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New mesogenic thiophene and furan derivatives

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The synthesis of novel liquid-crystalline heteroaromatic compounds incorporating the five membered thiophene and furan rings is described. The objective of the present work is to substitute the mesogenic units styrylthiophene, styrylfuran, phenylthiophene and phenylfuran for the aromatic structural units styrylbenzene and biphenyl in known mesomorphic compounds, thereby permitting a comparison of the effect of heterocyclic units on mesomorphic properties. The compounds synthesized with the mesogenic units styrylthiophene and phenylthiophene exhibited liquid-crystalline properties while compounds with the units styrylfuran and phenylfuran did not. The existence of mesophases in these compounds is closely associated with the configuration (linearity) of the molecule. The heterocyclic rings thiophene and furan are pentagonal and 2,5-disubstitution leads to non-collinear bonds which produce a deviation from linearity of the order of 32° and 54°, respectively.

1. Introduction

Over the past few years many new substances having liquid-crystalline properties have been synthesized. Synthesis of chemical compounds having a long extended rod-like molecular shape is still the fundamental premise and guarantee for the occurrence of a thermotropic liquid-crystalline phase [1, 2].

A great number of mesomorphic compounds containing heterocyclic units have been synthesized, and interest in such structures constantly grows [3, 4]. This is not only because of the greater possibilities with heterocyclics for the design of new mesogenic molecules, but also because the insertion of heteroatoms strongly influences the formation of mesomorphic phases. The effect of heteroatoms can change considerably the polarity, polarizability and sometimes the geometry of the molecule, thereby influencing the type of mesophase, the phase transition temperatures, dielectric constants and other properties of the mesogens [5, 6].

In this work, we have synthesized new compounds containing the five membered heteroaromatic rings, thiophene or furan. These rings may be incorporated into the principal structure of known calamitic mesogens with desired properties. Compounds containing the five membered thiadiazole or thiophene heteroaromatic rings have been reported [7–9] and compounds containing the apparently more mesogenic thiophene ring have recently been reported [10, 11].

We describe here the synthesis and the mesomorphic behaviour of the structural units *trans*-styrylthiophene **8a**, *trans*-styrylfuran **8b**, phenylthiophene **14(a, b, c)** and phenylfuran **14d**. We compare these compounds with the analogous isoelectronic compounds such as *trans*-stilbene and biphenyl derivatives. We also describe the behaviour of some Schiff's bases **9(a, b, c)**, using the same structural units.

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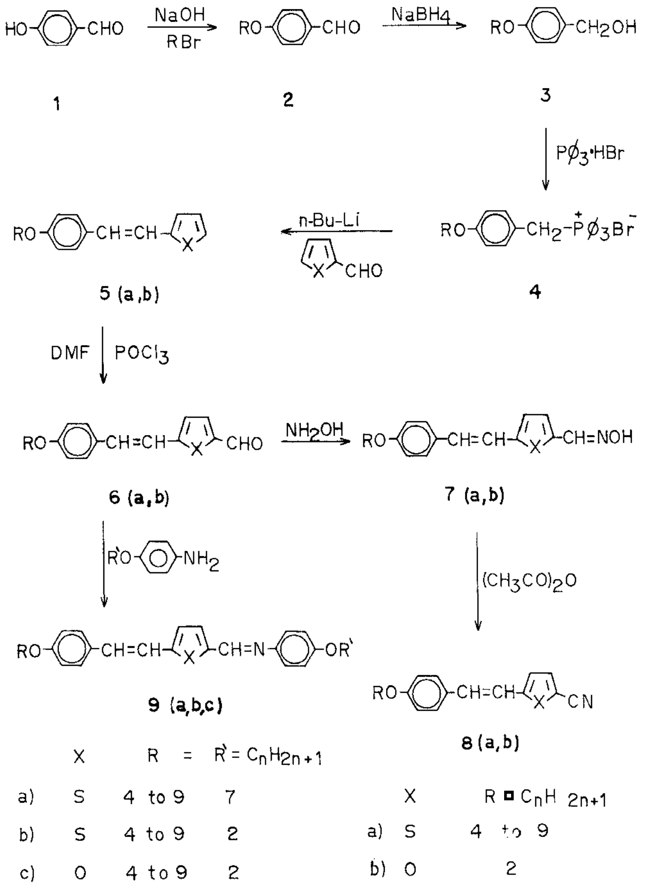
2. Synthesis

The route used for the synthesis of the new compounds **8(a, b)** and **9(a, b, c)** is shown in scheme 1.

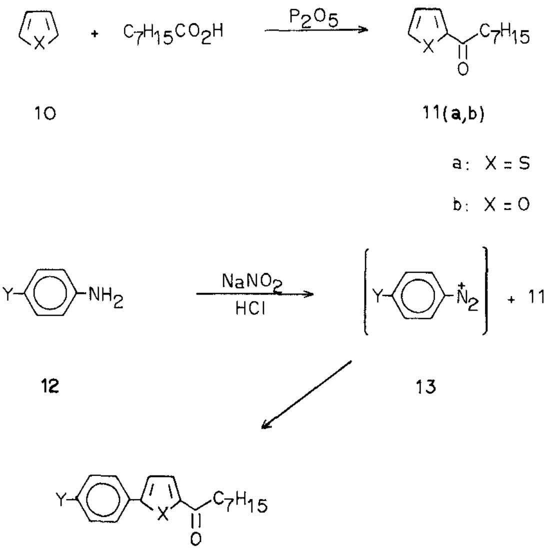


	X	R =	R' = C_nH_{2n+1}
a)	S	4 to 9	7
b)	S	4 to 9	2
c)	O	4 to 9	2

	X	R = C_nH_{2n+1}
a)	S	4 to 9
b)	O	2

The styrylthiophene **8a** and styrylfuran **8b** were synthesized in seven steps, starting with the alkylation of the 4-hydroxy-benzaldehyde **1**, and proceeding with the reduction of the aldehyde moiety with sodium borohydride. The phosphonic salt **4** was prepared from the triphenylphosphonic bromide and the alcohol **3**. In the preparation of these compounds, the purification becomes more difficult as the aliphatic chain increases. Purification is especially difficult for the compounds with eight and nine carbon atoms, which show amphilic properties. The following step is the ylidium preparation, *in situ* using *n*-butyl lithium, which reacts immediately with 2-tenaldehyde, leading to the formation of the olephinic product **5** [12]. The isolated product corresponds to the trans isomer by ^{1}H NMR spectroscopy. The vinyl system AB shows two sets of doublets centred at 6·97 and 7·01 ppm with $J_{AB} = 18$ Hz, which are typical values for the *trans* vinyl system. The following steps involve formilation reactions, oxime formation and dehydration with acetic anhydride. The Schiff's base series **9(a, b)** were obtained through condensation of aldehyde **6** with the corresponding alkoxyaniline.

The reaction pathway used to prepare the phenylthiophenes **14(a, b, c)** is shown in scheme 2.



14

	X	Y
a:	S	$-OR$
b:	S	$-Br$
c:	S	$-NO_2$
d:	O	$-OC_6H_{13}$

The acylation of the thiophene was done according to the method described in [13]. The transformation of the diazonium salt **13** into the desired product **14** requires the use of the Meerwein reaction [14] with 2-octanoylthiophene **11**. The short reaction sequences leading to the various substituted phenylthiophene and phenylfuran derivatives **14(a, b, c, d)**, will be described in details in the Experimental and require no comment. Although the yields are only moderate, 20–25 per cent, this reaction is very important because the product can be obtained in only one step.

3. Results and discussion

The transition temperatures were determined by optical texture observation using a polarizing microscope equipped with a hot stage, and are listed in tables 1–4. Table 1 summarizes the mesomorphic behaviour for 2-cyano-5-(4-alkoxystyryl)thiophene **8a** with various chain lengths. As can be observed in table 1, the melting point decreases slightly with increase in the chain length. The homologues with $n=6,7$ show enantiotropic nematic mesophases. However, the homologues with $n=5,8,9$ show monotropic nematic mesophases. The homologues with $n=9$, show crystalline and monotropic smectic polymorphism. The $n=4$ homologue is not a liquid crystal.

The nematic mesophase for all compounds in this series exhibit schlieren textures and the typical nematic droplets are observed on cooling from the isotropic liquid. The smectic phase observed at 82·5°C appears to be smectic A. The phase separates on cooling the nematic phase, in the form of batonnets and these batonnets coalesce to form a focal-conic fan texture; there is a strong tendency to assume a homeotropic texture.

Styrylthiophene compounds **8a** show a considerably lower thermal stability of the nematic phase than purely aromatic compounds having similar molecular structures

Table 1. Transition temperatures for the series 2-cyano-5-(4-*n*-alkoxystyryl)thiophene **8a**.†

n	C		C′		S_A		N		I
4			●	99·5°C	—		—		●
5			●	77·5°C	—		●	(74·5°C)	●
6			●	74·0°C	—		●	78·6°C	●
7			●	75·5°C	—		●	80·5°C	●
8			●	85·2°C	—		●	(83·6°C)	●
9	●	82·7°C	●	85·4°C	●	(82·5°C)	●	(84·0°C)	●

† Monotropic transitions in parentheses.

Table 2. Transition temperatures for the series 2-(4-*n*-alkoxystyryl)thienyliden-5-(4-*n*-heptoxyanilene) **9a**.

n	C		N		I	ΔT
4	●	144·8°C	●	166·8°C	●	22·0°C
5	●	144·8°C	●	159·2°C	●	14·4°C
6	●	155·5°C	●	160·0°C	●	4·5°C
7	●	157·5°C	●	(155·3°C)	●	—
8	●	151·6°C	●	155·7°C	●	4·1°C
9	●	143·8°C	●	152·7°C	●	8·9°C

such as 4-pentyl-4′-cyano *trans*-stilbenes [15] or 4-cyano-(4′-alkoxybenzyliden)aniline [16] for the first compound ΔT is 45·5°C [15] and for the second series ΔT varies from 12°C for $n=1$ to 47·6°C for $n=4$ [16]. The styrylfuran series **8b** showed no liquid-crystalline phases.

Probably, the low thermal stability of the styrylthiophene derivatives is due to the presence of the pentagonal heterocyclic ring which produces a non-linear substitution and thereby a molecular curvature which inhibits the formation of mesophases. In the majority of known liquid crystal compounds there is collinear 1,4-disubstitution of the benzene ring whereas compounds with the 2,5-disubstituted thiophene and furan rings are not linear. Using known bond angles, we estimate that for the 2,5-disubstituted thiophene ring that there is 32° deviation from the hard rod axis of the analogous compound with a phenyl ring and for the 2,5-disubstituted furan ring the deviation is on the order of 54°, giving compounds which are not mesogenic. The same behaviour is observed in the series of Schiff's bases **9(a, b, c)**, where the linearity of the molecule is increased by introducing an additional aromatic ring. Even so, none of the styrylfuran derivatives are liquid crystals and it seems that an increase in the aliphatic chain length causes an even larger deviation from linearity in the styrylfuran **9c**. This can be observed in the series **9(a, b)** which are nematogenic liquid crystals with a higher stability than the **8a** series, however between series **9a** and **9b** there are large changes in thermal stability. Their nematic isotropic transition temperatures show the usual odd–even alternation as the aliphatic chain length increases and the decrease of the thermal stability of the mesophase with chain length shows large deviations from linearity, especially for the first compounds of series **9a**.

The transition temperature and enthalpies for the series 2-octanoyl-5-(4-alkoxyphenyl)thiophene **14a** are given in table 4, and figure 1 shows the transition temperatures as a function of the number of carbon atoms (*n*) in the alkoxy chain. The melting point is relatively independent of the chain length, although a slight tendency

Table 3. Transition temperatures for the series 2-(4-*n*-alkoxystyryl)thienyliden-5-(4-ethoxyaniline **9b**.

n	C		N		I	ΔT
4	●	164·3°C	●	200·0°C	●	35·7°C
5	●	154·7°C	●	187·4°C	●	32·7°C
6	●	149·1°C	●	185·0°C	●	35·9°C
7	●	150·5°C	●	177·9°C	●	27·4°C
8	●	148·6°C	●	174·9°C	●	26·3°C
9	●	147·0°C	●	169·1°C	●	22·1°C

for a decrease in melting point with increasing chain length maybe observed. The enthalpies of fusion and of the smectic A–isotropic transition can be considered normal.

The first compound with $n=1$ is not a liquid crystal and for $n=3$ there is only a monotropic smectic A phase. The other homologues show an enantiotropic smectic A phase, and exhibit the normal pattern of alternation. The compound with $n=12$ shows a smectic A phase as well as a unidentified monotropic smectic phase, S_1; no attempt was made to identify the monotropic phase because the phase crystallizes almost immediately. The smectic A–isotropic transition temperature increases with an increase in the chain length and leads to a broadening of the smectic A mesophase range (2·3°C→21·6°C).

The texture observed with the polarizing microscope for the smectic S_A phase was focal-conic or homeotropic. The homeotropic texture observed in convergent light shows a centred uniaxial positive cross. The melting point for the series 4-*n*-alkoxy-4′-*n*-octanoylbiphenyl [16] are very similar to those of series **14a**. Both the phenylthiophene and biphenyl derivatives have melting points of the order 100°C to 129°C (see figures (*a*) and (*b*)). However, the biphenyl series (see figure (*b*)) shows dimorphism S_E–S_A for $n=2$ to 5 and for alkyl terminal chains with $n>5$ there is only a smectic S_A phase and a decrease in the smectic temperature range. This behaviour is opposite to that observed for the series **14a** (see figure (*a*)). The properties of series **14a** can be explained in terms of non-linear geometry and conjugative effects. The lone pair of the heteroatom may conjugate directly with the carbonyl group setting up a permanent dipole, a substantial component of which is directed laterally, and hence likely to increase the lateral intermolecular cohesive forces and the tendency to form smectic mesophases. The increase in the lateral dipole moment leads to a higher thermal stability for the smectic phase. The lower mesophase stability for the first homologue in this series can be explained by its non-linear geometry when compared with the analogous biphenyls. In a biphenyl derivative the ring substituent bonds are collinear but in the case of the thiophene ring there is deviation of approximately 32° from the hard rod axis of the biphenyl derivative.

As previously mentioned, we have also studied the derivatives of 2-octanoyl-5-(4-*n*-hexyloxyphenyl)furan **14d**. In contrast with the analogous thiophene derivatives, they do not exhibit mesomorphic properties and we suppose that such behaviour is caused by the deviation of the molecular shape from linearity and in this case, as previously mentioned, the non-linearity of the molecule is much more significant.

Finally, we synthesized the compounds **14(b, c)** in order to observe the mesomorphic behaviour with a terminal polar group. With the bromo terminal group, compound **14b**, only a smectic phase is observed. This phase was identified as a smectic

Table 4. Transition temperatures and transition enthalpy data for the series 2-octanoyl-5-(4-*n*-alkoxyphenyl)thiophene **14a.**

n	C		C′		S_1		S_A		I
1			●	109·8°C (31·60 kJ mol^{-1})	—		—		●
2			●	120·8°C (31·78 kJ mol^{-1})	—		—	123·1°C (5·29 kJ mol^{-1})	●
3			●	124·4°C (23·28 kJ mol^{-1})	—		●	[122·8°C]† (6·13 kJ mol^{-1})	●
4			●	127·6°C (24·57 kJ mol^{-1})	—		●	130·9°C (8·42 kJ mol)	●
5			●	120·5°C (22·16 kJ mol^{-1})	—		●	127·4°C (7·53 kJ mol^{-1})	●
6			●	120·0°C (22·99 kJ mol^{-1})	—		●	129·8°C (7·09 kJ mol^{-1})	●
7	●	105·0°C	●	113·0°C (21·49 kJ mol^{-1})‡	—		●	127·4°C (7·68 kJ mol^{-1})	●
8	●	103·0°C	●	109·5°C (18·07 kJ mol^{-1})‡	—		●	126·2°C (6·32 kJ mol^{-1})	●
9	●	103·0°C	●	107·5°C (21·31 kJ mol^{-1}‡	—		●	123·8°C (7·03 kJ mol^{-1})	●
12			●	100·6°C (23·67 kJ mol^{-1})	●	[93·8°C]† (3·27 kJ mol^{-1})	●	122·2°C (8·82 kJ mol^{-1})	●

† Monotropic transition.

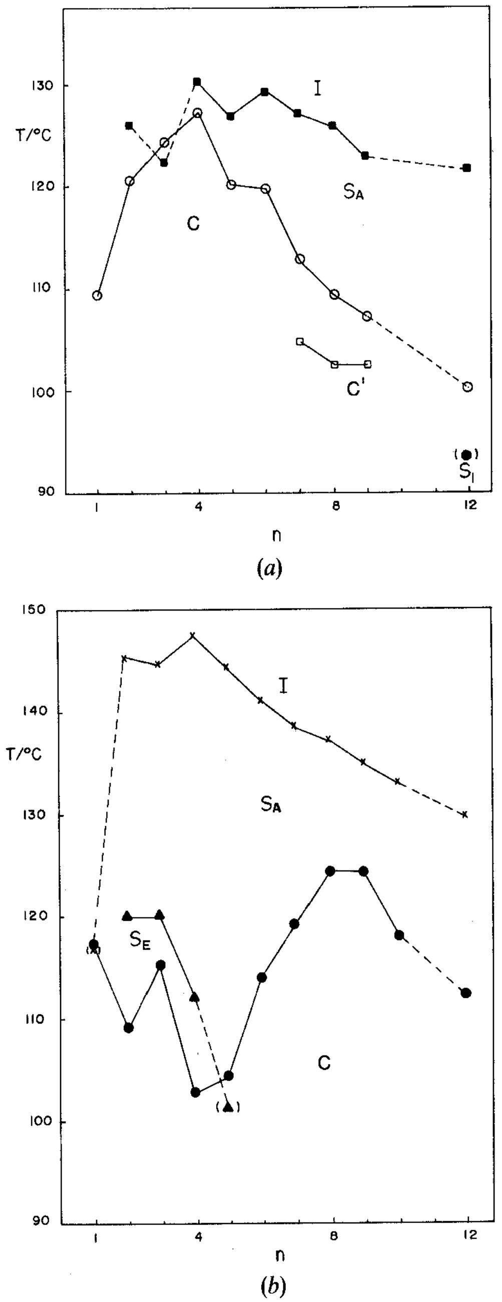
‡ Sum of the enthalpies of the C–C′ and C′–S_A transitions, where C and C′ are crystalline phases. S_1 is a smectic phase.

S_A by optical microscopy. The transition temperatures for this homologue are C 116·5°C S_A 125·0°C I. Compound **14c** with a terminal nitro group is not a liquid crystal. This may be due to a substantial decrease in the lateral dipolar interactions which would result from the conjugation between the heteroatom of the heterocyclic ring and the terminal nitro group.

4. Experimental

The transition temperatures for all compounds were determined by optical microscopy using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP 52 heating stage. The transition temperatures and enthalpies were also determined from DSC measurements using a Perkin–Elmer DSC-2. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard. The purity of the compounds was evaluated by thin layer chromatography and elemental analysis. The IR spectra were recorded using KBr discs with a Perkin–Elmer model 283 spectrometer, and the ^{1}H NMR and the ^{13}C NMR spectra were recorded at 60 MHz (Varian T-60), 80 MHz (Bruker WP-80) or 270 MHz (Bruker HX-270).

*(4-*n*-alkoxyphenyl)methyl triphenylphosphonium bromide* **4.** A solution of triphenylphosphine hydrobromide [17] (72·0 g, 0·21 mol), 4-*n*-alkoxybenzyl alcohol **3** and acetonitrile (400 ml) was refluxed gently for 3·5 h, cooled to room temperature and concentrated in a rotary evaporator to a volume of about 200 ml. The white precipitate was filtered off, washed with portions of cold ethyl acetate and dried at 50°C to give the desired Wittig reagent.



(*a*) Phase transition temperature for the series 2-octanoyl-5-(4-*n*-alkoxyphenyl)thiophene **14a** as a function of *n*. ○, C–S_A; ■, S_A–I; □, C′–C; ●, S_1 (monotropic phase). (*b*) Phase transition temperatures for the series 4-*n*-alkoxy-4′-*n*-octanoylbiphenyl as a function of *n*. ●, C–S_A; ×, S_A–I; ▲, S_E–S_A; (▲), S_E (monotropic); (×) S_A (monotropic phase).

Table 5. Yields and melting points of the (4-*n*-alkoxyphenyl)methyl triphenylphosphonium bromides **4**.

C_nH_{2n+1}	Yield %	mp °C
4	85	201·0–202·5
5	64	188·6
6	84	190·4–193·5
7	40	148·0–151·0
8†	—	—
9†	—	—

† The crude syrupy product was used without further purification.

IR (KBr) ν_{max}: 3020, 2910, 2820, 1600, 1570, 1500, 1465, 1420, 1385, 830, 735, 710 cm^{-1}.

4-n-Alkoxystyryl-2-thiophene **5a**. A solution of (4-*n*-alkoxy-phenyl)methyl triphenylphosphonium bromide (**4**) (0·123 mol) and anhydrous ether (800 ml) was added drop wise to a solution of *n*-butyl lithium (1·6 M in *n*-hexane) and the colour of the solution changed abruptly to red. The reaction mixture was stirred at room temperature for 2 h and then 2-thiophenecarboxaldehyde was added. The reaction mixture was heated for 4 h and a white solid formed. This mixture was stirred at room temperature overnight and filtered to remove the solid material. The organic layer was washed with sodium bicarbonate (2 × 100 ml) and water (200 ml), dried ($MgSO_4$), filtered and evaporated. The residue was purified on silica gel using a 4 : 1 hexane/ethyl acetate mixture as eluent and recrystallized from ethanol to give the pure product.

Data for $n=9$, IR(KBr)ν_{max}: 2910, 2840, 1590, 1460, 1375, 1230, 950, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 270 MHz): $\delta=7{\cdot}38$, 6·86 (AA′XX′, $J=7{\cdot}5$ Hz, 4 H), 7·08 (d, $J=18{\cdot}0$ Hz, 1 H), 6·87 (d, $J=18{\cdot}0$ Hz, 1 H), 7·14 (dd, $J=5$ Hz, 1 H), 7·01 (dd, $J=4$ Hz, 1 H), 6·97 (dd, $J=5$ Hz, 1 H), 3·95 (t, $J=8{\cdot}0$ Hz, 2 H), 1·82–1·73 (quint, $J=8{\cdot}0$ Hz, 2 H), 1·47–1·25 (m, 12 H), 0·88 ppm (t, $J=8{\cdot}0$ Hz, 3 H), ^{13}C NMR ($CDCl_3$, TMS, 50 MHz): 158·89, 143·32, 129·52, (3 C, quater.) 114·74, 1227·48 (4 C, Arom.), 128·08, 125·26, 123·63, 119·61 (2 C, vinyl, 3 C, thienyl), 68·09, 31·88, 29·54, 29·41, 29·27, 26·05, 14·11 ppm (8 C, aliphatic chain).

5-(4-n-Alkoxystyryl)-2-thiophenecarboxaldehyde **6a** were prepared according to [18].

Data for $n=4$, IR (KBr) ν_{max}: 2920, 2850, 1650, 1590, 1500, 1440, 1385, 940, 810 cm^{-1} ^{1}H NMR ($CDCl_3$, TMS, 270 MHz): $\delta=9{\cdot}80$ (s, 1 H), 9·80 (s, 1 H), 7·75–6·90 (m, 8 H), 4·05 (t, 2 H), 2·00–0·95 ppm (m, 7 H).

2-Hydroxyiminomethyl-5-(4-n-alkoxystyryl)thiophene **7a** were prepared using the same method described in [19].

Data for $n=7$, IR(KBr)ν_{max}: 3580–3250, 2900, 2840, 1590, 1500, 1460, 1250, 940, 820 cm^{-1}. ^{1}H NMR ($CDCl_3/D_3CCOCD_3$, TMS, 270 MHz): $\delta=8{\cdot}19$(s, 1 H), 7·37–6·85 (AA′XX′, $J=8{\cdot}6$ Hz, 4 H), 7·24 (s, 1 H), 7·04 (d, $J=4{\cdot}0$ Hz, 1 H), 6·98 (s, 1 H), 6·91 (d, $J=4{\cdot}0$ Hz, 1 H), 3·95 (t, $J=6{\cdot}4$ Hz, 2 H), 1·80–1·69 (m, 2 H), 1·39–1·23 (m, 8 H), 0·87 ppm (t, $J=6{\cdot}4$ Hz, 3 H).

Data for $n=4$, ^{13}C NMR ($CDCl_3$, TMS, 50 MHz): 161·50, 145·49, 145·15, 133·13, 130·52, 129·97, 129·09, 127·81, 125·43, 119·11, 114·81(11 C, sp^2), 67·78(1 C), 31·28, 19·24, 13·84 ppm (3 C, aliphatic chain).

Table 6. Yields and melting points of the 4-*n*-alkoxystyryl-2-thiophenes **5a**.

C_nH_{2n+1}	Yield %	mp °C
4	45	103·5–106·4
5	42	97·7–98·8
6	41	93·0–95·5
7	48	93·3–94·7
8	—	95·0–95·9
9	—	96·2–97·7

Table 7. Yields and melting points of the 5-(4-*n*-alkoxystyryl)-2-thiophenecarboxaldehydes **4a**.

C_nH_{2+1}	Yield %	mp °C
4	93	87·3
5	68	80·3
6	80	84·3
7	70	89·6
8	73	90·0
9	57	90·3

Table 8. Yields and melting points of the 2-hydroxyliminomethyl-5-(4-*n*-alkoxystyryl)thiophenes **7a**.

C_nH_{2n+1}	Yield %	mp °C
4	48	163·7–165·5
5	79	154·6–157·4
6	78	150·1–153·0
7	79	146·8–149·6
8	62	150·5–153·1
9	89	151·6–154·0

2-Cyano-5-(4-n-alkoxystyryl)thiophene **8a** were prepared using the same method described in [19] and purified by several recrystallizations from ethanol. The yields for all compounds were in the range 58–69 per cent.

Data for $n = 6$, IR (KBr)ν_{max}: 2900, 2840, 2200, 1600, 1240, 940, 810 cm^{-1}. ^{1}H NMR ($CDCl_3/D_3CCOCD_3$, TMS, 270 MHz): $\delta = 7{\cdot}47$ (d, $J = 4$ Hz, 1 H), 7·39, 6·87 (AA′XX′, $J = 8{\cdot}6$ Hz, 4 H), 7·23 (s, 1 H), 6·95 (d, $J = 4$ Hz, 1 H), 6·99 (s, 1 H), 3·95 (t, $J = 6{\cdot}6$ Hz, 2 H), 1·77 (m, 2 H), 1·53–1·31 (m, 6 H), 0·88 ppm (t, $J = 6{\cdot}6$ Hz, 3 H), ^{13}C NMR ($CDCl_3$, TMS, 50 MHz): 159·71, 150·41, 137·91, 132·18, 128·06, 127·97, 124·57, 117·32, 114·72, 106·10 (10 C, sp^2), 67·96 (1 C, $-OCH_2-$), 31·42, 29·03, 29·54, 22·45, 13·90 ppm (5 C, aliphatic chain).

2-cyano-5-(4-ethoxystyryl)furan **8b** was prepared according to [19]. (Yield 65 per cent, mp (105·0°C).

IR (KBr)ν_{max}: 3010, 2920, 2870, 2220, 1600, 1250, 955, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS 270 MHz): $\delta = 7{\cdot}41$, 6·87 (AA′XX′, $J = 9{\cdot}0$ Hz, 4 H), 7·18 (d, $J = 16{\cdot}0$ Hz, 1 H), 7·06 (d, $J = 3{\cdot}6$ Hz, 1 H), 6·69 (d, $J = 16{\cdot}0$ Hz, 1 H), 6·33 (d, $J = 3{\cdot}6$ Hz, 1 H), 4·05 (q, $J = 7{\cdot}0$ Hz, 2 H), 1·41 ppm (t, $J = 7{\cdot}0$ Hz, 3 H).

2-(4-n-Alkoxystyryl)thienylidene-5-4-n-alkoxyaniline **9a** was prepared according to [20].

Data for $n=4$ and 2, IR (KBr)ν_{max}: 3010, 2920, 2850, 1600, 1465, 1385, 1240, 935, 810, 720 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, 60 MHz): $\delta = 8{\cdot}50$ (s, 1 H), 7·50–6·70 (m, 12 H), 4·10–3·90 (2 t, 4 H), 1·90–0·90 ppm (m, 10 H, aliphatic chain).

2-(4-Ethoxystyryl)furfurylidene-5-4-n-alkoxyaniline **9b** was prepared according to [20]. For $n=5$, yield = 85 per cent, mp 124·0°C, for $n=9$, yield = 93 per cent, mp 121·3°C).

Data for $n=5$, IR (KBr)ν_{max}: 2920, 2860, 1600, 1455, 1380, 1240, 950, 840, 810, 720 cm^{-1} ^{1}H NMR (CDCl$_3$, TMS, 60 MHz): $\delta = 8{\cdot}24$ (s, 1 H), 6·41–7·47 (m, 12 H) 3·97 (m, 4 H), 1·68–0·93 ppm (m, 12 H, aliphatic chain).

2-Octanoylthiophene **11a** was prepared according to [13]. (Yield = 40 per cent, pe 126·0°C/0·5 mmHg).

IR (film)ν_{max}: 3080, 2910, 2840, 1660, 1520, 1455, 1380, 720 cm^{-1}. ^{1}H NMR(CDCl$_3$, TMS, 60 MHz): $\delta = 7{\cdot}66$ (m, 2 H), 7·06 (m, 1 H), 2·68 (t, 2 H), 1·65–0·65 ppm (m, 13 H, aliphatic chain).

2-Octanoylfuran **11b** was prepared according to [13]. Yield = 35 per cent, pe 118·0°C/2 mmHg).

IR (film)ν_{max}: 3110, 2900, 2840, 1670, 1560, 1450, 1385, 720 cm^{-1}.

2-Octanoyl-5-(4-alkoxyphenyl)thiophene **14a.** 4-*n*-Alkoxyaniline (0·03 ml) was dissolved in a mixture of 25 ml of concentrated hydrochloric acid and 15 g of ice. The mixture was cooled to 4·0°C in an ice bath and a solution of sodium nitrate (0·033 mol in 15 ml of water) was added in small portions. The mixture was stirred vigorously and maintained at below 5°C. The cold, filtered diazonium solution was transferred to a 300 ml beaker surrounded by ice-water, a solution of 2-octanoylthiophene (0·03 mol in 90 ml of acetone) was added, stirred vigorously and copper (II) chloride (0·0045 mol) was then added. The solution was heated and the temperature kept at 60°C for 3 h. After cooling the reaction mixture was extracted with diethyl ether (3 × 75 ml). The combined organic layers were washed with brine (2 × 100 ml), dried with magnesium sulphate, filtered and evaporated under slightly reduced pressure. The residue was purified by recrystallization from ethanol.

Data for $n=5$, IR (KBr)ν_{max}: 2900, 2840, 1640, 1600, 1260, 1020, 800 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, 270 MHz): $\delta = 7{\cdot}63$ (d, $J = 4$ Hz, 1 H), 7·56, 6·90 (AA′XX′, $J = 9$ Hz, 4 H), 7·19 (d, $J = 4$ Hz, 1 H), 3·98 (t, $J = 6$ Hz, 2 H), 2·86 (t, $J = 6$ Hz, 2 H), 1·79–1·32 (m, 16 H), 0·94 ppm (m, 6 H).

The following compounds were prepared using the same procedure:

2-octanoyl-5-(4-n-hexyloxyphenyl)furan **14d.** (Yield = 23 per cent, mp 68·9°C). IR (KBr)ν_{max}: 3100, 2900, 2830, 1640, 1600, 1575, 1240, 840, 720 cm^{-1}.

2-Octanoyl-5-(4-bromophenyl)thiophene **14b.** (Yield = 25 per cent, C 116·1°C S$_A$ 123·8°C I). IR (KBr)ν_{max}: 2900, 2820, 1650, 1600, 1380, 800 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, 270 MHz): $\delta = 7{\cdot}65$ (d, $J = 4$ Hz, 1 H), 7·53, 7·50 (AA′BB′, $J = 6$ Hz, 4 H), 7·29 (d, $J = 4$ Hz, 1 H), 2·87 (t, $J = 7$ Hz, 2 H), 1·78–1·28 (m, 10 H), 0·88 ppm (t, $J = 7$ Hz, 3 H). ^{13}C NMR (CDCl$_3$, TMS, 50 MHz): 194·0, 177·0, 151·0, 143·4, 132·5, 132·1, 127·6, 124·1, 123·0 (10 C, sp^2), 39·0, 31·6, 29·2, 29·0, 24·8, 22·5, 14·0 ppm (7 C, aliphatic chain).

2-Octanoyl-5-(4-nitrophenyl)thiophene **14c.** (Yield = 30 per cent, mp 100·0°C). IR (KBr)ν_{max}: 2900, 2830, 1650, 1585, 1505, 1460, 1380, 1325, 845, 805, 740 cm^{-1}.

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