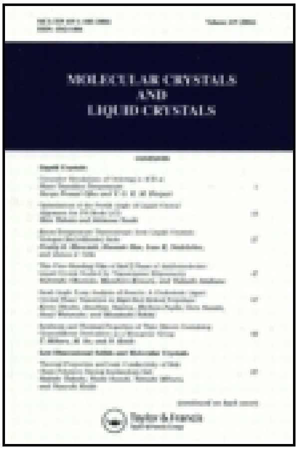

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Novel Bi- and Ter-Thiophenes Exhibiting Ferri- and Antiferro-Electric Behaviour

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Novel Bi- and Ter-Thiophenes Exhibiting Ferri- and Antiferro-Electric Behaviour

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Preliminary results of the synthesis and liquid crystalline properties of suitably substituted bi- and ter-thiophene-based chiral esters, derived from the appropriate thiophene-based carboxylic acid and either (*S*)-4-(1-methylheptyloxycarbonyl)phenol or (*S*)-1-methylheptyl-4'-hydroxybiphenyl-4-carboxylate are reported. The bithiophene ester comprising one phenyl ring exhibits monotropic smectic A, smectic C* ferro-, ferri- and antiferro-electric phase types. Increasing the number of rings, either thienyl or phenyl, increases both the melting point and thermal stability. The four ring compounds exhibit enantiotropic smectic A, smectic C* ferro-, ferri- and antiferro-electric phases together with underlying unknown phase type (S_X). The identity of the S_X phase is tentatively assigned as S_I* following free-standing film characterisation and miscibility study.

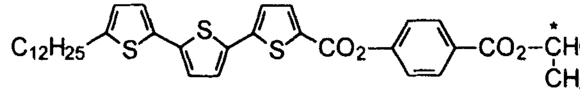
Keywords: thiophene; bithienyl; terthienyl; ferroelectric; ferrielectric; antiferroelectric

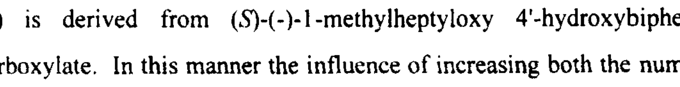
INTRODUCTION

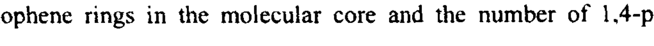
Since the reported occurrence of the ferri- and antiferro-electric phase types in 1989, there has been a rapid upsurge in this area of work primarily because the antiferroelectric phase participates in tristate switching via a sharp electric field threshold.[1,2] Although there are numerous references cited in the literature on the synthesis and characterisation of compounds which exhibit these phase types,[3-7] there are, however, relatively few examples based on thiophene.[4,5]

Thiophene is a five membered heterocycle comprising sulphur which readily undergoes electrophilic aromatic substitution at the 2- and 5-positions (*ortho-* to the sulphur atom). Despite the non-linear or bent nature of 2,5-disubstituted compounds, when suitably substituted they exhibit mesogenic properties.

Herein, we report our preliminary results on the synthesis and mesomorphic properties of novel bi- (**1**) and ter-(**2**, **3**) thiophene-based liquid crystalline compounds in order to investigate the occurrence of the ferro-, ferri- and antiferro-electric phase types in relation to molecular structure. The compounds (**1-3**) differ either in the number of thiophene rings, i.e., bithienyl versus terthienyl and/or the chiral moiety, i.e., (**1**) and (**3**) are derived from (*S*)-(-)-4-(1-methylheptyloxycarbonyl)phenol whereas


(**1**)


(**2**)

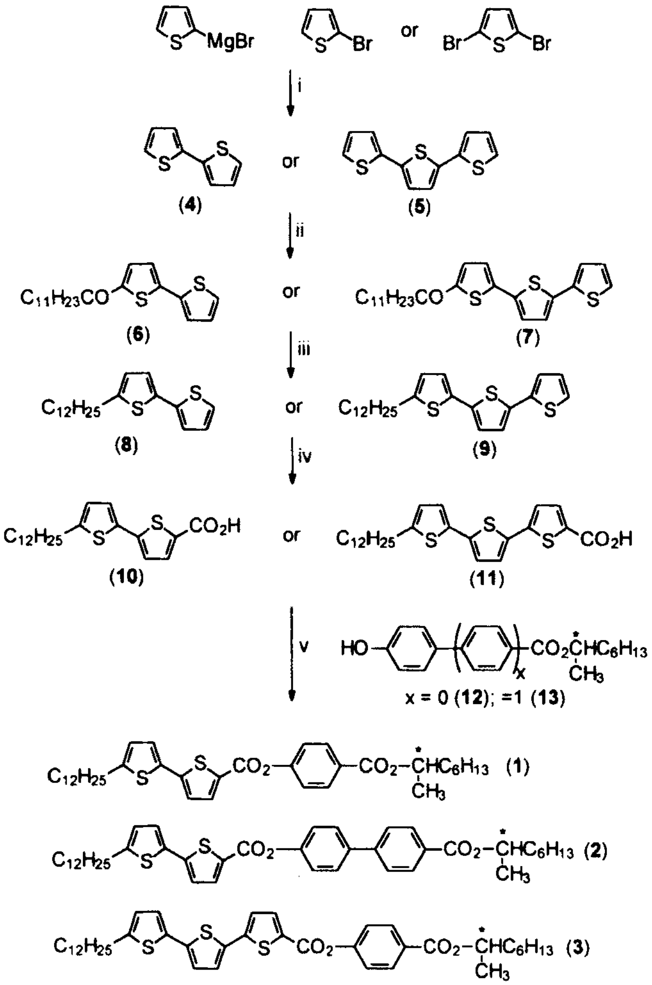

(**3**)

(**2**) is derived from (*S*)-(-)-1-methylheptyloxy 4'-hydroxybiphenyl-4-carboxylate. In this manner the influence of increasing both the number of thiophene rings in the molecular core and the number of 1,4-phenylene rings in the 'chiral phenol' on mesomorphic properties may be investigated. Increasing the number of rings, either thiophene or phenyl, is expected to enhance thermal stability.

SYNTHESIS

The synthetic pathway for the preparation of compounds (**1**-**3**) is summarised in Scheme 1 which relies on the successful synthesis of the desired two- and three-ring thiophene-based carboxylic acids, (**10**) and (**11**), which are then esterified with the appropriate chiral phenols (**12** or **13**). The latter were prepared according to the methods reported by Chin *et al.*[8] and Booth *et al.*[9]

Bi- (**4**) and ter-thiophene (**5**) were prepared in moderate to high yield (70 - 90%) using the nickel-catalysed cross-coupling methodology reported by Tamao *et al.*,[10] whereby, the Grignard reagent of 2-bromothiophene is coupled with either 2-bromothiophene to afford (**4**) or 2,5-dibromothiophene to afford (**5**). Subsequently, compounds (**4**) and (**5**) were subjected to Friedel-Crafts acylation with the appropriate alkanoyl chloride, catalysed by titanium(IV) tetrachloride to give the intermediate acyl-compounds (**6** and **7**). Wolff-Kishner (Huang-Minlon) reduction of compounds (**6** and **7**) generated the corresponding alkyl-compounds (**8** and **9**) which then were lithiated (1.6M BuLi, -78°C) and treated with an excess of solid carbon dioxide to furnish the desired two- (**10**) and three-ring (**11**) thiophene-based carboxylic acids. DCC esterification[11] of compounds (**10**



i. $[(C_6H_5)_2PCH_2CH_2CH_2(C_6H_5)]NiCl_2$, ether
ii. $TiCl_4$, $C_{11}H_{23}COCl$, CH_2Cl_2
iii. $NH_2NH_2.H_2O$, KOH, diethylene glycol
iv. a) 1.6 M BuLi, -78°C, N_2; b) CO_2, H^+
v. Dicyclohexylcarbodiimide (DCC), dimethylaminopyridine, CH_2Cl_2

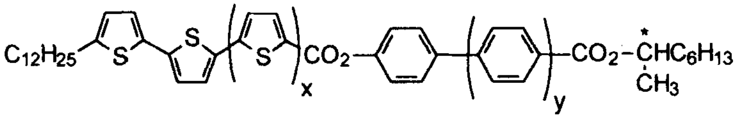
SCHEME 1

and **11**) with the appropriate chiral phenols (**12** or **13**) produced the required chiral esters (**1-3**).

RESULTS AND DISCUSSION

The mesomorphic properties of novel two- and three-thiophene ring containing chiral esters (**1-3**) are listed in Table 1. Compound (**1**) is low melting and exhibits poor mesogenic properties, i.e., monotropic phases. This may be attributed to a combination of poor geometry and possibly

TABLE 1 Transition temperatures (°C) and thermodynamic data (kJ/mol) (in italics) for novel bi- (**1**, **2**) and ter-thiophene (**3**) esters.



	x	y	m.p.	I-S_A	S_A-S_C*ferro	S_C*ferro-S_C*ferri	S_C*ferri-S_C*antiferro	S_C*antiferro S_X
1	0	0	57.5	(57)	(56)[a]	(56)[a]	(50)	-
			43	*1.1*	*[-]*[b]	*[-]*	*[-]*	
2	1	1	61[c]	142	135	116.3	110.7	94.8
			8.05	*6.7*	*0.34*	*[-]*	*[-]*	*5.63*
3	1	0	81.5[c]	139	132.4	118.2	116.2	(73.7)
			26.3	*6.0*	*0.4*	*[-]*	*[-]*	*0.9*

a. Transitions are very close. May be S_A-S_C*ferri
b. Too small to be evaluated
c. Obtained from DSC

poor molecular polarisability since the inclusion of an additional aromatic ring (either thienyl or phenyl), which increases the length to breadth ratio and polarisability, promotes mesogenity. Hence, the thermal stability (clearing point) of compounds (**2**) and (**3**) is higher by a magnitude of 85°C (influence of additional phenyl ring) and 82°C (influence of additional thienyl ring), respectively when compared with compound (**1**).

Compounds comprising a total of four rings, either bithienyl and biphenyl, i.e., (**2**) or terthienyl and phenyl, i.e., (**3**), exhibit the following sequence of phases, namely: I-S_A-S_C*ferro-S_C*ferri-S_C*antiferroelectric-S_X.

On cooling from the isotropic liquid, the S_A phase was characterised by the appearance of a classical focal-conic fan texture interspersed with homeotropic areas. At the S_A-S_C*ferroelectric transition, the fans adopt a golden-brown coloration and the previously dark homeotropic region develops an intense blue coloration (pseudohomeotropic). On further cooling of the S_C*ferroelectric phase, the pseudohomeotropic region changes colour from blue to red-green which is indicative of changes in pitch length with temperature, whilst the backs of the fans became heavily banded. The S_C* ferrielectric phase was characterised by the onset of milky-white shimmering texture, which is in constant motion, in the pseudohomeotropic regions. At the transition to the S_C*antiferroelectric phase, the shimmering ceases to leave a red-brown pseudohomeotropic region. The arc pattern across the fans becomes less pronounced and the fans closely resemble S_A with wishbone defects. Prior to the onset of crystallisation, fine lines (arcs) appear across the fans coupled with an intense Schlieren-mosaic texture in the previously pseudohomeotropic regions (S_X phase) which may correspond to either the S_I* phase or a smectic crystal phase such as either Cr E or Cr J. A possible explanation of this confusing texture may be the co-existence of both phase types which also accounts for the rather high enthalpy (compound (**2**), 5.63 kJ mol^{-1}) associated with the transition. The free-standing film texture of the S_X phase exhibits unfocussable schlieren contained within well defined mosaic regions (Plate 1) which suggests S_I*.

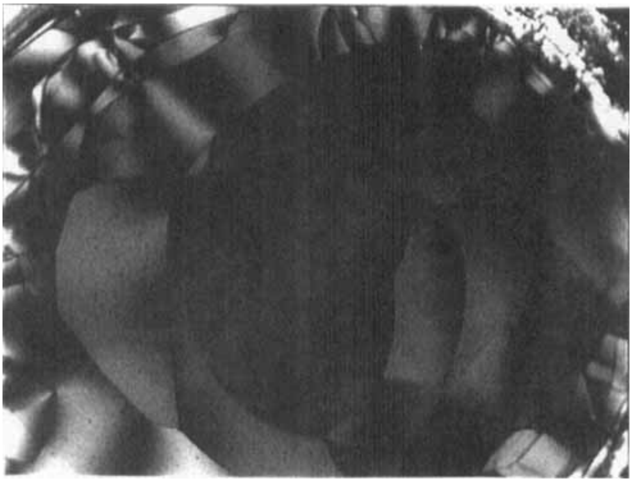


PLATE 1 Free standing film texture of the S_X phase for compound (**2**)
(See Color Plate IX at the back of this issue)

Miscibility study with the standard compound, i.e., (*R*)-4-(1-methylheptyloxycarbonylphenyl)-4'-nonyloxybiphenyl-4-carboxylate (**14**)[5] was under taken to further ascertain the identity of the S_X phase. Figure 1 shows continuous miscibility across the entire temperature range for the S_A, S_C*ferro-, S_C*ferri-, S_C*antiferro-electric and S_I* phase types. Despite the

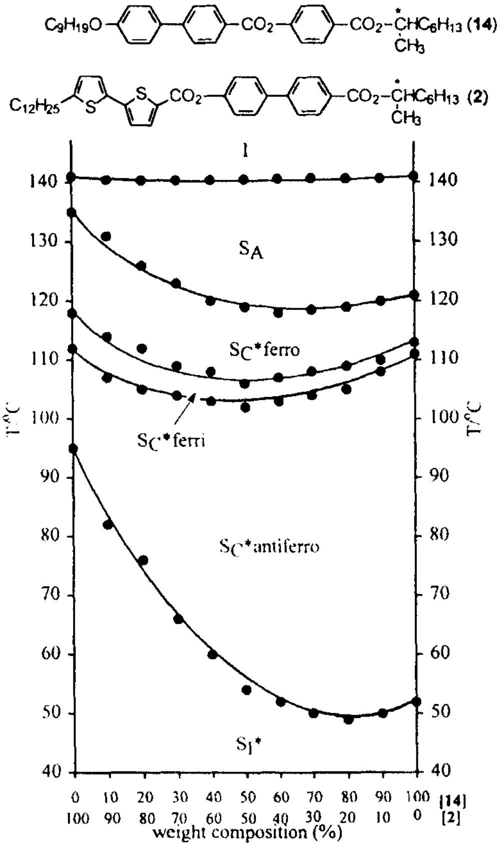


FIGURE 1 Miscibility diagram for compound (**2**) with the standard material (**14**).

seemingly continuous miscibility for the S_I* phase, further complimentary studies are required. Hence, at this stage, the unknown S_X phase may be tentatively assigned as S_I*.

Comparison of the four ring compounds, i.e., (**2**) versus (**3**), reveals that the thermal stability is slightly more favourable (3°C). However, a significant difference can be seen in the S_C*ferrielectric phase range: (**2**) phase range, 5.8°C; (**3**) phase range, 2°C.

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