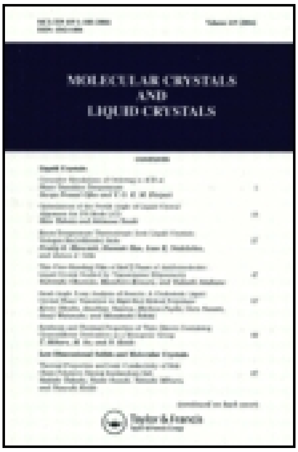

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Some Three-Ring Esters Containing aFive-Membered Heteroaromatic Ring. A Comparison of Liquid Crystal Properties

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Some Three-Ring Esters Containing a Five-Membered Heteroaromatic Ring. A Comparison of Liquid Crystal Properties†

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(*Received February 2, 1989; in final form April 12, 1989*)

Ninety compounds, over seventy of which are members of a number of homologous series of three-ring esters containing a 5-membered heteroaromatic ring, have been synthesized in order to establish how a change in the position of the heterocyclic ring influences liquid crystal behavior when compared with corresponding all-benzenoid esters. The liquid crystal properties of these esters, which show considerable variation, are discussed. One group of compounds shows unusual phase behavior, involving an unidentified (smectic?) phase and photomicrographs of optical textures of this phase are included.

INTRODUCTION

Mesogenic derivatives of 5-membered heteroaromatic ring systems, especially of pyrrole and furan, have not been extensively investigated.[1,2] Rather more mesogenic thiophene derivatives have been studied,[1,2] including some recently reported examples.[3,4] In this paper, the liquid crystal behavior of members of certain homologous series of three ring esters, (I), (II), (III) and (IV), containing a 5-membered heteroaromatic ring is reported. The position of the heterocyclic ring has been varied in order to establish the effect of this structural modification on liquid crystal properties compared with the corresponding 4-*n*-alkoxyphenyl biphenyl-4-carboxylates (V)[5] and the 4′-*n*-alkoxybiphenyl-4-yl benzoates (VI), which contain only benzenoid rings.

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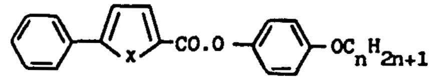
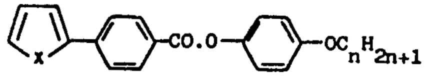
†Presented at the 12th International Liquid Crystal Conference, University of Freiburg, Freiburg, Federal Republic of Germany, 15th–19th August 1988.



(I) X = O,S



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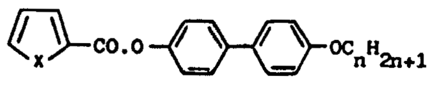
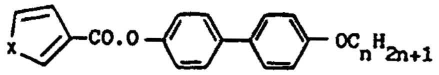
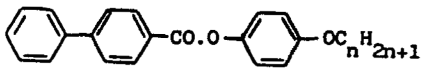


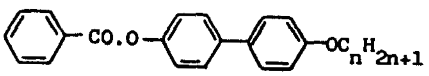
(III) X = O,S,NH,NMe



(IV) X = O,S



(V)



(VI)

A wide variation in liquid crystal behavior is shown by these compounds. Transition temperatures for members of the various series are shown plotted against the number of C atoms, n, in the alkyl chain in Figures 1–10, and are listed in corresponding Tables. Smectic phase types were identified from optical textures observed during thermal microscopy. In a few instances the assignments made by this method are rather tentative and future miscibility studies will be necessary to confirm the identity of these smectic phases.

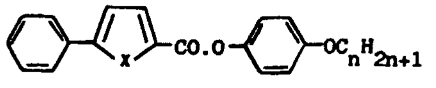
In the following discussion the liquid crystal thermal stabilities of the series have been compared using the average N–I (n = 7, 8) or S–I (n = 8, 9) transition temperatures, denoted by $T_{N(7,8)}$, or $T_{S(8,9)}$.

DISCUSSION

Esters of type (I) (X = S, O)

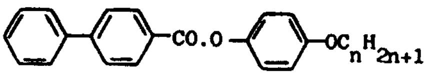
In these compounds, the heterocyclic ring occupies a central position. Conjugation is possible between the hetero-atom of the ring and both adjacent substituents, the ester function and the benzene ring.

None of the compounds studied in either the furan or the thiophene series gives rise to liquid crystal phases. The esters are relatively low melting compared with the analogous biphenyl esters and there is no evidence for monotropic liquid crystal phases on cooling the isotropic melts. In contrast, the analogous biphenyl esters (V) (Figure 1) give rise to enantiotropic nematic phases for which $T_{N(7,8)}$ is 128.8°C.



(I)

		m.p.
X = S:	n = 6	100°C
	n = 8	96.5
	n = 14	106.5
X = O:	n = 6	71
	n = 8	78
	n = 12	74.5



(V)

$T_{N(7,8)}$ = 128.8°C

	C–N	N–I
n = 6	125.5°C	134°C
n = 7	111	129
n = 8	114	128.5
n = 12	111.5	119
n = 14	114	116

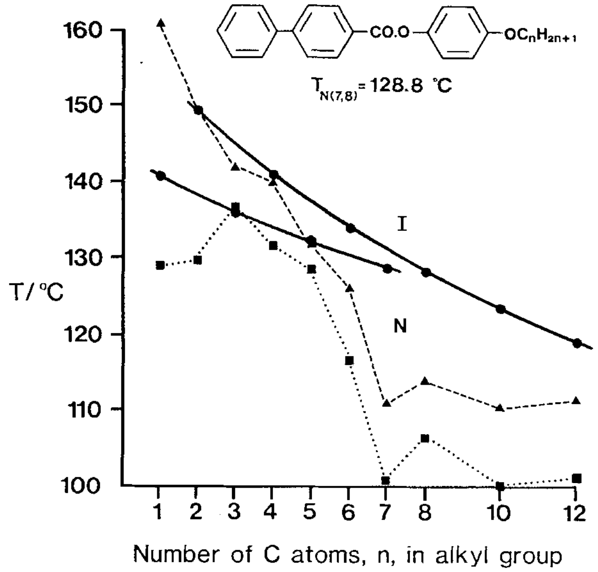


FIGURE 1 4-*n*-Alkoxyphenyl biphenyl-4-carboxylates

In this and subsequent Figures, where they are relevant, symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A smectic A, etc.

▲------▲ indicate m.p.'s

■·····■ represent temperatures at which recrystallization occurs at a cooling rate of approximately 1–5°/min.

Average N–I (for heptyloxy and octyloxy compounds) or S–I (for octyloxy and nonyloxy compounds) transition temperatures are denoted, where relevant, by $T_{N(7,8)}$ and $T_{S(8,9)}$.

In a 1,4-phenylene ring the ring-substituent bonds are colinear, but are inclined at an angle of approximately 35° in a 2,5-disubstituted furan or thiophene ring. Thus the probable reason for the lack of mesogenic properties of the phenylthienyl and phenylfuranyl esters (I) is that the substitution of the heterocyclic ring introduces a bend into the system which is not conducive to liquid crystal formation by interfering with efficient space filling properties of the molecules.

Esters of type (II) (X = S, O)

In these esters the positions of the directly linked rings are interchanged. With the heterocyclic ring located in a terminal position, the presence of the 1,4-phenylene ring restores linearity to the molecule and leads to much reduced conjugation between the hetero-atom and the ester function.

Both the thienyl- and furanyl-benzoates (III, X = S, O) give rise to nematic phases, the plots of transition temperature against *n* (Figures 2 and 3) showing broadly similar trends to the plot for the biphenyl analogues (V) (Figure 1). The

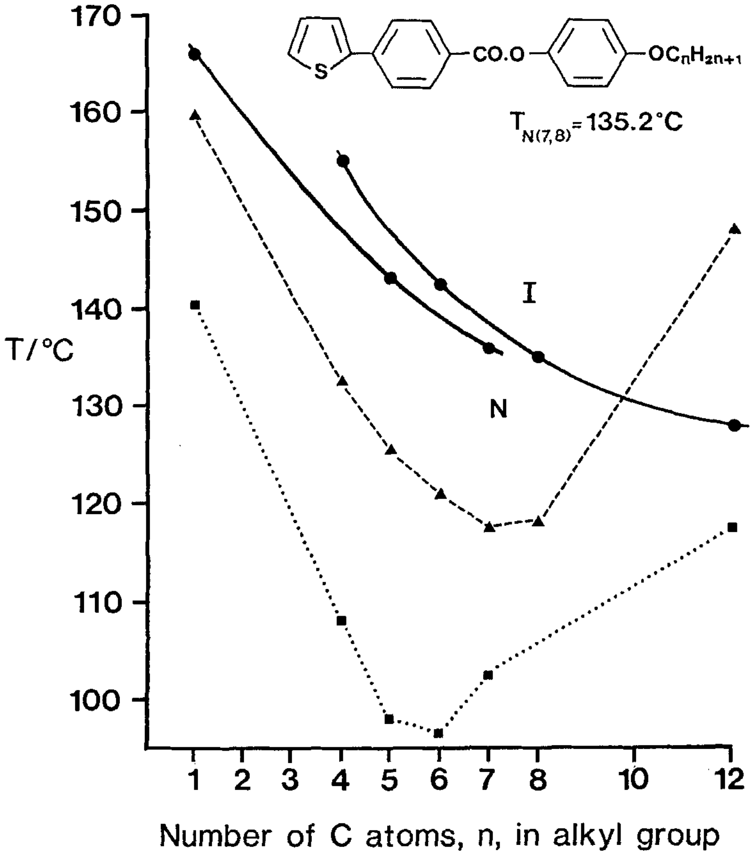


FIGURE 2 4-*n*-Alkoxyphenyl 4-(2-thienyl)benzoates

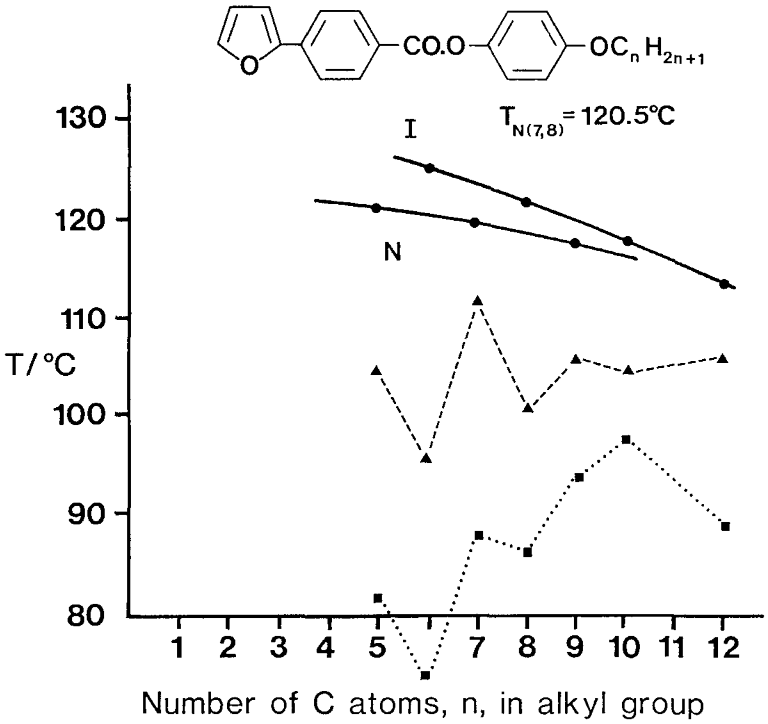
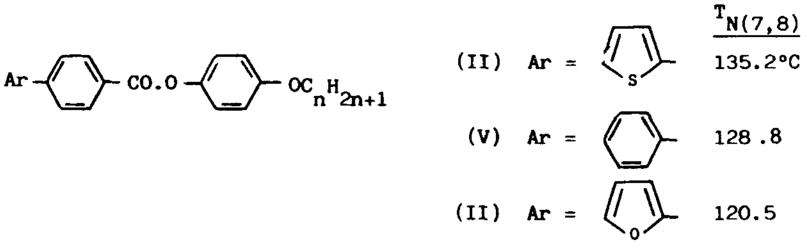


FIGURE 3 4-*n*-Alkoxyphenyl 4-(2-furanyl)benzoates

thienylbenzoates have a greater nematic thermal stability than the furanylbenzoates with the biphenyl carboxylates (V) having an intermediate value.



When the Ar substituent is replaced by cyclohexyl the thermal stability of the series is much reduced, only two members (*n* = 5 and 6) giving rise to nematic phases (Figure 4).

Esters of type III (X = S, O, NH, NMe) and type IV (X = S, O)

In these esters in which the phenolic moiety is a half-ether of 4,4′-dihydroxybiphenyl, the heterocyclic ring is also located in a terminal position. The lone pair of the hetero-atom may conjugate directly with the ester function setting up a permanent dipole, a substantial component of which is laterally disposed and hence

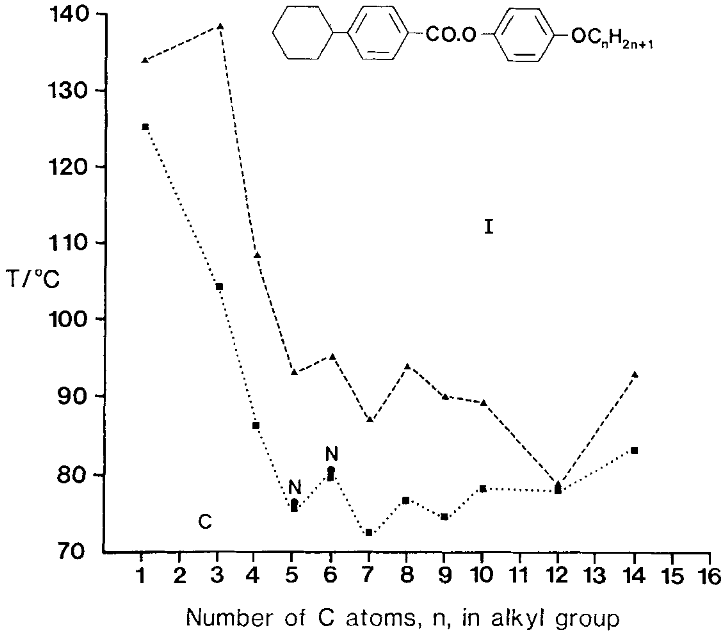
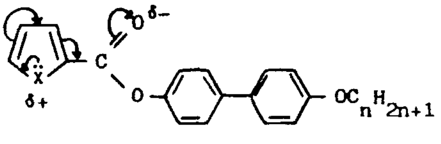


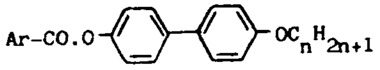
FIGURE 4 4-*n*-Alkoxyphenyl 4-cyclohexylbenzoates

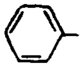
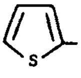
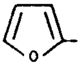
likely to increase the lateral intermolecular cohesive forces and the tendency to form smectic mesophases.



(III)

However, the general form of the transition temperature plots for the furan- and thiophene-2-carboxylates (III, X = S, O) (Figures 5 and 6) and for the corresponding benzoates (VI) (Figure 7) is very similar and there is no evidence for enhancement of smectic thermal stability of the heterocyclic esters. The three series are predominantly nematic in character but show differing types of smectic behavior between $n = 7$ and 14. Both nematic and smectic thermal stability of these esters increase in the order furan-2-carboxylates < thiophene-2-carboxylates < benzoates.



			$T_{N(7,8)}$	$T_{S(8,9)}$
(VI)	Ar =		135°C	114.1°C
(III)	Ar =		114.7	93.8
(III)	Ar =		108.7	89.9

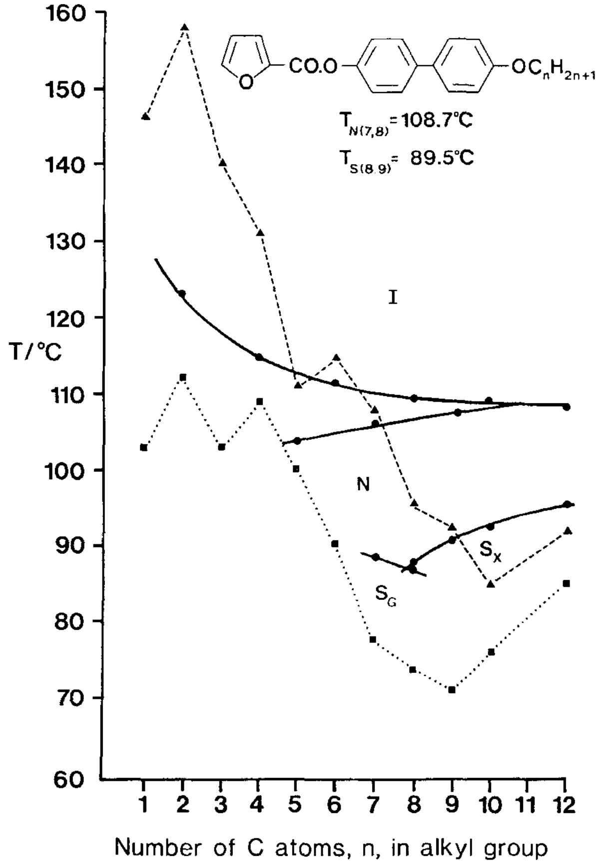


FIGURE 5 4′-*n*-Alkoxybiphenyl-4-yl furan-2-carboxylates

The benzoates predominantly form S_C and S_B phases. One member (*n* = 14) gives only an S_A phase. The points (Figure 7) for the S_C–N transition temperatures lie on a gently rising curve (*n* = 9, 10, 12) above a similar, shallow curve for the S_B–S_C (or N) transition temperatures (*n* = 8, 9, 10, 12). On cooling from the nematic phase, one member (*n* = 12) of the thiophene-2-carboxylates (Figure 6) gives rise to an S_C (schlieren texture), followed immediately by an S_B phase just prior to the onset of crystallization. Other members (*n* = 8, 9, 10) form S_B phases just before crystallization occurs and the points for the N–S_B transition temperatures lie on a shallow rising curve. The furan-2-carboxylates (Figure 5) reveal quite different smectic polymorphism. The early members (*n* = 7, 8) form S_G phases, whereas later members (*n* = 8, 9, 10, 12) give an unidentified (smectic?) phase (S_X). The points for the N–S_G and N–S_X transition temperatures lie, respectively, on falling and on rising curves. The optical textures shown by the unidentified S_X phase have some characteristics of S_F or S_I (banded focal conic texture) and of S_C and S_I (schlieren texture), and are discussed more fully later together with the behavior observed on cooling the nematic phase of the homologue *n* = 8.

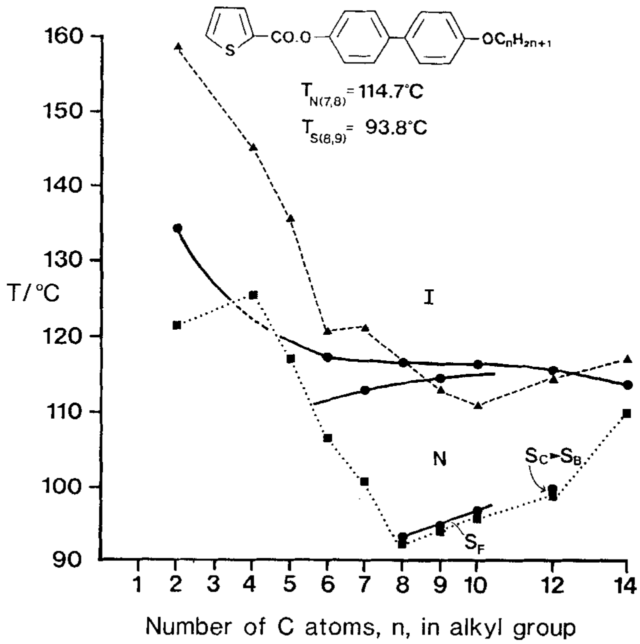


FIGURE 6 4′-*n*-Alkoxybiphenyl-4-yl thiophene-2-carboxylates

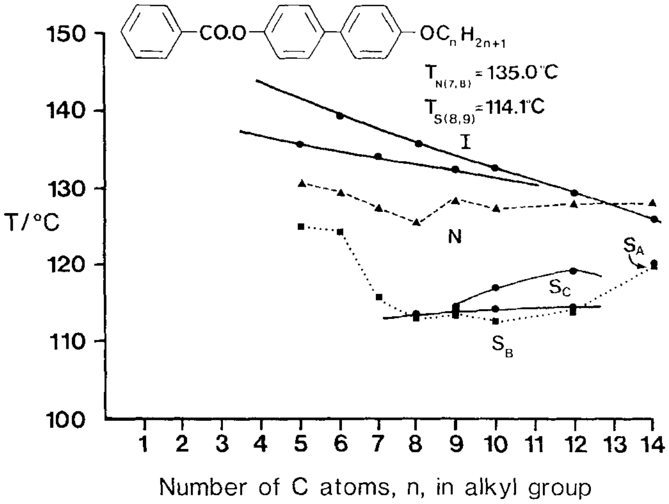
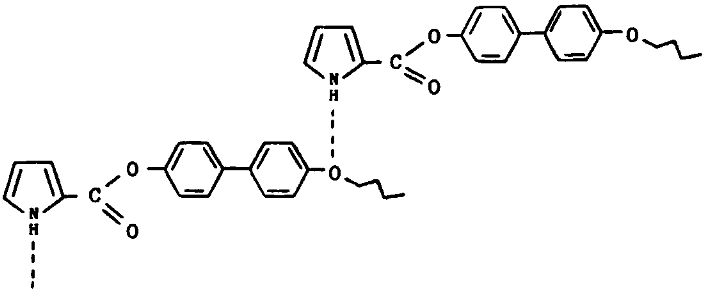


FIGURE 7 4′-*n*-Alkoxybiphenyl-4-yl benzoates

The corresponding pyrrole-2-carboxylates (III), (X = NH) (Figure 8) are not smectogenic and have a much higher nematic thermal stability presumably due to stabilization of the nematic phase by intermolecular H-bonding.



H-bonding cannot occur in the corresponding N-methylpyrroles which do not give rise to liquid crystal phases, although slightly impure samples of these esters reveal a very short nematic phase just before crystallization occurs on cooling the isotropic melt.

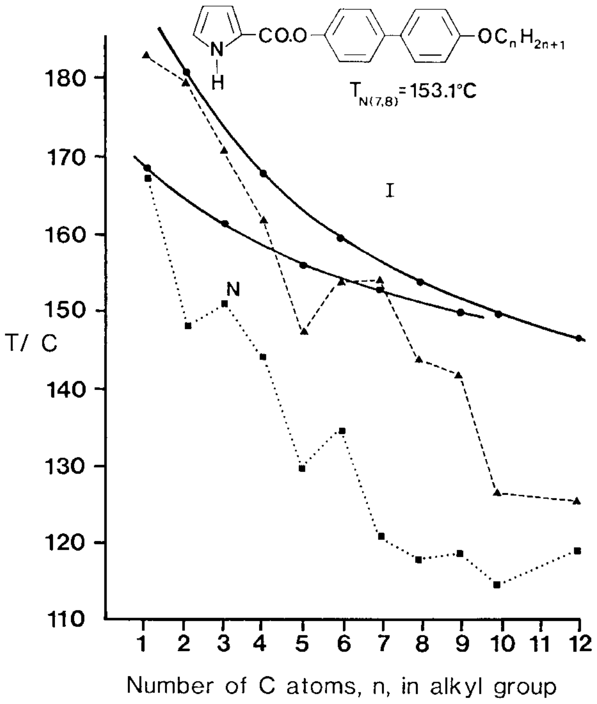
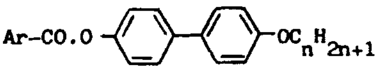
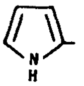


FIGURE 8 4'-*n*-Alkoxybiphenyl-4-yl pyrrole-2-carboxylates

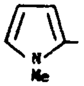


(III) Ar =



$T_{N(7,8)}$ 153.1°C

(III) Ar =



	C–I	I–C
n = 7	100.5°C	76.2°C
n = 8	96	72
n = 9	103.5	81.5

Esters of type (IV) (X = S, O)

Both the thiophene- and furan-3-carboxylates show rather similar mesomorphic behavior (Figures 9 and 10). The nematic phase shown initially ($n = 2$) is obscured for other lower members of the series ($n = 3, 4, 5$ for X = O, $n = 3$–7 for X = S) by their rather high m.p. and temperature of crystallization, but reappears for later members. In these esters the hetero-atom of the terminal heterocyclic ring behaves rather like a terminal substituent, increasing nematic thermal stability by extending the molecular length, but not the breadth, and increasing the anisotropy of molecular polarizability by conjugation with the rest of the molecule. The furan-3-carboxylates ($T_{N(7,8)} = 130.8°$) have a slightly higher nematic thermal stability than the thiophene-3-carboxylates ($T_{N(7,8)} = 125.8°$), these values being of roughly the same order as for the corresponding benzoates (VI) and substantially higher than for the corresponding 2-carboxylates (III) confirming the influence of the terminally disposed hetero-atom.

In addition, the 3-carboxylates are significantly more smectogenic than the 2-carboxylates. This may be due to a more substantial increase in the lateral dipolar

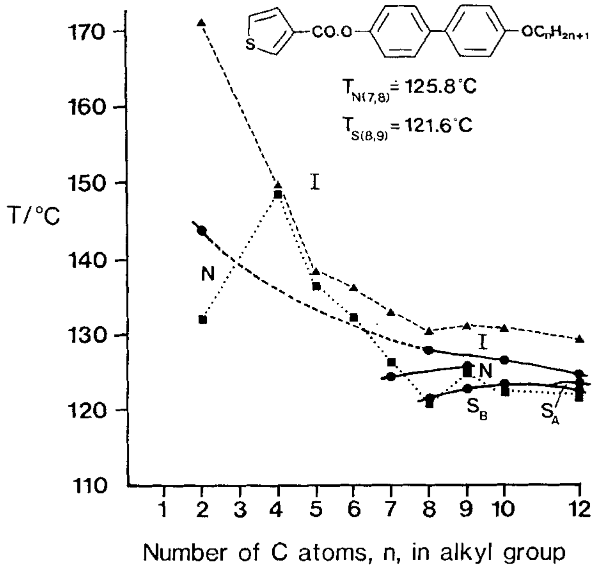


FIGURE 9 4′-n-Alkoxybiphenyl-4-yl thiophene-3-carboxylates

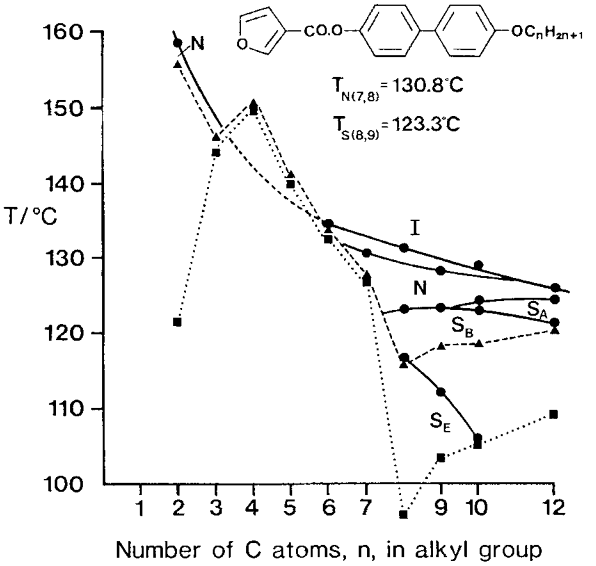
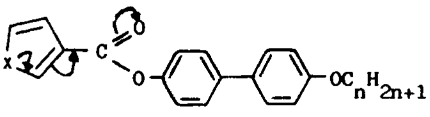


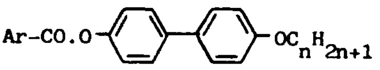
FIGURE 10 4′-*n*-Alkoxybiphenyl-4-yl furan-3-carboxylates

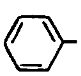
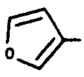
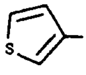
interactions resulting from conjugation between the hetero-atom of the heterocyclic ring and the ester function of the 3-carboxylates.



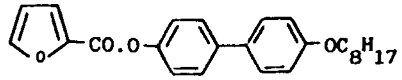
(IV)

On cooling the nematic melts of the thiophene-3-carboxylates (Figure 9), one member ($n = 12$) forms an S_A then an S_B phase just prior to the occurrence of crystallization. Other members ($n = 8, 9, 10$) also give an S_B phase, the points for the N–S_B transition temperatures lying on a shallow rising curve. The furan-3-carboxylates (Figure 10) reveal similar though more complex behavior. The ester $n = 12$ gives an S_A folowed by an S_B phase, and the ester $n = 10$ behaves similarly, though the S_A phase is much shorter and an S_E phase is formed from the S_B phase just before crystallization occurs. The esters $n = 8, 9$, show similar behavior but do not form S_A phases. The points for the S_B–S_E transition temperatures lie on a curve which falls sharply as n increases.



		$T_{N(7,8)}$	$T_{S(8,9)}$
(VI)	Ar = 	135°C	114.1°C
(IV)	Ar = 	130.8	123.3
(IV)	Ar = 	125.8	121.6

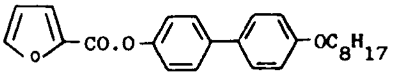
Textures of the smectic phases of

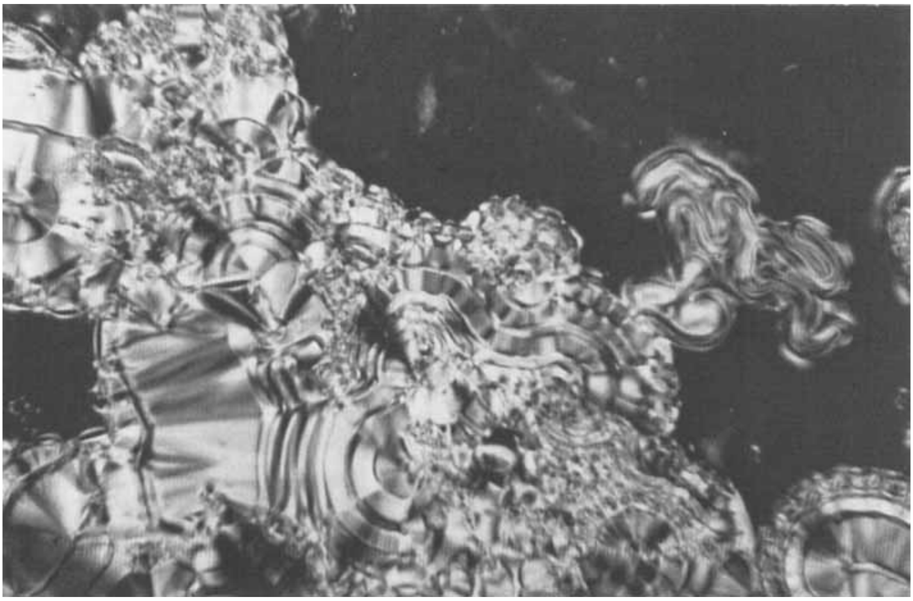


When the nematic phase (in its homeotropic texture) of this compound is slowly cooled the unidentified (S_X) phase begins to form at 87.6°C. Growth commences simultaneously at various discontinuities in the sample, e.g. at an air bubble or interfaces between the slide and the edge of the cover slip. If the temperature is maintained at 87.6°C, growth of the phase continues slowly, but actively, in an unusual manner giving several different textures. Some areas form in a spiral fashion from mobile ribbons or strings which either settle to give a concentric lace-like texture or are pulled back (presumably by surface forces) into the homeotropic nematic and disappear. Other areas of growth reveal a rather ill-defined schlieren texture, or give rise to a fan texture with continuous bands across the fans which have a characteristic, almost transparent appearance. The phase is generally only weakly colored. Figures 11, 12 and 13 show these textures of the S_X phase. Later members ($n = 9, 10, 12$) of this series also give an S_X phase showing similar behavior and textures. Some of these textural features are reminiscent of those reported by Attwood, Lydon, and Jones[6] for the chromonic M phases of drug and dye/water systems.

Growth of the S_X phase within the nematic phase occurs relatively slowly, and when the temperature of the nematic phase of the ester $n = 8$ is lowered to approximately 1°C below the N–S_X transition, dendrites rapidly fill the field of

Plates showing textures of smectic phases of





FIGURES 11, 12 and 13. Formation of S_X phase from nematic phase at 87.6°C. See Color Plate I.

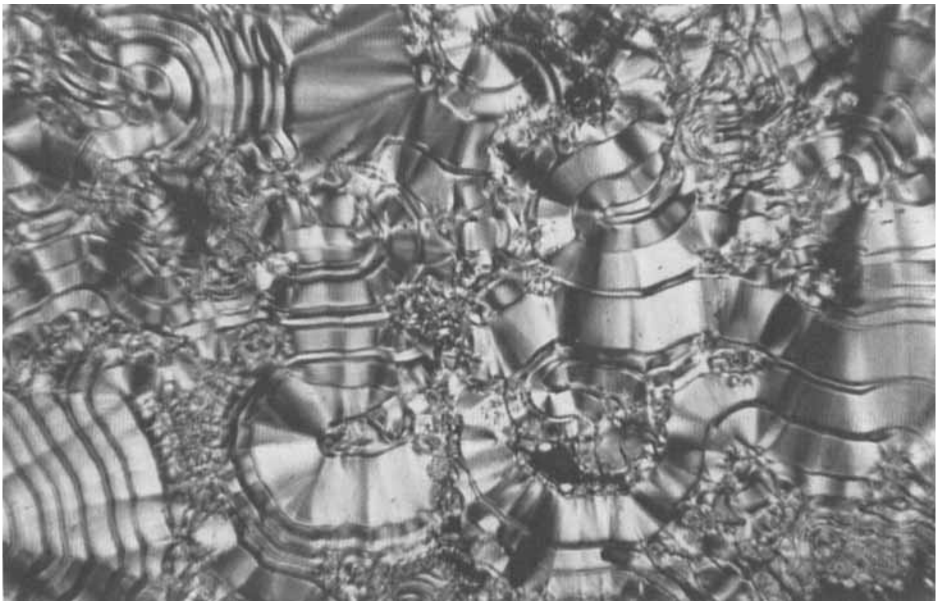


FIGURE 12
See Color Plate II.

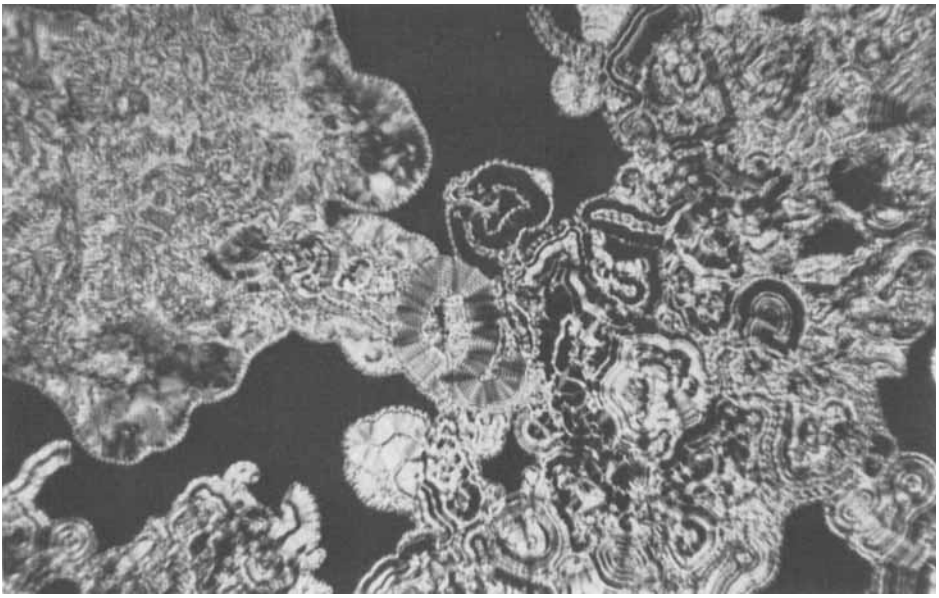


FIGURE 13
See Color Plate III.

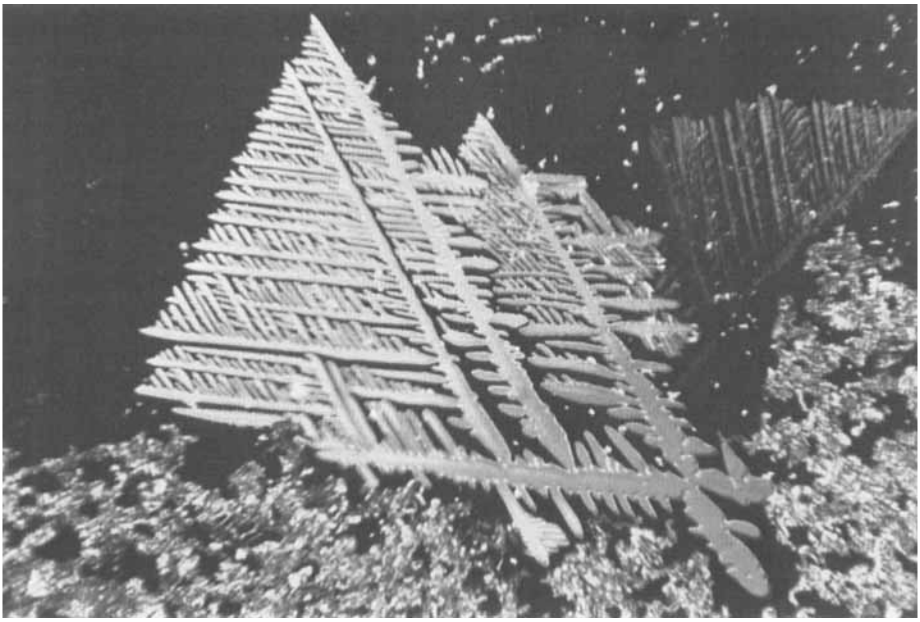


FIGURE 14. Formation of dendrites from nematic phase at 86.7°C, with S_X phase continuing to form. See Color Plate IV.

view and give rise to the formation of a brightly colored mosaic texture typical of an S_G phase. This is illustrated in Figure 14. However this phase is metastable with respect to the S_X phase which invades the mosaic texture and slowly grows as described above, until the mosaic is completely displaced. The dendrites and mosaic revert back to the homeotropic nematic phase if the temperature is raised, but growth of the S_X phase continues unless the temperature is increased above the S_X–N transition.

SUMMARY

The liquid crystal properties of these esters show considerable variation and no distinct trends in the relationship between molecular structure and liquid crystal behavior are apparent except as follows.

The esters containing a centrally positioned heterocyclic ring do not form liquid crystals. Purely nematic behavior is shown by esters containing the heterocyclic ring in a terminal position, but separated from the ester function by a benzene ring. When the terminal heterocyclic ring is directly attached to the ester function, the esters generally also show smectic properties (smectic polymorphism in some instances).

One compound, 4′-*n*-octyloxybiphenyl-4-yl furan-2-carboxylate, forms an S_G phase and an unidentified (smectic?) phase (S_X), on cooling the nematic phase. These mesophases coexist over a small temperature range.

TABLES OF TRANSITION TEMPERATURES

The following notes, where relevant, apply to Tables I–X.

[a]Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic A, etc. Thus C–S_A represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

[b]Temperature of recrystallization.

[c]Values in parentheses are for monotropic transitions.

Table I. Values are taken from D. J. Byron, D. Lacey and R. C. Wilson, *Mol. Cryst. Liq. Cryst.*, **51**, 265 (1979).

Table V. The phase denoted by S_X has not yet been identified. For the octyloxy compound, the S_G–N and S_X–N transition temperatures were obtained on *cooling* from the nematic phase.

Table IX. Phase transitions marked by an asterisk were obtained by optical examination of small isolated areas after recrystallization of the main bulk of sample had occurred.

Average N–I (for heptyloxy and octyloxy compounds) or S–I (for octyloxy and nonyloxy compounds) transition temperatures are denoted by $T_{N(7,8)}$ and $T_{S(8,9)}$.

TABLE I

4-*n*-Alkoxyphenyl biphenyl-4-carboxylates

	Transition temperature (°C)[a]			
n-alkyl group	C–I	N–I	I–C[b]	
CH_3	161.0	(140.5)[c]	129	
C_2H_5	149.5	149.5	129.5	
C_3H_7	142.0	136.5	136.5	
	C–N			
C_4H_9	140.0	141.0	131.5	
C_5H_{11}	132.0	132.5	128.5	
C_6H_{13}	125.5	134.0	117.0	
C_7H_{15}	111.0	129.0	101.0	
C_8H_{17}	114.0	128.5	106.5	
$C_{10}H_{21}$	110.5	123.5	100.0	
$C_{12}H_{25}$	115.5	119.0	101.0	$T_{N(7,8)}$ = 128.8°C

TABLE II

4-*n*-Alkoxyphenyl 4-(2-thienyl)benzoates

	Transition temperature (°C)[a]			
n-alkyl group	C–I	N–I	I–C[b]	
CH_3	159.4	166.0	140.0	
C_4H_9	132.5	155.1	107.0	
C_5H_{11}	125.3	143.1	98.0	
C_6H_{13}	120.5	142.1	97.0	
C_7H_{15}	118.7	135.4	102.0	
C_8H_{17}	117.3	135.0	103.0	
$C_{12}H_{25}$	147.7	(132.9)[c]	117.0	$T_{N(7,8)}$ = 135.2°C

TABLE III

4-*n*-Alkoxyphenyl 4-(2-furanyl)benzoates

	Transition temperature (°C)[a]			
n-alkyl group	C–I	N–I	N–C[b]	
C_5H_{11}	104.2	121.0	81.0	
C_6H_{13}	95.5	124.8	73.8	
C_7H_{15}	101.8	119.5	87.6	
C_8H_{17}	100.3	121.4	86.2	
C_9H_{19}	105.8	117.2	93.9	
$C_{10}H_{21}$	104.8	117.6	97.5	
$C_{12}H_{25}$	106	113.0	88.7	$T_{N(7,8)}$ = 120.5°C

TABLE IV

4-*n*-Alkoxyphenyl 4-cyclohexylbenzoates

	Transition temperature (°C)[a]		
n-alkyl group	C–I	N–I	I–C[b]
CH_3	134.0		125.7
C_3H_7	138.4		104.2
C_4H_9	108.7		86.4
C_5H_{11}	93.0	(75.9)[c]	75.5
C_6H_{13}	95.2	(80.0)	79.8
C_7H_{15}	87.0		72.4
C_8H_{17}	94.0		76.9
C_9H_{19}	90.0		74.8
$C_{10}H_{21}$	89.7		78.3
$C_{12}H_{25}$	79.0		78.0
$C_{14}H_{29}$	93.0		83.0

TABLE V

4′-*n*-Alkoxybiphenyl-4-yl furan-2-carboxylates

	Transition temperature (°C)[a]				
n-alkyl group	C–I	S_G–N	S_X–N	N–I	S_G/S_X/N/I–C[b]
CH_3	146.5				103.4
C_2H_5	158.5			(123.5)[c]	112.7
C_3H_7	140.3				103.4
C_4H_9	131.5			(115.0)	109.2
C_5H_{11}	111.5			(104.3)	100.4
C_6H_{13}	115.1			(112.0)	90.9
C_7H_{15}	108.2	(88.0)		(106.6)	78.1
	C–N				
C_8H_{17}	96.0	(86.7)	(87.6)	110.8	74.3
	C–I				
C_9H_{19}	92		(91.4)		71.8
	C–S_X				
$C_{10}H_{21}$	85.6		92.5		76.5
$C_{12}H_{25}$	92.6		96.0		85.5

$T_{N(7,8)}$ = 108.7°C
$T_{S(8,9)}$ = 89.5°C

TABLE VI

4′-*n*-Alkoxybiphenyl-4-yl thiophene-2-carboxylates

	Transition temperature (°C)[a]				
n-alkyl group	C–I	S_B–S_C	S_F–N	N–I	S_F/S_B/N/I–C[b]
C_2H_5	158.7			(134.2)[c]	121.7
C_4H_9	145.0				125.3
C_5H_{11}	135.5				117.0
C_6H_{13}	120.8			(117.1)	106.7
C_7H_{15}	121.1			(112.9)	100.5
	C–N				
C_8H_{17}	116.7		(93.0)	(116.5)	93.0
C_9H_{19}	113.0		(94.6)	114.5	94.6
$C_{10}H_{21}$	110.8		(96.5)	116.0	96.5
			S_C–N		
$C_{12}H_{25}$	114.6	(99.6)	(99.7)	115.2	99.6
	C–I				
$C_{14}H_{29}$	116.7			113.2	110.0

$T_{N(7,8)}$ = 114.7°C
$T_{S(8,9)}$ = 93.8°C

TABLE VII

4′-*n*-Alkoxybiphenyl-4-yl benzoates

n-alkyl group	Transition temperature (°C)[a]				
	C–I	S_B–S_A	S_B–N	N–I	S_B/S_A/N–C[b]
C_5H_{11}	130.3			135.7	125.0
C_6H_{13}	129.7			139.5	124.2
C_7H_{15}	127.4			134.3	115.9
C_8H_{17}	126.6		(113.6)[c]	135.7	112.9
			S_C–N		
C_9H_{19}	128.3	(113.6)	(114.5)	132.5	113.6
$C_{10}H_{21}$	127.2	(114.3)	(117.1)	132.7	112.9
$C_{12}H_{25}$	128.0	(114.6)	(119.8)	129.8	114.6
			S_A–N		
$C_{14}H_{29}$	128.1		(120.5)	(126.3)	120.3

$T_{N(7,8)} = 135.0°C$
$T_{S(8,9)} = 114.1°C$

TABLE VIII

4′-*n*-Alkoxybiphenyl-4-yl pyrrole-2-carboxylates

n-alkyl group	Transition temperature (°C)[a]		
	C–I	N–I	N–C[b]
CH_3	182.6	(168.2)[c]	167.0
	C–N		
C_2H_5	179.3	180.8	147.8
	C–I		
C_3H_7	170.5	(161.4)	150.9
	C–N		
C_4H_9	161.7	167.8	143.5
C_5H_{11}	147.3	155.6	129.8
C_6H_{13}	153.2	154.0	134.1
	C–I		
C_7H_{15}	153.5	(152.8)	130.2
	C–N		
C_8H_{17}	143.5	153.4	117.9
C_9H_{19}	141.1	149.9	118.1
$C_{10}H_{21}$	126.0	149.2	114.3
$C_{12}H_{25}$	125.0	146.2	118.9

$T_{N(7,8)} = 153.1°C$

TABLE IX

4′-n-Alkoxybiphenyl-4-yl thiophene-3-carboxylates

	Transition temperature (°C)[a]					
n-alkyl group	C-I	S_B-S_A	S_B-N	N-I	S_B/N/I-C[b]	
C_2H_5	171.2			(143.7)[c]	132.0	
C_4H_9	149.4				148.5	
C_5H_{11}	138.1				136.3	
C_6H_{13}	136.1				132.0	
C_7H_{15}	132			(124.0)*	126.3	
C_8H_{17}	130.4		(121.3)	(127.6)	121.2	
C_9H_{19}	131		(121.9)*	(125.4)	125.0	
$C_{10}H_{21}$	130.5		(123.0)	(126.6)	122.5	
			S_A-N			
$C_{12}H_{25}$	129.1	(122.8)	(123.7)	122.8		$T_{N(7,8)}$ = 125.8°C $T_{S(8,9)}$ = 121.6°C

TABLE X

4′-n-Alkoxybiphenyl-4-yl furan-3-carboxylates

	Transition temperature (°C)[a]						
n-alkyl group	C-N	S_E-S_B	S_B-S_A	S_B-N	N-I	S_B/S_A/N/I-C[b]	
C_2H_5	155.8				158.5	121.5	
	C-I						
C_3H_7	146.1					144.5	
C_4H_9	150.7					149.0	
C_5H_{11}	141.0					139.0	
	C-N						
C_6H_{13}	133.8				134.4	132.8	
C_7H_{15}	127.5				130.3	126.5	
	C-S_E						
C_8H_{17}	116.0	116.8		123.1	131.2	95.6	
	C-S_B						
C_9H_{19}	118.2	(111.8)[c]		123.4	128.2	103.4	
				S_A-N			
$C_{10}H_{21}$	118.9	(105.8)	122.8	124.6	129.1	105.8	
$C_{12}H_{25}$	120.7		121.3	124.2	125.8	109.4	$T_{N(7,8)}$ = 130.8°C $T_{S(8,9)}$ = 123.3°C

EXPERIMENTAL

Thermal optical microscopy, carried out with a Vickers M 75 polarizing microscope in conjunction with a Mettler FP 52 hot-stage and FP 5 control unit, was used to measure transition temperatures and to identify mesophase types from their optical textures. Miscibility studies are being undertaken to confirm some assignments of phase types and the results of this work, together with details of the synthetic procedures for preparation of the esters, will be given in future publications.

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