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Reentrant phenomena in cyano substituted biphenyl esters containing flexible spacers

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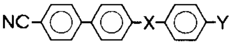
A number of 4′-substituted phenyl 4-(4′-cyano-4-oxybiphenyl)butanoates have been synthesized to study the effects of the $-O-(CH_2)_3COO-$ inter-ring linkage on mesomorphic behaviour. Transition temperatures have been determined and are compared with those of the phenyl cyanobiphenylmethanoate analogues. In general, the butanoates exhibit lower melting points but in all cases, a lower nematic–isotropic transition is observed. An interesting feature of some members of the butanoate series is the presence of several reentrant mesophases. A unique phenomenon observed while studying the behaviour of one of the butanoates was the appearance of smectic filaments from the isotropic liquid on cooling. These filaments, through an unusual process, eventually form the typical smectic A texture. Formation of an S_A phase from the isotropic liquid or the nematic phase in this fashion has not been reported previously.

1. Introduction

Recently, a great deal of emphasis has been placed on the synthesis and characterization of mesomorphic compounds which contain the terminal cyanobiphenyl moiety. Interest in this class of compounds results from the desirable properties for use in optical devices, low melting points, wide nematic ranges and high positive dielectric anisotropies. In addition, these compounds may also exhibit unique and interesting reentrant liquid crystal phases.

A survey of analogous compounds [1] indicates that, in general, varying the inter-ring linkage affects the number and nature of observed liquid crystal phases as well as transition temperatures of the mesophases. Several investigators [2–5] have synthesized mesogenic molecules containing the cyanobiphenyl moiety and a number of inter-ring linkages with the general structure:



where

$$X = -COO-, -OCH_2-, \text{ or } -CH_2-CH_2-$$

$$Y = \text{alkyl, alkoxy, or other substitutents.}$$

It has been reported that the mesomorphic compounds with $X = -COO-$ have higher melting points and clearing points than either of the $-OCH_2-$ or $-CH_2-CH_2-$

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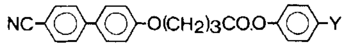
analogues. Also, the compounds in this series exhibit a limited number of smectic mesophases.

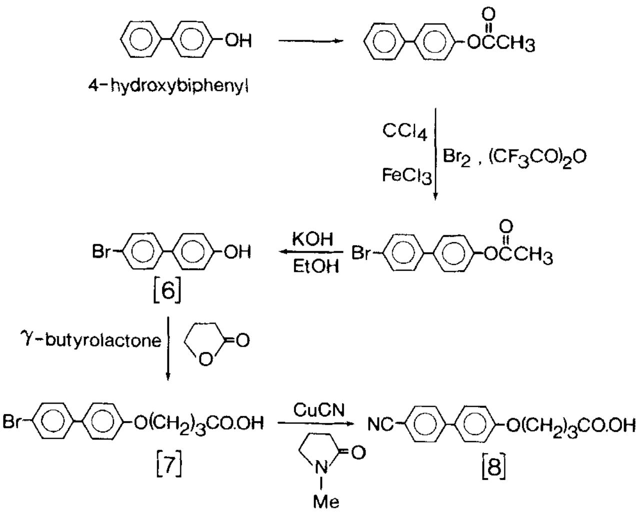
With these studies in mind, it was considered of interest to synthesize a series of compounds containing a $-O(CH_2)_3COO-$ inter-ring linkage. This is, in a sense, incorporating a single linkage which combines the ester, ether and $-CH_2-$ units in the inter-ring linkage. To our knowledge compounds containing this inter-ring linkage have not been reported previously. Comparisons of the butanoates synthesized in the present study with the previously reported $-COO-$, $-OCH_2-$ and $-CH_2-CH_2-$ analogues will be made to further understand the affects of the inter-ring linkage on the mesogenic behaviour of this class of compounds.

2. Synthesis

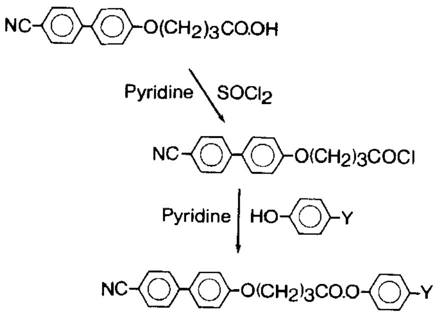
Synthesis of the 4′-*Y*-phenyl 4-(4′-cyano-4-oxybiphenyl)butanoates of the general structure



involves two schemes:



Scheme 1. Synthesis of 4-(4′-cyano-4-oxybiphenyl)butanoic acid.



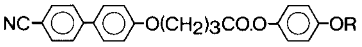
Scheme 2. Preparation of 4′-*Y*-phenyl 4-(4′-cyano-4-oxybiphenyl)butanoates [9].

3. Results and discussion

Table 1 summarizes the mesomorphic behaviour for 4′-*n*-alkoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoates with varying chain lengths. In the methoxy terminally substituted compound, only a monotropic nematic phase is observed. For chain lengths with C_2–C_5 in the terminal alkoxy group, an enantiotropic nematic phase is observed exclusively. The C_7–C_{10} butanoates, however, exhibit interesting mesomorphic behaviour which will now be described in detail.

For the 4′-*n*-heptoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoate, both a smectic and a nematic phase are observed on heating. Cooling gives rise to an enantiotropic smectic (S_1) phase and two additional monotropic smectic (S_2 and S_3) phases. The S_1 observed at 120°C (see table 1) appears to be smectic A while the S_2 and S_3 phases were difficult to identify. These are, at present, under investigation and the results will be published separately.

Table 1. Transition temperatures (in °C) of 4′-*n*-alkoxyphenyl 4-(4′-cyano-4-oxybiphenyl)-butanoates).



R	C–S_6, S_5 S_4, S_3, S_2, S_1 N or I	S_6–S_5	S_5–S_4	S_4–S_3	S_3–S_2	S_2–S_1	S_1–N or I	N–I
CH_3	146·0	–	–	–	–	–	–	(144·3)
C_2H_5	134·0	–	–	–	–	–	–	146·6
C_4H_9	123·0	–	–	–	–	–	–	136·2
C_5H_{11}	106·5	–	–	–	–	–	–	126·6
C_7H_{15}	75·9	–	–	–	(39·2)	(45·0)	120·0	124·0
C_8H_{17}	81·7	(44·0)	(49·3)	(50·6)	(52·8)†	(54·6)	124·7	125·2
$C_{10}H_{21}$	71·5	–	–	–	(60·6)†	126·0	131·2	–

( ) Monotropic transition.
† Reentrant mesophase.

4′-*n*-Octoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoate is an interesting compound in that it exhibits two enantiotropic and five monotropic liquid crystal phases. The mesophase observed at the highest transition temperature (125·2°C) is a nematic phase having a very narrow range. It is preceded by an S_1 phase which has a strong tendency to become homeotropic and appears to be smectic A. Of the five monotropic mesophases exhibited by this compound, S_3 appears to be a smectic C and S_4 a reentrant nematic. It is difficult to identify the S_6, S_5 and S_2 mesophases at present; textures of S_5 and S_6 suggest that they may also be reentrant. The nature of these phases, once characterized and identified, will be reported in a future communication.

The final compound in the series, 4′-*n*-decoxyphenyl 4-(4′-cyano-4-oxybiphenyl)-butanoate, exhibits two enantiotropic smectic phases and a monotropic mesophase. The monotropic phase observed at 60·6°C is either smectic C or reentrant nematic as shown in figure 1. The enantiotropic phase observed at 131·2°C for this compound has the typical smectic A texture (see figure 2). The second smectic phase (71·5°C) also has a typical fan texture but with the ends broken.

A unique phenomenon observed with this compound is the formation of a smectic A phase from the isotropic liquid on cooling. In most cases, the S_A phase separates out on cooling the isotropic or nematic phase in the form of batonnets. These

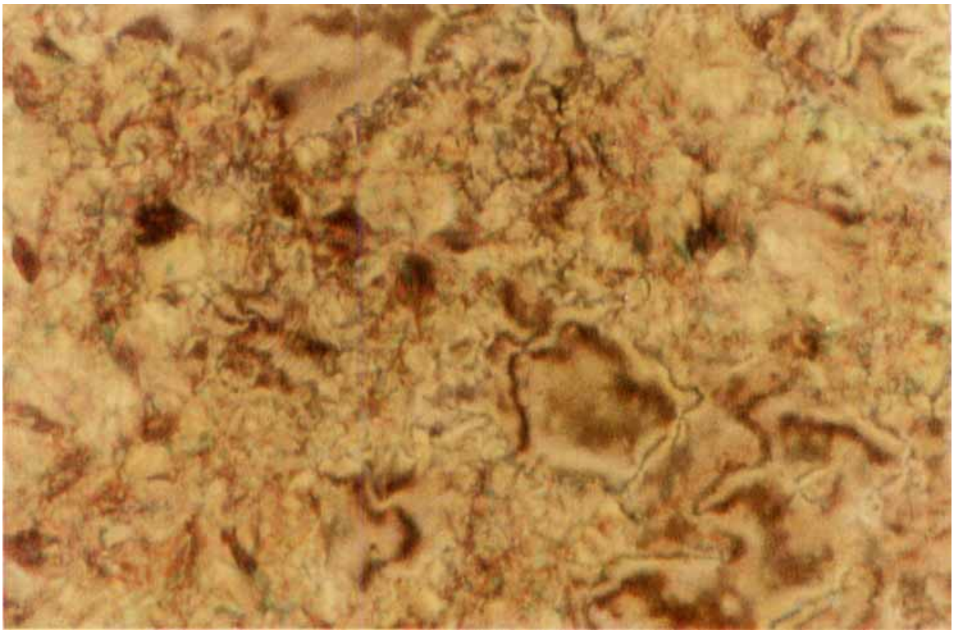


Figure 1. Smectic C or reentrant nematic phase of 4′-decoxyphenyl 4-(4′-cyano-4-oxybiphenyl)-butanoate observed on cooling at 60·6°C through a polarizing microscope with crossed polarizers. Magnification × 320.

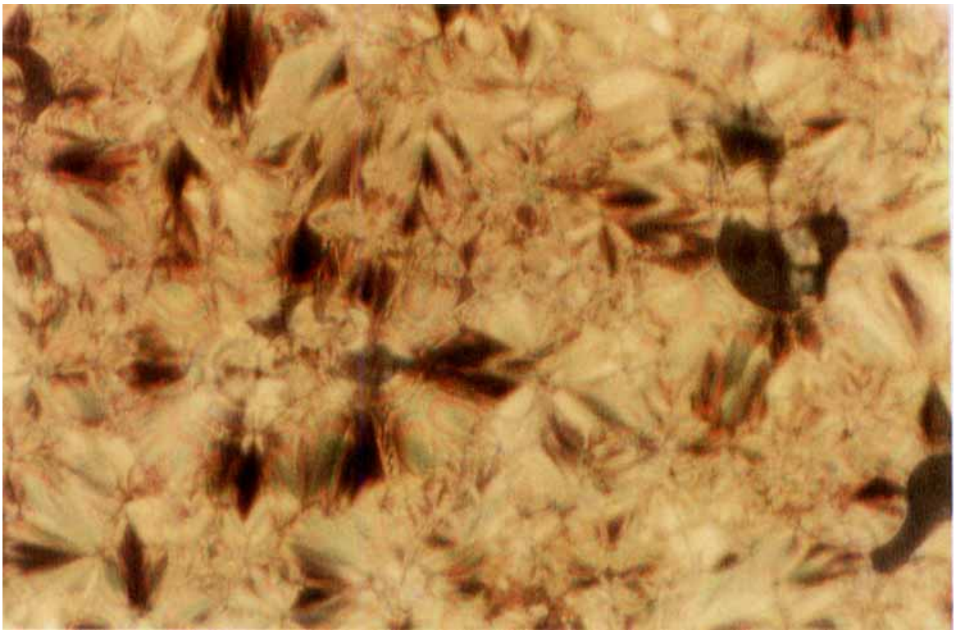
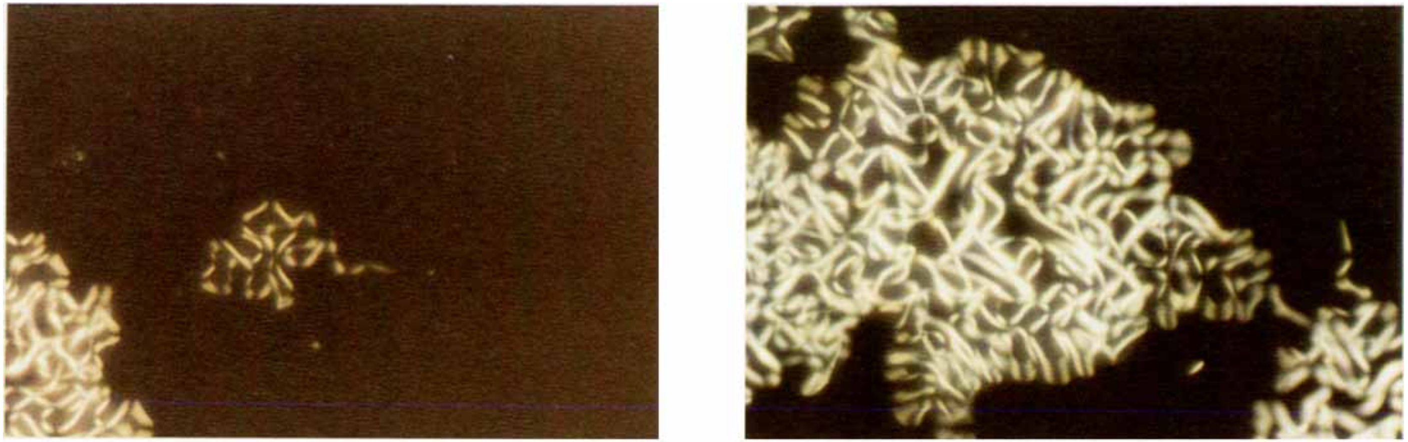


Figure 2. Smectic A phase of 4′-decoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoate at 131·2°C.



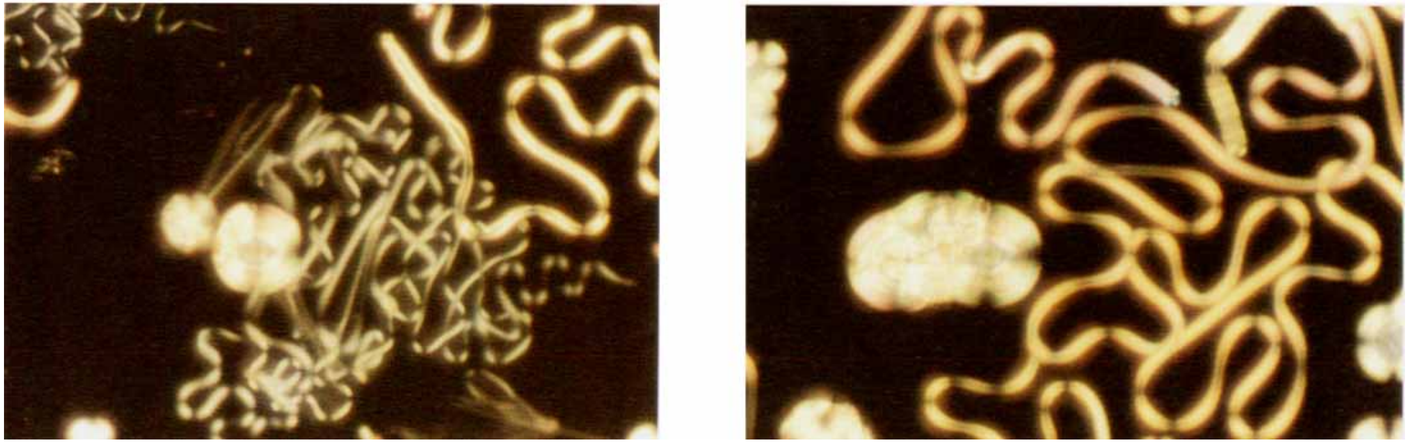


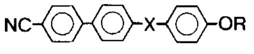
Figure 3. Appearance of smectic filaments from the isotropic liquid of 4′-decoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoate.

Figure 4. Smectic filaments formed from the isotropic liquid of 4′-decoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoate.

bâtonnets then coalesce to form the focal-conic fan texture. When the isotropic liquid phase of the C_{10} butanoate is cooled, the formation of the smectic regions is unusual. Microscopic observations give the following typical sequence of events. First, filaments of the S_A phase, a few microns in diameter, form and grow in length. After some time, these filaments are suddenly and rapidly pulled into compact, nearly circular regions, which formed concurrently. These domains eventually merge to form the typical S_A phase (see figures 3(*a*), (*b*) and 4(*a*), (*b*)). A detailed description of this process will be reported elsewhere.

Table 2 lists transition temperatures for several 4′-alkoxyphenyl(cyano-oxybiphenyl)butanoates and analogous 4′-alkoxyphenyl(cyanobiphenyl)methanoates (X = -COO-). Careful examination of the data in table 2 indicates that the methanoates have higher N–I transition temperatures and, in most cases, higher melting points. The higher N–I transition temperatures can be attributed to the enhanced anisotropies of molecular polarizability afforded by the participation of the -COO- linkage in the overall conjugation of the molecule. The presence of three methylene units in the inter-ring linkage of the butanoates, causes separation of the polarizable moieties of the molecules. This separation in turn strongly suppresses nematic properties. However, the presence of O and -COO- in the butanoate inter-ring linkage produces strong lateral intermolecular attractions which are further enhanced by the presence of a long chain terminal alkoxy group. Weak terminal attractions, in addition to these characteristics, increase the chances considerably for formation of smectic phases. It may be due to these reasons that the 4′-*n*-heptoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoates exhibit more smectic phases than analogous methanoates.

Table 2. Effect of exchange of the X linkage in 4′-*n*-alkoxyphenyl 4-(4′-cyano-4-biphenyl)-*n*-alkanoates on the transition temperatures (in °C).

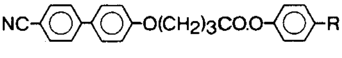


R	X	$C–S_3$, S_2, S_1, N or I	$S_3–S_2$	$S_2–S_1$	S_1–N	N–I
CH_3	$O(CH_2)_3COO$	146·0	–	–	–	(144·3)
	COO	158·0 [2]	–	–	–	315·0
C_2H_5	$O(CH_2)_3COO$	134·0	–	–	–	146·6
	COO	161·0 [2]	–	–	–	308·0
C_4H_9	$O(CH_2)_3COO$	123·0	–	–	–	136·2
	COO	114·5 [2]	–	–	–	272·0
C_5H_{11}	$O(CH_2)_3COO$	106·5	–	–	–	126·6
	COO	110·5 [2]	–	–	(98·2)	258·2
C_7H_{15}	$O(CH_2)_3COO$	75·9	(39·2)	(45·0)	120·0	124·0
	COO	121·5 [2]	–	–	(108·5)	241·0

( ) Monotropic transition.

The mesophase transition temperatures and observed phases for several alkylphenyl(cyano-oxybiphenyl)butanoates are presented in table 3. A comparison of the mesomorphic properties of the cyano-oxybiphenylbutanoates (see table 3) with the terminal alkoxy substituted compounds (see table 1) indicates, as expected, lower

Table 3. Transition temperatures (in °C) of 4′-*n*-alkylphenyl 4-(4′-cyano-4-oxybiphenyl)-butanoates.



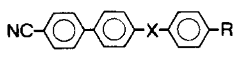
R	C–S_2, S_1, N or I	S_2–S_1	S_1–N or I	N–I
CH_3	123·5	–	–	(112·0)
C_2H_5	109·5	–	–	(107·9)
C_3H_7	85·0	–	–	105·0
C_4H_9	88·0	–	–	110·0
C_8H_{17}	69·0	98·0	116·0	–

( ) Monotropic transition.

transition temperatures for the alkyl substituted compounds. Also, there are fewer smectic phases observed for the 4′-*n*-octylphenyl 4-(4′-cyano-4-oxybiphenyl)-butanoate when compared to the analogous octoxyphenyl(cyanooxybiphenyl)-butanoate (see table 1). The S_1 phase of the 4′-*n*-octylphenyl 4-(4′-cyano-4-oxy-biphenyl)butanoate has the typical fan texture of smectic A. It separates out, on cooling, to form bâtonnets and not as smectic filaments as observed for the 4′-*n*-decoxyphenyl 4-(4′-cyano-4-oxybiphenyl)butanoate. The S_2 phase observed for this C_8 butanoate may be smectic C, but this has yet to be verified.

Table 4 lists the mesomorphic properties of analogous alkylphenyl(cyano-biphenyl)butanoates and methanoates. Inspection of the data in table 4 reveals that the transition temperatures for the methanoates are higher than for the corresponding butanoates. This is similar to the results presented which compared the alkoxy substituted esters (see table 2).

Table 4. Effect of exchange of the *X* linkage in 4′-*n*-alkylphenyl 4′-cyano-4-biphenyl-*n*-alkanoates on the transition temperatures (in °C).

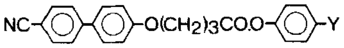


R	*X*	C–N or I	N–I
CH_3	$O(CH_2)_3COO$	123·5	(112·0)
	COO	189·0 [2]	272·0
C_2H_5	$O(CH_2)_3COO$	109·5	(107·9)
	COO	147·0 [2]	257·0
C_3H_7	$O(CH_2)_3COO$	85·0	105·0
	COO	125·8 [2]	245·0
C_4H_9	$O(CH_2)_3COO$	88·0	110·0
	COO	108·5 [2]	225·0

( ) Monotropic transition.

Table 5 summarizes the results for studies involving several 4′-phenyl substituted cyano-oxybiphenylbutanoates. All of the compounds listed exhibit only a nematic phase which in some cases is monotropic.

Table 5. Transition temperatures (in °C) of 4′-*Y*-phenyl 4-(4′-cyano-4-oxybiphenyl)-butanoates.



Y	C–N or I	N–I
CH_3	123·5	(112·0)
OCH_3	146·0	(144·3)
$COCH_3$	128·5	159·5
COC_2H_5	110·0	153·4
C_6H_5	192·0	(191·8)
CN	179·0	(156·2)

( ) Monotropic transition.

4. Experimental

The transition temperatures were determined with a Leitz polarizing microscope using a Mettler FP-2 heating stage. The melting points (solid–liquid or solid–liquid crystal transition) are those recorded on heating. The uncertainty of the temperature measurements is estimated to be less than ±2°C.

The esters prepared, by the synthetic route presented previously, were recrystallized several times from an appropriate solvent until the transition temperatures remained constant.

For purified compounds, the transition between mesophases and from the isotropic liquid to the mesophase were sharp and reversible. The transition temperatures determined by optical microscopy on heating and cooling differed only by a few tenths of a degree.

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