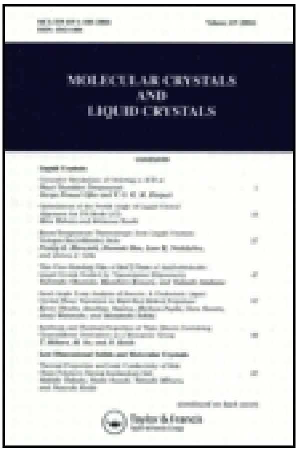

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The Synthesis and Liquid Crystal Properties of Certain 5,5″-Disubstituted 2,2′:5′,2″-Terthiophenes

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THE SYNTHESIS AND LIQUID CRYSTAL PROPERTIES OF CERTAIN 5,5″-DISUBSTITUTED 2,2′:5′,2″-TERTHIOPHENES

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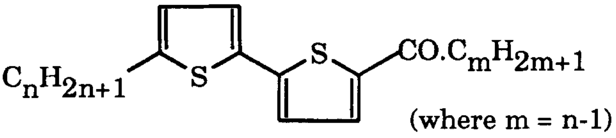
Abstract The synthesis and liquid crystal properties of eight members of an homologous series of 5-n-alkanoyl-5″-n-alkyl-2,2′:5′,2″-terthienyls and the corresponding eight 5,5″-di-n-alkyl-2,2′:5′,2″-terthienyls are reported. The disposition of the three thiophene rings is sufficiently linear that suitably substituted compounds are mesomorphic, and the liquid crystal transition temperatures of related members of the two series are compared. Corresponding 5,5′-disubstituted 2,2′-bithienyls are not liquid crystalline.

INTRODUCTION

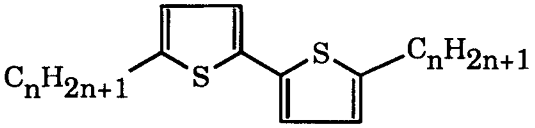
At present, there is growing interest in the liquid crystal properties of disubstituted thiophenes and bithiophenes[1-4]. The mesogenic properties of these compounds are dependent on the linearity of the system which is determined by the relative disposition of the substituents and of the thiophene rings with respect to each other. Cai *et al.*[2,5] have reported that 2,5-disubstitution of thiophene produces a non-linear molecule with an exocyclic bond angle of 148°. Thus, the conventional lath-like packing arrangement usually associated with structures containing 1,4-phenylene, in which the exocyclic bond angle is 180°, is severely disrupted in the case of thiophene-based molecules. Due to a reduction in the packing efficiency of the molecules, the compounds are generally lower melting than their analogous 1,4-phenylene counterparts. In addition, thiophene-based systems possess a strong lateral dipole within their structure due to the presence of lone pairs of electrons on the sulphur atom. This is an important feature when tailoring molecules for display applications which require a large negative dielectric anisotropy as it eliminates the need for lateral substituents such as cyano- and fluoro- which also have the disadvantage of increasing the molecular breadth and viscosity of the system.

Most of the relatively few 2,2′-disubstituted bithiophenes reported in the literature contain elongated terminal substituents which are able to conjugate with the bithienyl core, e.g. diesters and divinylenes[6]. We have synthesised a range of 5-n-alkanoyl-5′-n-alkyl- (**1**) and 5,5′-di-n-alkyl-2,2′-bithienyls (**2**) but these compounds are not mesomorphic, presumably due to poor molecular geometry and low molecular polarisability. However, it was envisaged that the incorporation of an additional thiophene ring into the molecule, giving a 2,2′:5′,2″-terthienyl core, would be conducive to liquid crystal formation due to improved molecular geometry and an increase in the molecular polarisability.



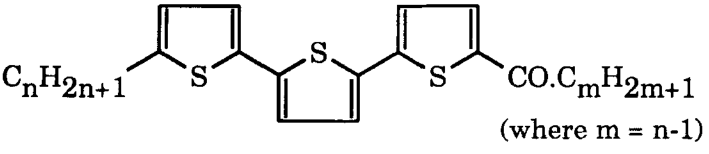
(where m = n-1)

(**1**)



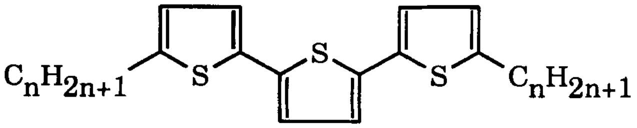
(**2**)

Accordingly, following our preliminary communication[7], we now report the synthesis and liquid crystal properties of members of an homologous series of 5-n-alkanoyl-5″-n-alkyl- (**3**) and the corresponding 5,5″-di-n-alkyl-2,2′:5′,2″-terthienyls (**4**). The properties of these compounds are also compared with analogous 5,5′-disubstituted bithienyls and 4,4″-disubstituted 1,1:4′,1″-terphenyls.



(where m = n-1)

(**3**)



(**4**)

SYNTHESIS

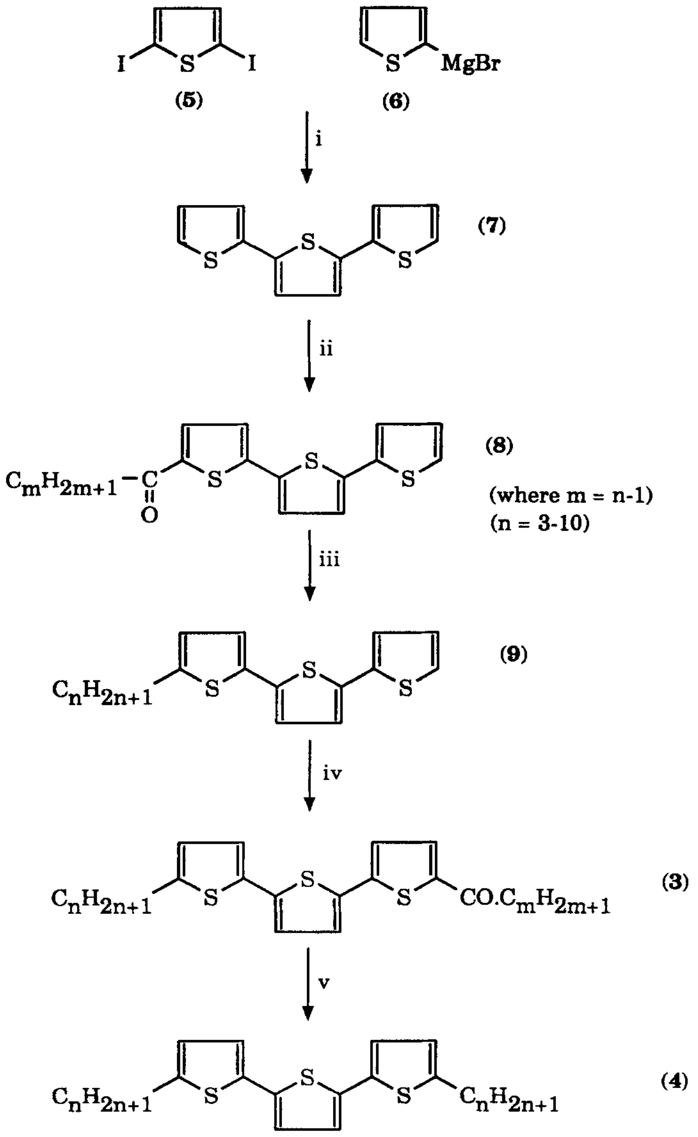
The method of preparation of eight homologues (n=3-10) of series (3) and the corresponding members of series (4) is outlined in Scheme 1. The analogous two-ring compounds, the 5,5′-disubstituted 2,2′-bithienyls, were also synthesised in a similar manner and the physical constants for these compounds are given the experimental section.

The Nickel-catalysed cross-coupling reaction[8] between 2,5-diiodothiophene (5) and the Grignard reagent (6), derived from 2-bromothiophene, afforded 2,2′:5′,2″-terthienyl (7) in low to moderate yield (33%). This is a particularly useful 'one-pot' coupling reaction with additional advantageous features, such as short reaction time and ease of separation and purification of the desired product. Friedel-Crafts acylation of compound (7) with the appropriate acid chloride, catalysed by titanium(IV) tetrachloride, yielded the compounds (8) which on Wolff-Kishner (Huang-Minlon) reduction gave the intermediate 5-n-alkyl-2,2′:5′,2″-terthienyls (9). Friedel-Crafts acylation of the compounds (9) with the appropriate acid chloride afforded the members of the 5-n-alkanoyl-5′-n-alkyl-2,2′:5′,2″-terthienyls, series (3). Subsequent reduction of members of series (3) gave the corresponding 5,5″-di-n-alkyl-2,2′:5′,2″-terthienyls, series (4).

RESULTS AND DISCUSSION

Eight members (n=3-10) of homologous series (3) and eight members (n=3-10) of the corresponding homologous series (4) were prepared. The liquid crystal transition temperatures and thermodynamic data for members of series (3) and (4) are listed in Tables I and II, respectively.

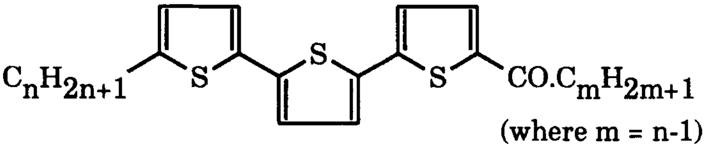
The disposition of the three thiophene rings of 2,2′:5′,2″-terthienyl is such that when suitable 5- and 5″-substituents are present the molecular geometry is sufficiently linear to sustain mesomorphic behaviour. All the members of both series (3) and series (4) are liquid crystalline. Reduction of the carbonyl group of members of series (3) leads to a lowering of the melting point of the corresponding members of series (4) and an increase in the occurrence of tilted smectic phases. The liquid crystal phase types



i. $[(C_6H_5)_2PCH_2CH_2CH_2(C_6H_5)_2)]NiCl_2$, ether, reflux.
ii + iv. $RCOCl$, $TiCl_4$, CH_2Cl_2.
iii + v. $NH_2NH_2.H_2O$, KOH, diethylene glycol, reflux.

SCHEME 1

TABLE I Liquid crystal transition temperatures and enthalpies of transition for the 5-n-alkanoyl-5″-n-alkyl-2,2′:5′,2″-terthienyls (3)[a]



(3)

(where m = n-1)

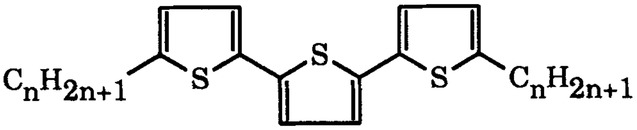
n	m	C-S_C/S_A	S_C-S_A[b]	S_C/S_A-I
3	2	155.5	-	166.5
		(20.96)		(7.60)
4	3	148.3	-	155.7
		(24.58)		(7.64)
5	4	137.2	-	163.0
		(15.57)		(6.36)
6	5	138.4	-	162.0
		(25.86)		(10.70)
7	6	132.0	138.9	161.8
		(30.29)	-	(12.22)
8	7	133.0	151.0	159.7
		(25.09)	-	(11.32)
9	8	129.4	154.2	158.7
		(34.04)	-	(13.12)
10	9	127	-	152.0
		(36.48)		(13.25

[a] For each compound the first row gives transition temperatures (°C) and the second row (in parentheses) gives enthalpies of transition (kJ mol^{-1}) on heating (DSC scan rate 10°C min^{-1}). [b] The enthalpy of the second-order S_C-S_A transition was too small to be evaluated.

were studied by thermal optical microscopy and differntial scanning calorimetry (DSC). The compounds of series (3) give rise to S_A and S_C phases, and S_C, S_F, and S_G phases are formed by members of series (4)

The liquid crystal transition temperatures of the members of series (3) and (4) are represented graphically in Figures 1 and 2, respectively, as a plot against n, the number of carbon atoms in the alkyl group. For series (3), the early homologues

TABLE II Liquid crystal transition temperatures and enthalpies of transition for the 5,5″-di-n-alkyl-2,2′:5′,2″-terthienyls (4)[a]

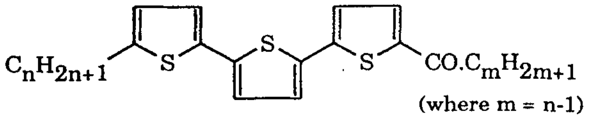


(4)

n	C-S_X/S_G/S_F	S_G-S_F	S_F-S_C	S_G/S_C-I
3	50	-	-	74
	(18.01)			(12.38)
4	50	-	-	75
	(20.99)			(16.32)
5	53	-	-	77
	(22.07)			(12.37)
6	51	-	-	82
	(20.15)			(19.94)
7	55	78	83	89
	(19.31)	(3.92)	(0.99)	(10.21)
8	65	72	87	91
	(24.62)	(3.78)	(0.78)	(10.02)
9	64	(62)[b]	91	95
	(29.74)	(10.49)[c]	(1.91)	(13.59)
10	71	-	95	96
	(40.05)		(-)[d]	(21.83)[e]

[a] For each compound the first row gives transition temperatures (°C) and the second row (in parentheses) gives enthalpies of transition (kJ mol^{-1}) on heating (DSC scan rate 10°C min^{-1}). [b] Monotropic transition. [c] Enthalpy of transition on cooling. [d] The enthalpy of the S_F-S_C transition could not be determined due to masking by the S_C-I transition. [e] This value includes the enthalpy for the S_F-S_C transition.

(n=3,4,5,6) exhibit an S_A phase, whereas for the higher homologues (n=7,8,9) both S_A and S_C phases are observed. The S_A phase separates from the isotropic liquid as bâtonnets which coalesce to form an elongated focal-conic fan texture. At the S_A-S_C transition, the fans shatter and schlieren develops in the areas which were homeotropic in the S_A phase, both textures being characteristic of the S_C phase. The DSC



(3)

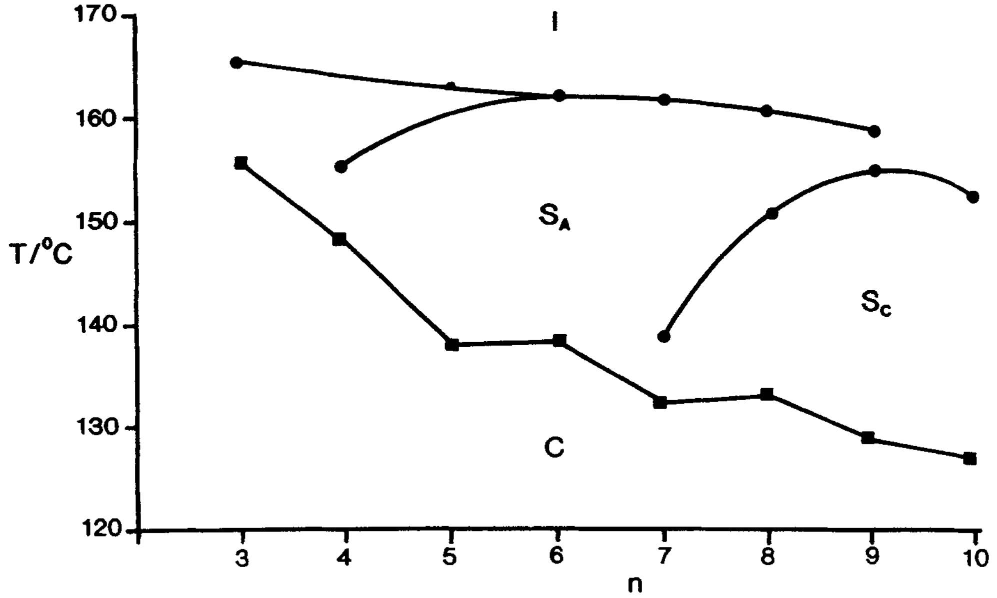


FIGURE 1 5-n-Alkanoyl-5″-n-alkyl-2,2′:5′,2″-terthienyls (3): transition temperatures against n, the number of carbon atoms in the alkyl chain.

■——■ crystal to mesophase transition

●——● mesophase to mesophase; mesophase to isotropic transition

thermogram (Figure 3) recorded at a cooling rate of 10°C min^{-1} shows a small peak corresponding to a second order transition. For the n=10 homologue the S_A phase is extinguished and only an S_C phase is observed.

For series (4), the S_A phase is not observed. The early homologues (n=3,4,5,6) exhibit a phase ('S_X') which, on cooling from the isotropic liquid, appears, at first sight, to be the onset of crystallisation and which is associated with a large enthalpy of transition*. Large, 'splinter-like' lancets rapidly cross the field of view forming a mosaic texture with irregularly shaped and sized constituents, mostly angular, sharp-cornered in appearance and often highly coloured (Figure 4). We believe this 'S_X' phase to be an ordered, crystal phase, most probably S_G. However, in Figure 2,

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*For example, n=4 homologue. DSC cooloing cycle: 70°C, ΔH=16.2 kJ mol^{-1}; 22°, ΔH=18.

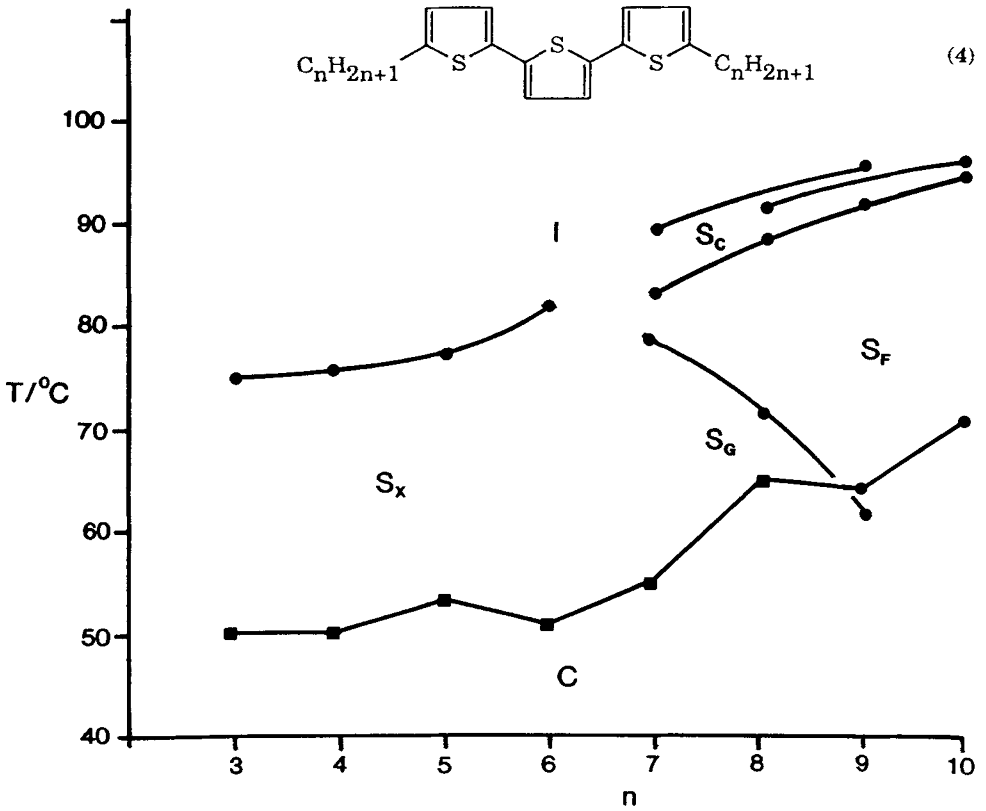


FIGURE 2 5,5″-Di-n-alkyl-2,2′:5′,2″-terthienyls (4): transition temperatures against n, the number of carbon atoms in the alkyl chain.

■——■ crystal to mesophase transition

●——● mesophase to mesophase; mesophase to isotropic transition

we have chosen not to connect the points for the transition temperatures I-S_X (n=3,4,5,6) with those for S_F-S_G (n=7,8,9) because of the clear discontinuity between n=6 and n=7. Further work to establish the identity of the 'S_X' phase is necessary. The later homologues (n=7,8,9) exhibit S_C, S_F and S_G phases. The S_F phase was characterised by closely observing the schlieren-mosaic texture formed either on cooling the S_C phase or on heating the S_G phase. At the phase transition, the schlieren-mosaic texture could be brought into optical focus[9], thus indicating an S_F phase (Figure 5) rather than an S_I phase. Following the S_F-S_G transition (n=7,8,9) the focal-conic fans become severely broken and many have a 'chequerboard' appearance. The schlieren-mosaic texture of the preceding S_F phase becomes a coloured mosaic with quite small mosaic areas. On

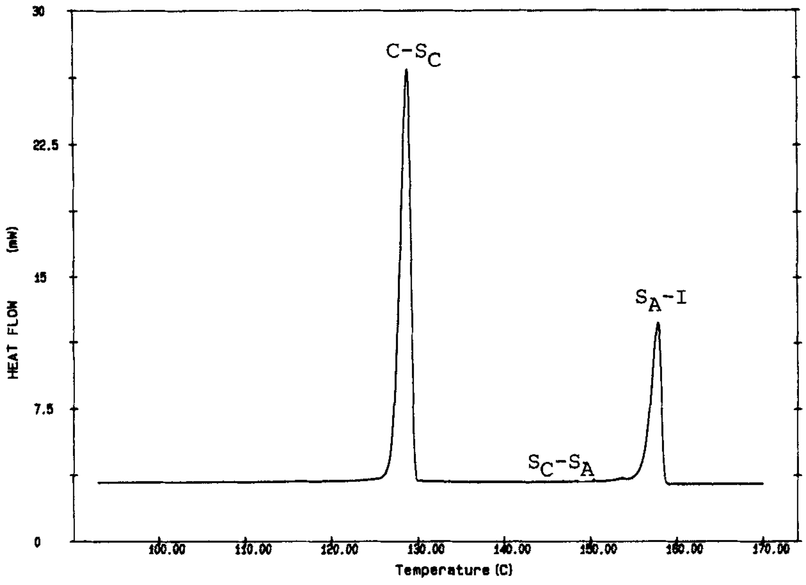


FIGURE 3 DSC thermogram of the n=9 homologue of series (**3**)

cooling the n=10 homologue from the isotropic liquid, an extremely short S_C phase is observed (which persists over a range of only 1°C) and this is followed immediately by an S_F phase. No S_G phase is formed on further cooling.

Tables III and IV list the transition temperatures for certain analogous two-ring 5,5′-disubstituted 2,2′-bithienyls and 4,4′-disubstituted biphenyls. The data show that the 5-n-alkanoyl-5′-alkyl-[10a] and 5,5″-di-n-alkyl-2,2′-bithienyls[11] are not liquid crystalline, whereas the corresponding 4,4′-disubstituted biphenyls are mesomorphic and exhibit smectic phases. The most likely reason for this is the distorted molecular geometry of the bithienyl core resulting in a relatively non-linear structure which does not lend itself to mesophase formation. By comparison, in the 5,5″-disubstituted-2,2′:5′,2″-terthienyls, e.g. members of series (**3**) and (**4**), the extra thiophene ring, in addition to increasing the molecular polarisability, appears to modify the molecular geometry so that it is sufficiently linear to be conducive to liquid crystal formation. In 2,2′-bithiophene the two sulphur atoms lie *trans* with respect to each other[11] and it is assumed that the three rings of 5,5″-disubstituted-2,2′:5′,2″-terthiophene are probably disposed in a similar 'up-down-up' manner in a nearly linear conformation.

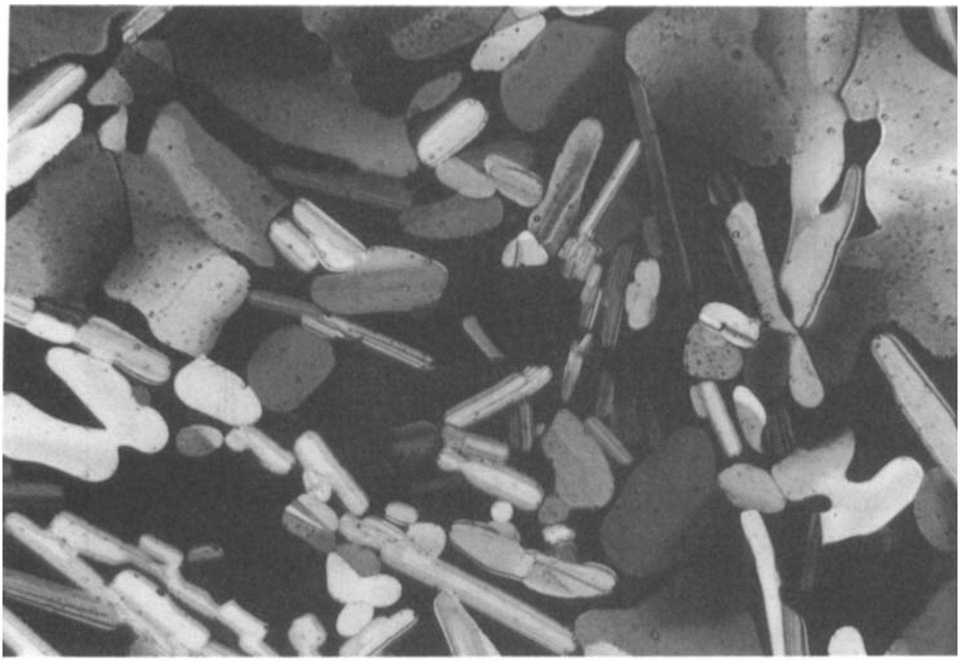


FIGURE 4 Photomicrograph of the mosaic texture of the 'S_X' phase of the n=4 homologue of series (4). See Color Plate III.

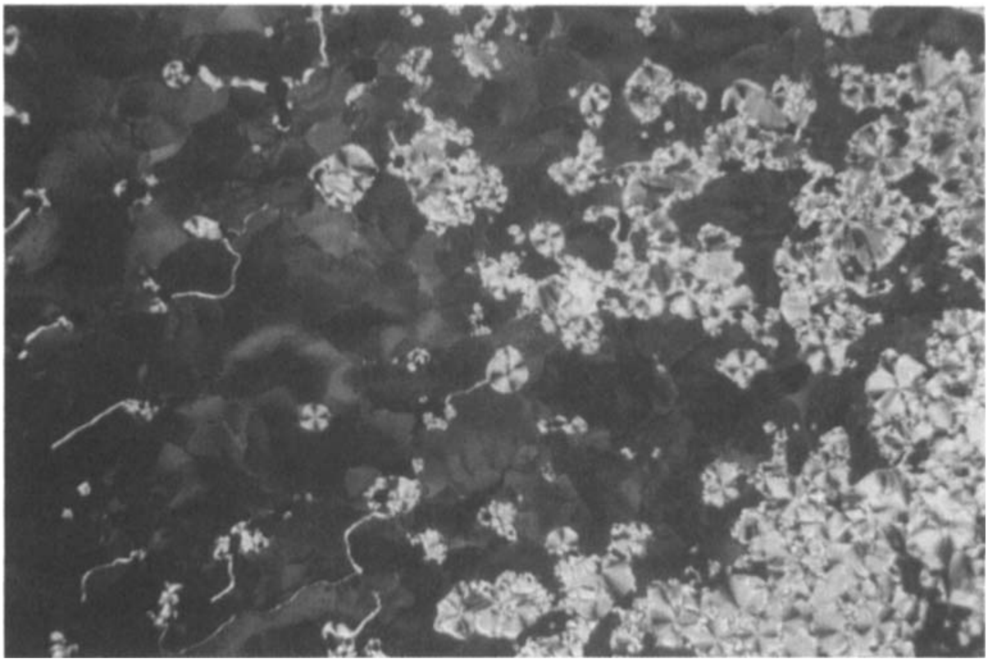
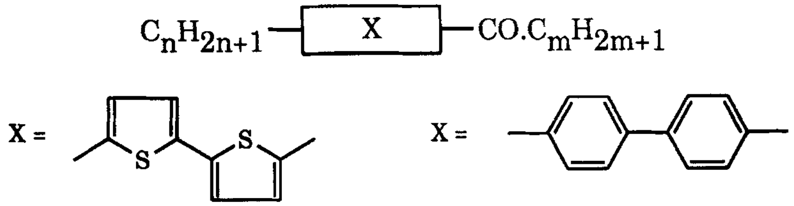


FIGURE 5 Photomicrograph of the S_F phase of the n=9 homologue of series (4) showing the schlieren-mosaic texture. See Color Plate IV.

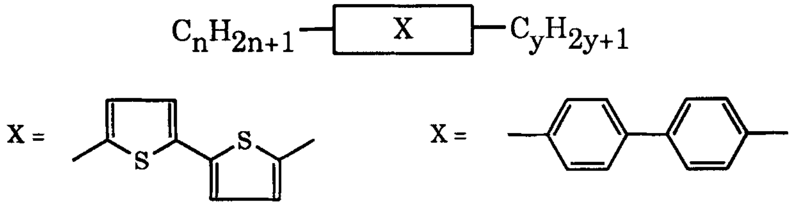
TABLE III Transition temperatures (°C) of certain 5-n-alkanoyl-5′-alkyl-2,2′-bithienyls and analogous 4-n-alkanoyl-4′-n-alkylbiphenyls[10a]



n	m	C-I
7	6	89-90
8	7	95-95
9	8	92-93
10	9	102-103

n	m	C-S_1	S_1-S_2	S_1/S_2-C
7	5	95	98	105
8	5	87.5	93.5	102.5
9	5	83	90.5	101
10	5	77	89	100.5

TABLE IV Transition temperatures (°C) of certain 5,5′-di-n-alkyl-2,2′-bithienyls and analogous 4,4′-di-n-alkylbiphenyls[11]

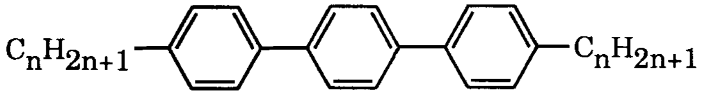


n	y	C-I
7	7	56
8	8	43
9	9	56
10	10	52

n	y	C-S_E	S_E-S_B	S_B-I
5	5	12	47	52
6	6	35	39.5	53.5
7	4	-15	16.5	38.5

Table V lists the transition temperatures for the analogous 4,4″-di-n-alkyl-1,1′:4′,1″-terphenyls[10b] enabling a comparison with the members of series (4) to be made. Relative to the terphenyl analogues, the presence of three thiophene rings considerably lowers the melting point (the average melting point for members n=6-10 is 61.2°C) and mesophase stability (the average clearing point for members n=6-10 is 90.6°C). Again, the lowering of the thermal stability of the terthienyl relative to their terphenyl analogues may be attributed to the significant deviation from linearity within the terthienyl core which disrupts the lamellar packing arrangement of the molecules in the mesophases.

TABLE V Transition temperatures (°C) of certain 4,4″-di-n-alkyl-1,1′:4′,1″-terphenyls[10b]



n	C-S	S-I
6	193	218
7	181	205
8	176	181
9	166	185
10	161	181

The results of further investigation of the mesomorphic behaviour of 5,5″-disubstituted-2,2′:5′,2″-terthienyls and related three-ring heterocyclic compounds containing the bithienyl unit will be reported in a future publication.

EXPERIMENTAL

Structural confirmation of the structures of the intermediates and the products was obtained by ^{1}H NMR spectroscopy (JEOL FX60Q 270 MHz spectrometer) and infrared spectroscopy (Perkin-Elmer FT 1605 spectrophotometer). Measurements of transition temperatures and microscopic observations of mesophase textures were made using a Vickers M75 polarising microscope in conjunction with a Mettler FP52 hot stage and

FP5 control unit. These were confirmed by thermal analysis which was carried out with a Perkin-Elmer DSC7 differential scanning calorimeter at heating and cooling rates of 10°C min^{-1}.

2,2′:5′,2″-Terthienyl (7)

The Grignard reagent (6), prepared by dropwise addition of 2-bromothiophene (30.0 g, 0.184 mol) in dry ether (200 ml) to magnesium turnings (4.9 g, 0.202 mol) in an atmosphere of nitrogen, was cooled to 0°C and added, dropwise, to a solution of 2,5-diiodothiophene (5) (20.0 g, 0.092 mol) and [1,3-bis(diphenylphosphino)-propane]nickel(II) chloride (0.5 g, 0.90 mmol) in dry ether (150 ml) ensuring that the temperature did not exceed 10°C. The reaction mixture was then stirred under reflux for 10 h and poured into ice-cold saturated aqueous ammonium carbonate (200 ml). The aqueous layer was extracted with ether (4x150 ml) and the combined extracts were washed with water (200 ml), dried ($MgSO_4$), and the solvent removed in *vacuo*. The crude product was crystallised from a mixture of 1:1 ethanol : light petroleum (b.p. 40-60°C) affording the desired 2,2′:5′,2″-terthienyl (7), 7.2 g (33%), m.p. 92-94°C (lit.[8] 93-95°C) as a yellow solid.

δ_H ($CDCl_3$) 7.0-7.3 (8H, m, ArH); ν_{max} (KBr) 3036w (C-H str.), 1496w, 1422w (C=C str.), 844w, 833m, 798s, 688s, 676s (C-H o.o.p.d.) cm^{-1}.

2,2′-Bithienyl was prepared in a similar manner from 2-bromothiophene (33 g, 0.2 mol), C_4H_3SMgBr (0.245 mol), Ni(dppp)Cl_2 (1.1g, 0.002 mol). Distillation of the residue afforded the 2,2′-bithienyl, 31.6 g (94%), b.p. 100°C/0.2 mmHg (lit.[8] 144°C/25 mmHg), as a colourless liquid which solidified on standing, m.p. 31-32°C.

5-n-Alkanoyl-2,2′:5′,2″-terthienyls (8)

Titanium(IV) chloride (1.3 ml, 0.012 mol) was added in portions, with stirring, to a mixture of the appropriate acid chloride (0.012 mol) and 2,2′:5′,2″-terthienyl (7) (2.0 g, 0.008 mol) in dry dichloromethane (100 ml), maintained at -10°C. After the addition, the reaction mixture was stirred for 6 h at room temperature, then poured into a mixture of ice/concentrated hydrochloric acid (100 ml) and stirred for a further 1 h. The aqueous phase was extracted with dichloromethane (3x150 ml) and the combined organic layers were washed with saturated aqueous sodium hydrogen carbonate (200 ml), water (200 ml), and then dried ($MgSO_4$) and the solvent removed under reduced pressure. The crude product was purified by a column chromatography on silica gel, eluting with 4:1 chloroform : light petroleum ether (b.p. 40-60°C), followed by recrystallisation of the resulting solid from ethanol to yield the desired product (**8**) (50-65%) as pale yellow crystals, m.p.s: C_2H_5CO, 136-137°C; C_3H_7CO, 123-125°; C_4H_9CO, 127-129°; $C_5H_{11}CO$, 133-134°; $C_6H_{13}CO$, 128-129°; $C_7H_{15}CO$, 131-132°; $C_8H_{17}CO$, 127-128°; $C_9H_{19}CO$, 130-131°.

The following spectroscopic data for 5-n-pentanoyl-2,2':5',2"-terthienyl are typical of the series:

δ_H ($CDCl_3$) 1.0 (3H, t, CH_3), 1.2-1.8 (4H, m, $2CH_2$), 2.9 (2H, t, $COCH_2$), 7.0-7.6 (7H, m, ArH); ν_{max} (KBr) 3061w (arom. C-H str.), 2926m, 2866m (aliph. C-H str.), 1654s (C=O str.), 1457m, 1443 m (C-H str.), 794s, 694m, 685m (C-H o.o.p.d.) cm^{-1}.

The 5-n-alkanoyl-2,2'-bithienyls were prepared in a similar manner, m.p.s : $C_5H_{11}CO$, 77-78°C; $C_6H_{13}CO$, 82-83°; $C_7H_{15}CO$, 76-77°; $C_8H_{17}CO$, 88-89°.

5-n-Alkyl-2,2':5',2"-terthienyls (9)

A solution of the appropriate ketone (0.010 mol) and hydrazine hydrate (10 ml, 0.20 mol) in diethylene glycol (150 ml) was heated gently under reflux for 2 h. The excess of hydrazine hydrate was then distilled off and the temperature of the reaction mixture was increased to and maintained at 210°C for 1 h. After cooling the reaction mixture to room temperature, potassium hydroxide pellets (11.2 g, 0.20 mol) were added, and the mixture then reheated to 160°C for 3 h. and poured into a mixture of ice/concentrated hydrochloric acid (100 ml). The product was extracted with chloroform (3x100 ml), washed with water (200 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with 1:4 chloroform : light petroleum (b.p. 40-60°C), followed by recrystallisation from ethanol affording the desired 5-n-alkyl-2,2':5',2"-terthienyl (**9**) as a pale yellow solid (75-90%), m.p.s: C_3H_7, 56-57°C; C_4H_9, 54-55°; C_5H_{11}, 58-59°; C_6H_{13}, 63-61°: C_7H_{15}, 73-74°; C_8H_{17}, 74-75°; C_9H_{19}, 74-75°; $C_{10}H_{21}$, 70-71°.

The following spectroscopic data, which are typical of the series, refer to 5-n-pentyl-2,2':5',2"-terthienyl:

δ_H ($CDCl_3$) 0.9 (3H, t, CH_3), 1.2-1.8 (6H, m, $3CH_2$), 2.8 (2H, t, CH_2), 6.6-7.2 (7H, m, ArH); ν_{max} (KBr) 3062w (arom. C-H str.), 2918s, 2853m (aliph. C-H str.), 1449m, 1426m (C-H str.), 834m, 797s, 680s (C-H o.o.p.d.) cm^{-1}.

The analogous 5-n-alkyl-2,2'-bithienyls were prepared in a similar manner and were purified by vacuum distillation (Kugelrohr), b.p.s: C_7H_{15}, 170°C/0.6 mmHg; C_8H_{17}, 170°/0.01; C_9H_{19}, 205°/0.05; $C_{10}H_{21}$, 225°/0.3.

5-n-Alkanoyl-5"-n-alkyl-2,2':5',2"-terthienyls (3)

Friedel-Crafts acylation of the appropriate 5-n-alkyl-2,2':5',2"-terthienyl (9) (4.0 mmol) with the appropriate acid chloride (4.3 mmol) in the presence of titanium(IV) chloride (0.82 g, 4.3 mmol) was carried out by the method described for the preparation of compound (8). The crude product was subjected to column chromatography on silica gel, eluting with 4:1 chloroform : light petroleum ether (b.p. 40-60°C), and then recrystallised from ethanol affording the desired product (3) as a yellow solid (50-60%). The mesomorphic transition temperatures for these ketones are listed in Table 1.

The following data for 5-n-butanoyl-5"-n-butyl-2,2':5',2"-terthienyl are typical of the series:

Found: C, 63.94; H, 5.91%. $C_{20}H_{22}OS_3$ requires C, 64.17; H, 5.88%; δ_H($CDCl_3$) 1.0 (6H, m, $2CH_3$), 1.4-1.8 (6H, m $3CH_2$), 2.9 (4H, m $2CH_2$), 6.7-7.6 (6H, m, ArH); ν_{max} (KBr) 3065w (arom. C-H str.), 2923s, 2852m (aliph. C-H str.), 1647s (C=O str.), 1450m, 1439m (C-H str.), 795s (C-H o.o.p.d.) cm^{-1}.

5,5"-Di-n-alkyl-2,2':5',2"-terthienyls (4)

Reduction of the appropriate ketone (3) (6.0 mmol) with hydrazine hydrate (20.0 mmol) in diethylene glycol (50 ml) was achieved by the method described for the preparation of compound (9). Purification by column chromatography on silica gel eluting with 1:9 chloroform : light petroleum (b.p. 40-60°C), followed by recrystallisation from ethanol afforded the required 5,5"-di-n-alkyl-2,2':5',2"-terthienyl (4) as pale yellow crystals (75-85%). The mesomorphic transition temperatures of the dialkyl compounds are listed in Table II.

The following data refer to 5,5"-di-n-decyl-2,2':5',2"-terthienyl and are typical of the series: Found: C, 72.72; H, 9.08%. $C_{32}H_{48}S_3$ requires C, 64.17; H, 9.46%; δ_H($CDCl_3$) 0.9 (6H, t, $2CH_3$), 1.2-1.8 (32H, m, $16CH_2$), 2.8 (4H, t, $2CH_2$), 6.6-7.2 (6H, m, ArH);

ν_{max} (KBr) 3064w (arom. C-H str.), 2917s, 2848s (C-H str.), 1472m, 1446m (C-H str.), 854m, 793s, 784m (C-H o.o.p.d.) cm^{-1}.

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