupled). The cyanoalkoxyhydroxybiphenyls have a stable symmetrical C_1 phase which undergoes more rapidly [than for the dicyanomethoxybiphenyl] a transformation into the less symmetrical C_2 form. Besides the C_1-C_2 polymorphism in the solid state, some of this cyanophenols have a mesomorphic phase of weak stability. Binary mixtures between dicyanoalkoxybiphenyls and cyanoalkoxyhydroxybiphenyls reveal an interesting potentiality for inducing mesophases from the disorganization of a crystalline arrangement.

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