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# New liquid crystalline compounds based on 2-arylthiophenes and 2-(biphenyl-4-yl)thiophenes

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A general and versatile route to the 2-alkyl-5-(4′-cyanophenyl)thiophenes was established, involving the condensation of an aryl vinyl ketone with an aldehyde in the presence of a thiazolium catalyst (Stetter procedure) to give a 1,4-diketone which with Lawesson's reagent undergoes ring-closure to give the corresponding arylthiophene. In the final step the exchange of a bromo substituent on the phenyl ring for a cyano group is accomplished by copper(I) cyanide in *N*,*N*-dimethylformamide at reflux. The same sequence afforded 2-alkyl-5-(4″-cyanobiphenylyl)thiophenes. Several of the 1,4-diketones were obtained by conjugate addition of nitroalkanes to aryl vinyl ketones, and treatment of the γ-nitroketones with silica gel-supported potassium permanganate. Three alkyl 5-(4-cyanophenyl)thiophene-2-carboxylates were prepared by condensing β-chlorovinylaldehydes with thioglycolates. The cyanophenylthiophenes exhibited only monotropic phases, but incorporation of an additional phenyl ring provided cyanobiphenylylthiophenes of wide nematic ranges. Transition temperatures of binary mixtures of the cyanophenylthiophenes with 4-*n*-pentyl-4′-cyanobiphenyl were measured, and extrapolated virtual nematic–isotropic transition temperatures were determined.



## 1. Introduction

The work reported in this paper was stimulated by a desire to produce low melting liquid crystal materials formed from molecules having transverse dipole moments. To avoid the problem of lateral substituents disrupting mesophase formation, we focused on heterocyclic systems, where the transverse dipole is part of the core ring structure. An additional potential advantage of using heterocycles as part of a two-ring or three-ring core structure is that the symmetry of the molecule is reduced, resulting in lower melting points and low temperature mesophases.

There have been many reports of liquid crystal compounds containing various heterocyclic ring systems. In this paper we restrict attention to mesogens containing the five-membered sulphur-containing thiophene ring. Again there is an extensive literature on such mesogens [1–6], and a conclusion is that the non-linearity of 2,5-disubstituted thiophenes generally results in a disruption of mesophase properties when compared with 1,4-disubstituted phenyl analogues. Use of thiophenes as terminal groups [1] can result in the formation of smectic phases. Homologous series of three-ring esters containing thiophene have been reported [7], and it was found that compounds with a centrally-positioned thiophene ring did not form mesophases, but that nematic phases could be generated if the thiophene ring acted as a terminal group

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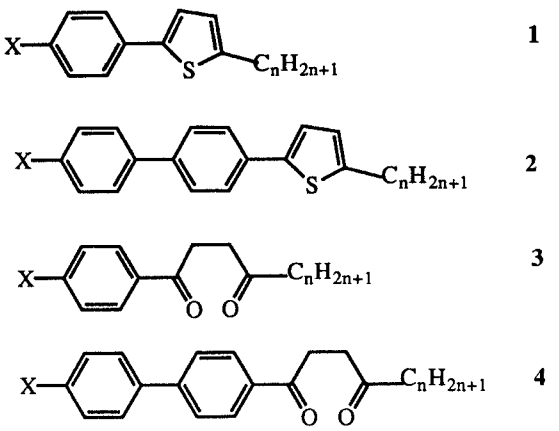
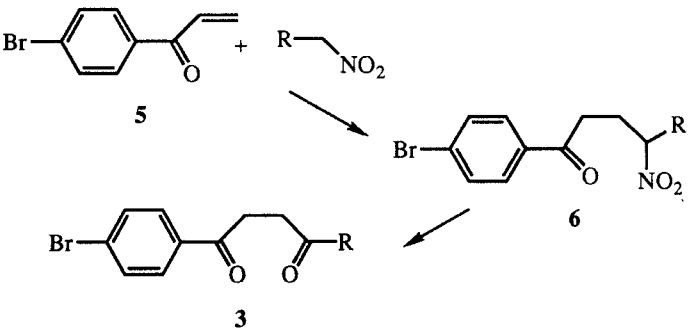
separated from the ester function by a phenyl ring. Where the thiophene ring was terminal and directly attached to the ester function, mostly smectic phases were formed. The usefulness of the thiophene ring as part of the core structure has also been discussed [8].

## 2. Synthesis

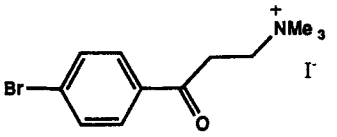
In this paper we report the synthesis of a series of compounds of the type **1** and **2** ($X = CN$) via diketone intermediates **3** and **4**, and their evaluation for use as liquid crystals. A preliminary account of part of this work has been published [9]. To avoid




possible problems due to the cyano group, which had been encountered in attempts to prepare the 1,4-diketone **3** ($n = 5$; $X = CN$) from 4-cyanophenacyl bromide and ethyl 3-oxooctanoate [10], the chosen route involved the preparation of a series of 1-(4-bromophenyl)- and 1-(4′-bromobiphenylyl)-1,4-dioxoalkanes **3** and **4** ($X = Br$) which could then be converted via the 2-alkyl-5-(4-bromophenyl)- or 2-alkyl-5-(4′-bromobiphenyl-4-yl)-thiophenes **1** and **2** ($X = Br$) into the desired 2-alkyl-5-(4-cyanophenyl)- and 2-alkyl-5-(4′-cyanobiphenyl-4-yl)thiophenes **1** and **2** ($X = CN$). Initially we chose to prepare the 1,4-diketones **3** ($X = Br$) by the route shown in scheme 1. A Mannich reaction on 4-bromoacetophenone, followed by quaternization with iodomethane [11], gave the Mannich base methiodide **7**. Direct condensation of **7** with




Scheme 1.

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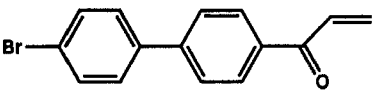
1-nitrohexane, in the presence of potassium fluoride and 18-crown-6 [12], gave the desired nitroketone **6** ($R = CH_3(CH_2)_3CH_2$–), but only in 16 per cent yield, and it was found necessary to isolate the enone **5** and use a different catalyst to obtain an acceptable yield for the Michael addition. By keeping strict control of the temperature, the duration of the reaction, the concentrations of the reagents, and the amount of base, it was eventually possible, using sodium hydrogen carbonate as the base [13], to achieve a yield of 78 per cent in the preparation of **5**. The use of potassium hydroxide, as described in the literature [11], gave only a 28 per cent yield. When the enone **5** was stirred with 1-nitrohexane, in hexane, in the presence of alumina [14], the desired 4-nitroketone **6** ($R = CH_3(CH_2)_3CH_2$–) was obtained (61 per cent).

Transformation of the 4-nitroketone **6** ($R = CH_3(CH_2)_3CH_2$–) into the 1,4-diketone **3** ($X = CN$; $n = 5$) was achieved in 50 per cent yield using silica gel-supported potassium permanganate [12], of a loading of *c.* 0·2 mmol $g^{-1}$ [15]. Other reagents, including 30 per cent aqueous hydrogen peroxide in methanol [16], cetyltrimethylammonium permanganate in the presence of triethylamine in dichloromethane [17] and titanium(III) chloride [18] were much less efficient and convenient. Similar results were obtained when the route described by scheme 1 was used to prepare the diketones **3** ($X = Br$; $n = 7$, 9 and 11). Those nitroalkanes which were not available commercially were prepared in 60–67 per cent yield from the corresponding iodoalkanes and sodium nitrite in *N*-*N*-dimethylformamide [12]; the co-produced nitrite esters were separated by column chromatography.

Following these experiments, attention was turned to the Stetter reaction [19] for the preparation of the 1,4-diketones **3** and **4**. Reaction of the enone **5** with an alkanal in the presence of 3-benzyl-5-(2′-hydroxyethyl)-4-methyl-1,3-thiazoline chloride and anhydrous sodium acetate in dry ethanol under nitrogen for 1·5 h gave the desired 1,4-diketones **3** ($X = Br$; $n = 3$–8, and 10) in yields varying from 76 to 87 per cent. Two of the diketones **3** ($X = Br$; $n = 5$ and 7) were prepared by both routes; the nitroketone route (scheme 1) gave overall yields from the enone **5** of only 28–29 per cent.

The 2,5-disubstituted thiophenes **1** ($X = Br$; $n = 3$–11) were prepared from the 1,4-diketones **3** ($X = Br$; $n = 3$–11) in 58–71 per cent yield by heating at reflux for 4 h with Lawesson's reagent in toluene [19]. The crude products were purified by flash chromatography, followed by several recrystallizations, until pure material, as judged by TLC and $^1H$ NMR spectroscopy, was obtained. Synthesis of the target cyano compounds **1** ($X = CN$; $n = 3$–11) was completed by reaction of the bromo compounds with copper(I) cyanide. Poor yields were obtained with the commonly used [20] solvent pyridine, but after 6 h heating at 190°C in *N*,*N*-dimethylformamide [21], the crude cyano compounds were obtained in 75–85 per cent yield. The pure materials were obtained by warming with iron(III) chloride-hydrochloric acid (to oxidize the copper(I) to copper (II) which does not complex), followed by extraction into warm toluene, column chromatography and further purification steps.

Three compounds in the biphenyl series **2** ($X = CN$; $n = 4$–6) were prepared in similar overall yields from 4′-bromobiphenyl vinyl ketone **8** by the Stetter reaction with the appropriate alkanals followed sequentially by reaction with Lawesson's reagent

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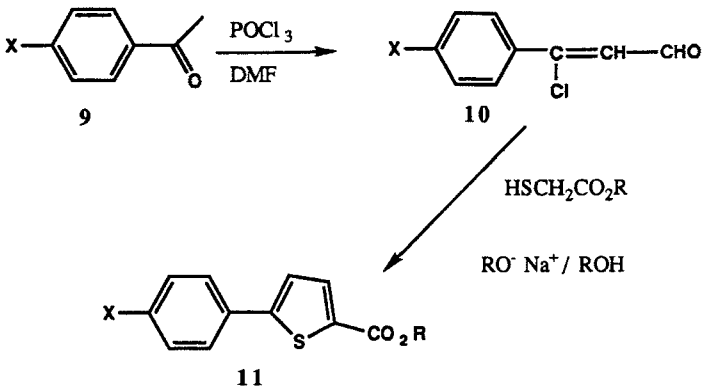
and copper(I) cyanide. The enone **8** was prepared by the Friedel–Crafts acylation of 4-bromobiphenyl with acryloyl chloride in carbon disulphide in the presence of aluminium chloride. The intermediate thiophenes **2** ($X = Br$; $n = 4$–6) were sparingly soluble in light petroleum (bp 60–80°C). In order to purify them by column chromatography they were supported on silica gel by dissolving the crude material in warm toluene, adding silica gel, and evaporating the slurry to dryness. The resultant powder was poured on to the top of a silica gel chromatography column. Elution with light petroleum (bp 60–80°C) then permitted the pure thiophene to be obtained. This tedious procedure had to be adopted because eluants of higher polarity led to material contaminated with impurities which could not be eliminated subsequently by recrystallization.

We also report the synthesis of three other thiophenes **11** ($X = CN$; $R = Et$), **11** ($X = CN$; $R = CH_3(CH_2)_4CH_2$– and **11** ($X = CH_3(CH_2)_4CH_2O$–; $R = Et$) from the corresponding 4-substituted acetophenones [22], using the thiophene synthesis employing the reaction of β-chlorovinylaldehydes and thioglycolates [23] (see scheme 2).




**9** **10** **11**

Scheme 2.

Reaction of the 4-substituted acetophenone **9** ($X = CN$ or $C_6H_{13}O$–) with *N*,*N*-dimethylformamide-phosphorus oxychloride, followed by work-up with 10 per cent aqueous sodium acetate, gave a mixture of the (*Z*)-and (*E*)-isomers of the corresponding β-chlorocinnamaldehydes, in which, as expected [24], the (*Z*)-isomer predominated. In the case of 4-cyano-β-chloro-cinnamaldehyde **10** ($X = CN$) the pure (*Z*)-isomer could be separated from the 10 per cent of the (*E*)-isomer by crystallization from cyclohexane; the liquid mixture containing 84 per cent of the (*Z*)-isomer of the two forms of 4-hexyloxy-β-chlorocinnamaldehyde **10** ($X = C_6H_{13}O$–) was used in the next step without further purification. Condensation with ethyl or hexyl thioglycolate then gave the desired thiophene esters **11**. Ethyl 5-(4-hexyloxyphenyl)thiophene **11** ($X = C_6H_{13}O$–; $R = Et$) has been reported previously [25]; it was prepared by the condensation of *N*,*N*-dimethyl-3-chloro-3-(4-hexyloxyphenyl)propeniminium perchlorate with ethyl thioglycolate, but was not fully characterized.

## 3. Mesophase properties

### 3.1. *2-n-Alkyl-5-(4-bromophenyl)thiophenes*

Nine homologues of this series from propyl to undecyl were prepared and characterized. All except the propyl derivative exhibited polymorphism, as detected by differential scanning calorimetry and relatively low melting points, but the phases formed were not liquid crystalline: thermal data are given in table 1.

### 3.2. *2-n-Alkyl-5-(4-bromobiphenylyl)thiophenes*

Only three members of this series were prepared, and all exhibited a simple melting from crystal to isotropic at temperatures in excess of 200°C. Thermal data are included in table 2.

### 3.3. *2-n-Alkyl-5-(4-cyanophenyl)thiophenes*

The thermal data for the nine members of the homologous series synthesized in this work have already been reported [9]. The compounds all had low melting points,

Table 1. Thermal data for the 2-*n*-alkyl-5-(4-bromophenyl)thiophenes.

| *n*† | Transition | $T_{OPT}$/°C | $T_{DSC}$/°C | $\Delta H$/kJ mol$^{-1}$ | $\Delta S$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|
| 3 | C→I | 88·8 | 87·2 | 15·7 | 43·6 |
| 4 | C→C′ | † | 76·0 | 0·71 | 2·03 |
| | C′→I | 84·6 | 82·1 | 13·2 | 37·1 |
| 5 | C→C′ | ‡ | 58·3 | 6·79 | 20·5 |
| | C→C″ | ‡ | 76·0 | 0·62 | 1·78 |
| | C″→I | 80·2 | 79·0 | 15·0 | 42·6 |
| 6 | C→C′ | ‡ | 3·3 | 2·49§ | 9·01 |
| | C′→C″ | ‡ | 34·1 | 3·64§ | 11·8 |
| | C″→I | 78·3 | 76·2 | 14·5§ | 41·6 |
| 7 | C→C′ | ‡ | 45·8 | 19·6 | 61·4 |
| | C′→I | 76·7 | 74·6 | 15·2 | 43·8 |
| 8 | C→C′ | ‡ | 67·4 | 33·0‖ | 96·9 |
| | C′→I | 72·9 | 70·8 | 14·1 | 41·1 |
| 9 | C→C′ | ‡ | 52·6 | 28·0 | 85·8 |
| | C′→C″ | ‡ | 56·9 | 1·10 | 3·34 |
| | C″→I | 71·3 | 70·0 | 15·0 | 44·0 |
| 10 | C→C′ | ‡ | 68·9 | 26·5 | 77·6 |
| | C′→I | 70·7 | 72·2 | 26·4 | 76·5 |
| 11 | C→C′ | ‡ | 62·1 | 19·3‖ | 57·7 |
| | C′→I | 66·3 | 62·5 | 18·1 | 53·8 |

† *n* indicates the number of carbon atoms in the chain.
‡ Not determinable by optical microsopy.
§ Total values of $\Delta H$ for 1st and 2nd heating cycles are 42·2 and 20·7 kJ mol$^{-1}$, respectively.
‖ Overlapped peaks.

Table 2. Thermal data for the 2*n*-alkyl-5-(4-bromobipheylyl)thiophenes.

| *n* | Transition | $T_{OPT}$/°C | $T_{DSC}$/°C | $\Delta H$/kJ mol$^{-1}$ | $\Delta S$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|
| 4 | C→I | 234 | 228·2 | 21·4 | 42·7 |
| 5 | C→I | 231 | 227·7 | 23·6 | 47·1 |
| 6 | C→I | 230 | 223·4 | 22·0 | 44·3 |

below 60°C, and homologues with 3, 4, 5, 6 and 8 alkyl chain lengths had monotropic isotropic liquid–nematic transitions, and for $n=8$ a smectic A phase was also detected; one derivative ($n=4$) was stable as a clear liquid at room temperature. Data for these mesophase transitions are summarized in table 3.

### 3.4. *2-n-Alkyl-5-(4-cyanobiphenylyl)thiophenes*

These compounds all had wide nematic ranges above 100°C, and showed a strong tendency to form homeotropic alignment on untreated microscope slides. Thermal data for these materials are listed in table 4.

## 4. Discussion

Introduction of a thiophene ring in place of a phenyl ring in the rigid core of a molecule results in a lowering of melting points and mesophase transition temperatures. This can be attributed to the non-linearity introduced by the 2,5-disubstituted thiophene, and the entropic effect due to the asymmetry of the thiophene structures. The cyanophenyl thiophenes only showed monotropic phases, albeit at low temperatures, while inclusion of another phenyl ring in the cyanobiphenyl thiophenes gives materials having wide nematic ranges. In order to investigate more fully the



Table 3. Transition temperatures for the 2-*n*-alkyl-5-(4-cyanophenyl)thiophenes.

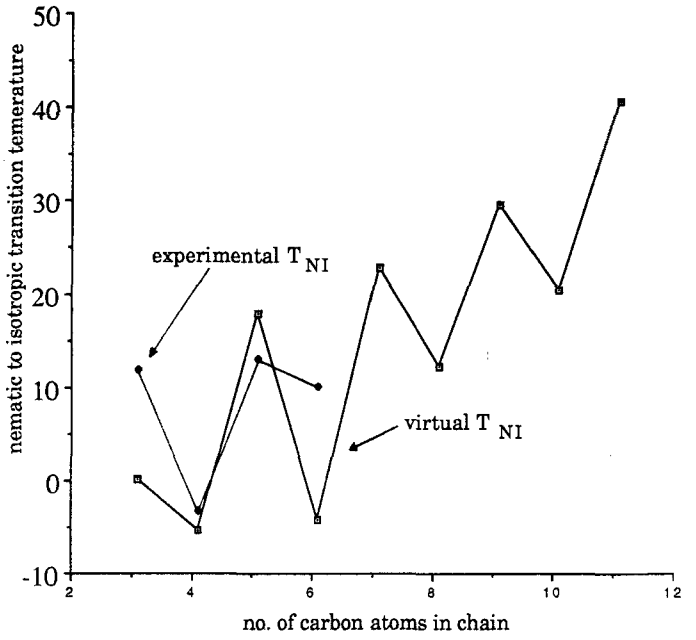
| *n* | Transition | $T_{OPT}$/°C | *n* | Transition | $T_{OPT}$/°C |
|---|---|---|---|---|---|
| 3 | C→C′ | 44·0 | 7 | C→I | 42·2 |
| | C→I | 44·7 | 8 | C→I | 49·9 |
| | C′→I | 51·4 | | (N→I)† | 22·2 |
| | (N→I)† | 11·3 | | ($S_A$→N)† | 20·8 |
| 4 | C→I | 29·2 | 9 | C→I | 57·2 |
| | (N→I)† | −3·9 | 10 | C→I | 53·4 |
| 5 | C→I | 42·0 | 11 | C→C′ | 50·0 |
| | (N→I)† | 12·3 | | C→I | 56·0 |
| 6 | C→C′ | 2·5 | | C′→I | 62·0 |
| | C′→C″ | 8·6 | | | |
| | C″→C‴ | 13·5 | | | |
| | C″→I | 18·9 | | | |
| | C‴→I | 24·0 | | | |
| | (N→I)† | 9·5 | | | |

†Monotropic transition.

Table 4. Thermal data for the 2-*n*-alkyl-5-(4-cyanobiphenylyl)thiophenes.

| *n* | Transition | $T_{OPT}$/°C | $T_{DSC}$/°C | $\Delta H$/kj mol$^{-1}$ | $\Delta S$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|
| 4 | C→N | 163 | 155·3 | 11·2 | 26·1 |
| | N→I | 206 | 200·8 | 0·83 | 1·74 |
| 5 | C→N | 154 | 149·9 | 12·0 | 28·4 |
| | N→I | 204 | 197·1 | 0·66 | 1·41 |
| 6 | C→C′ | † | 63·4 | 0·71 | 2·11 |
| | C′→N | 151 | 145·9 | 10·6 | 25·2 |
| | N→I | 194 | 189·0 | 0·81 | 1·75 |

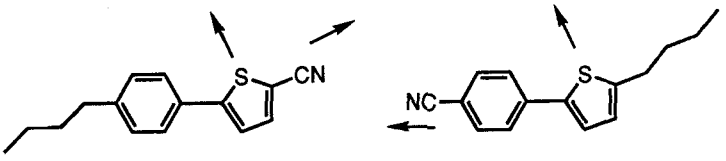
† Not observable by optical microscopy.




Nematic to isotropic transition temperatures for the 2-*n*-alkyl-5-(4′-cyanophenyl)thiophenes.

mesogenicity of cyanophenyl thiophenes, the transition temperatures of their binary mixtures with 4-*n*-pentyl-4′-cyanobiphenyl were measured, and extrapolated virtual nematic–isotropic transition temperatures were determined. These are plotted in the figure along with the monotropic transition temperatures determined experimentally. The latter differ to some extent from the virtual transition temperatures, but these results indicate that all the cyanophenyl thiophenes have potentially low mesophase transition temperatures.

It is interesting to compare our results for alkylcyanophenylthiophenes with the isomeric 2-cyano-5-(4)-alkylphenyl)thiophenes reported by Hitachi Limited [26]. The transition temperatures for the *n*-butyl derivatives are:




(I) C→I
55°C

(II) C→[N→]I
29°C −3·9°C

Our explanation of the higher melting point of (I) is that there is a stronger dipole moment localized at one end of the molecular core. The lack of a mesophase for (I) is attributed to the non-linear core which includes the cyano group as a centre of anisotropic attractive forces. These studies have shown that combining a thiophene into the core of a molecule can result in mesomorphic behaviour. Of particular interest for the compounds reported is the low mesophase transition temperatures for the alkyl cyanophenyl thiophenes. When used as components in mixtures [27] for display applications, these thiophenes can produce low viscosity materials having good optical contrast, yet operating at low voltages.

## 5. Experimental

Moisture-sensitive reactions were conducted in flame-dried glassware under nitrogen using solvents freshly distilled under a continuous stream of nitrogen over molecular sieves (type 4 Å). Solvents were dried and purified according to literature methods [16]. Thin layer chromatography was used to monitor reactions and to establish the purity of samples; it was performed on aluminium sheets precoated with silica gel (Merck $60F_{254}$). The plates were inspected using UV light, and then developed with iodine vapour. Column chromatography separations were performed with silica gel (Merck 60) as the stationary phase. Organic solutions were dried over anhydrous magnesium sulphate, unless otherwise stated.

Low resolution mass spectra were recorded using a Kratos MS 25 mass spectrometer. IR spectra were recorded with either Perkin–Elmer 457 or Perkin–Elmer 684 spectrophotometers using KBr pellets, liquid samples between NaCl plates or chloroform solutions. $^1$H NMR spectra were recorded using a Bruker AM250 (250 MHz) spectrometer (unless the use of a Perkin–Elmer R34 (220 MHz) instrument is indicated) with tetramethylsilane as the internal standard and for solutions in deuteriochloroform. The chemical shifts are recorded as follows: $\delta$ in p.p.m. (number of protons, multiplicity, coupling constants, assignment). The multiplicity of the signals is designated as follows: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet; dt, doublet of triplets; td, triplet of doublets. Coupling constants ($J$) are given in Hz. $^{13}$C NMR spectra were recorded with a Bruker AM250 instrument operating at 62·9 MHz (unless the use of a Bruker WH400 instrument operating at 100·6 MHz is indicated), for solutions in deuteriochloroform. Chemical shifts are given in p.p.m. from tetramethylsilane.

Optical microscopy data were obtained by hot stage polarizing microscopy using a Zeiss Universal microscope equipped with crossed polarizers and a Linkam hot stage with an integrated temperature controller. Heating and cooling rates were usually 5 or $10°\,min^{-1}$. Phase assignments were made by reference to literature textures [28]. Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer DSC-7 at scan rates of $10°\,min^{-1}$. Sample masses of between 1 and 2 mg were typically used. Onset peak temperatures were taken as transition temperatures and they and associated thermodynamic parameters, $\Delta H$ in $kJ\,mol^{-1}$ and $\Delta S$ in $J\,mol^{-1}\,K^{-1}$, are normally quoted from a second heating cycle. Elemental analyses were performed by the University of Sheffield Microanalytical Services.

### 5.1. *Enones*

#### 5.1.2. *4-Bromophenyl vinyl ketone*

A slurry of sodium hydrogen carbonate (15 g) and 3-dimethylamino-4′-bromopropiophenone methiodide (30 g, 75 mmol) [11] in water (225 ml) and dichloromethane (400 ml) was vigorously stirred at 20–30°C for approximately 90 min, until the suspension became clear. The organic layer was separated and the aqueous layer shaken with dichloromethane (2 × 50 ml). The combined organic layers were washed successively with 0·1 M hydrochloric acid (2 × 100 ml) and water (200 ml), dried, filtered through a pad of silica gel and evaporated to give 4-bromophenyl vinyl ketone (12·4 g, 78 per cent) as an oil; (lit., [1] mp 55–56°C); $\delta_H$ 7·80 and 7·61 (each 2 H, $A_2X_2$ system, $J_{AX}$ 8, $-C_6H_4-$), 7·10 (1 H, dd, $J$ 18, 11, $H_{gem}$), 6·44 (1H, dd, $J$ 18, 11, $H_{cis}$), 5·95 (1 H, dd, $J$ 11, 1·5, $H_{trans}$).

5.1.3. *4'-Bromobiphenylyl vinyl ketone*

Acryloyl chloride (4·52 g, 0·05 mol) was added dropwise at room temperature to a stirred suspension of aluminium chloride (8 g, 0·06 mol) in dry carbon disulphide (10 ml) under nitrogen. The mixture was then cooled to ice bath temperature and 4-bromobiphenyl (11·65 g, 0·05 mol) in dry carbon disulphide (25 ml) was added dropwise. The resulting mixture was stirred at 20°C for 6 h and then poured into ice (100 g) and 10 M hydrochloric acid (25 ml) and shaken with dichloromethane (3 × 100 ml). The combined extracts were washed with 0·1 M hydrochloric acid (100 ml), saturated aqueous sodium hydrogen carbonate (100 ml) dried and evaporated. The crude product was purified by flash column chromatography using dichloromethane–light petroleum (bp 60–80°C) (1 : 1) as eluant and recrystallized from 95 per cent ethanol to give the desired vinyl ketone (8 g, 56 per cent). (Found: C, 62·8; H, 3·8; Br, 27·7 per cent. $C_{15}H_{11}BrO$ requires C, 62·7; H, 3·9; Br, 27·8 per cent); $\nu_{max}$ (KBr) 1665 (CO), 780 $cm^{-1}$ (*p*-substituted phenyl); $\delta_H$ 8·03 and 7·66 (each 2H, $A_2X_2$ system, $J_{AX}$ 8, *p*-Br–$C_6H_4$–), 7·60 and 7·49 (each 2H, $A'_2X'_2$ system, $J_{A'X'}$ 8, –$C_6H_4$–CO), 7·21 (1 H, dd, *J* 17, 11, $H_{gem}$), 6·48 (1H, dd, *J* 17, 1·5, $H_{cis}$), 5·96 (1 H, dd, *J* 11, 1·5, $H_{trans}$); $\delta_C$ 190·3, 144·4, 138·8, 136·3, 132·3, 132·1, 130·1, 129·4, 128·8, 127·1, 122·7.

## 5.2. *Nitroketones*

5.2.1. *Preparation of nitroalkanes* [2]

(i) 1-Iodooctane (24 g, 0·1 mol) and sodium nitrite (13·8 g, 0·2 mol) were stirred in dry *N*,*N*-dimethylformamide (160 ml) at 20°C for 4 h. The mixture was quenched with ice (200 g) and the solution shaken with dichloromethane (3 × 50 ml). The combined organic extracts were washed with 10 per cent aqueous sodium sulphite (2 × 50 ml) and water (100 ml), dried and evaporated. Chromatography using light petroleum (bp 60–80°C) as eluant yielded 1-nitrooctane (10·15 g, 64 per cent); $\nu_{max}$ 1550 ($NO_2$ asym.), 1380 $cm^{-1}$ ($NO_2$ sym); $\delta_H$ (220 MHz)) 4·38 (2 H, t, $CH_2NO_2$), 2·00 (2H, m, $CH_2CH_2NO_2$), 1·30 (10 H, m, $(CH_2)_5CH_3$), 0·86 (3H, m, $CH_3$). Similarly prepared were:

(ii) *1-Nitrodecane* (60 per cent); $\nu_{max}$ 1550 and 1380 $cm^{-1}$; $\delta_H$ (220 MHz), 4·40 (2 H, t, $CH_2NO_2$), 2·00 (2H, m, $CH_2CH_2NO_2$), 1·30 (14 H, m, $(CH_2)_7CH_3$), (0·85, t, $CH_3$).

(iii) *1-Nitrododecane* (67 per cent); $\nu_{max}$ 1560 and 1380 $cm^{-1}$; $\delta_H$ (220 MHz) 4·38 (2 H, t, $CH_2NO_2$), 2·00 (2H, m, $CH_2CH_2NO_2$), 1·30, (18 H, m, $(CH_2)_9CH_3$), 0·85 (3H, m, $CH_3$).

5.2.2. *1-(4-Bromophenyl)-4-nitrononan-1-one*

(i) 1-Nitrohexane (1·69 g, 13·0 mmol) was added to 4-bromophenyl vinyl ketone (2·99 g, 14·2 mmol) in dry hexane (3 ml) at 0°C under nitrogen. After stirring for 10 min, basic alumina (5·38 g), previously dried at 160°C for 24 h, was added in one portion. Stirring was continued, at 40–50°C for 18 h, and after cooling to room temperature, the alumina was collected by filtration and extracted with dichloromethane for 12 h using a Soxhlet apparatus. The combined filtrate and extract was washed with water, dried and evaporated. Column chromatography using dichloromethane–hexane (3 : 2) as eluant, and subsequent recrystallization from 95 per cent ethanol gave the desired nitroketone (2·7 g, 61 per cent), mp 63–64°C. (Found: C, 52·4; H, 5·9; N, 4·1; Br, 23·6 per cent. $C_{15}H_{20}BrNO_3$ requires C, 52·6; H, 5·4; N, 4·1; Br, 23·35 per cent); $\nu_{max}$1690 (CO) and 1555 $cm^{-1}$ ($NO_2$); $\delta_H$ 7·79 and 7·61 (each 2H, $A_2X_2$ system, $J_{AX}$ 8, –$C_6H_4$–), 4·61 (1 H, m, $CHNO_2$), 2·99 (2H, m, $COCH_2CH_2CHNO_2$), 2·12–1·96 and 1·85–1·71 (each 1H, m,

$CH(NO_2)C\underline{H}_2(CH_2)_3CH_3$), 1·50–1·20 (6H, m, $(C\underline{H}_2)_3CH_3$), 0·89 (3H t, $CH_3$); $\delta_C$ 196·9, 135·1, 132·0, 129·5, 128·6, 88·1, 34·2, 34·0, 31·0, 27·7, 25·3, 22·3, 13·8. Similarly prepared† were:

(ii) *1-(4-bromophenyl)-4-nitroundecan-1-one* (56 per cent), mp 61–62°C. (Found: C, 55·0; H, 6·3; N 3·5; Br, 21·7 per cent. $C_{17}H_{24}BrNO_3$ requires C, 55·1; H, 6·35; N, 3·8; Br, 21·6 per cent.)

(iii) *1-(4-Bromophenyl)-4-nitrotridecan-1-one* (53 per cent), mp 59–60°C. (Found: C, 57·2; H, 6·9; N, 3·4; Br, 20·4. $C_{19}H_{28}BrNO_3$ requires C, 57·3; H, 7·1; N, 3·5; Br, 20·1 per cent.)

(iv) *1-(4)-Bromophenyl)-4-nitropentadecan-1-one* (57 per cent). (Found: C, 59·2; H, 7·6; N, 3·1; Br, 18·8 per cent. $C_{21}H_{32}BrNO_3$ requires C, 59·1; H, 7·6; N, 3·3, Br, 18·7 per cent.)

### 5.3. *Diketones*

#### 5.3.1. *Preparation of 1,4-diketones from nitroketones*

(i) A suspension of 1-(4-bromophenyl)-4-nitrononan-1-one (2 g, 5·8 mmol) and freshly prepared silica gel-supported potassium permanganate (20 g: *c.* 0·2 mmol $g^{-1}$) in dry benzene (40 ml) was stirred at reflux temperature under nitrogen for 48 h. The mixture was then filtered, and the solid residue extracted into dichloromethane for 12 h using a Soxhlet apparatus. The combined extracts were washed with water, dried and evaporated. Column chromatography of the crude product on silica gel using dichloromethane–light petroleum (bp 60–80°C) (3:2) as eluant afforded 1-(4-bromophenyl)nonane-1,4-dione (0·85 g, 47 per cent), mp 82°C. (Found: C, 57·8; H, 6·1; Br, 25·8 per cent. $C_{15}H_{19}BrO_2$ requires C, 57·9; H, 6·15; Br, 25·7 per cent; $\nu_{max}$ 1710 (CO) and 1670 $cm^{-1}$ (conj. CO); $\delta_H$ 7·85 and 7·61 (each 2H, $A_2X_2$ system $J_{AX}$ 8, $BrC_6H_4CO$–), 3·23 and 2·86 (each 2 H, m, $COC\underline{H}_2CH_2CO$), 2·52 (2H, t, *J* 7, $COCH_2CH_2(CH_2)_2CH_3$), 1·62 (2 H, m, $COCH_2CH_2(CH_2)_2CH_3$), 1·36–1·25 (4H, m, $COCH_2CH_2(CH_2)_2CH_3$), 0·90 (3H, t, $CH_3$); $\delta_C$ 209·5, 197·6, 135·5, 131·8, 129·5, 128·2, 42·9, 36·1, 32·2, 31·4, 23·5, 22·4, 13·9. Similarly prepared were:

(ii) *1-(4-bromophenyl)undecane-1,4-dione* (50 per cent), mp 74°C. (Found: C, 60·2; H, 6·8; Br, 23·55 per cent $C_{17}H_{23}BrO_2$ requires C, 60·2; H, 6·8; Br, 23·55 per cent.)

(iii) *1-(4-bromophenyl)tridecane-1,4-dione* (51 per cent), mp 78°C. (Found: C, 62·5; H, 7·3; Br, 22·0 per cent $C_{19}H_{27}BrO_2$ requires C, 62·1; H, 7·4; Br, 21·75 per cent.)

(iv) *1-(bromophenyl)pentadecane-1,4-dione* (50 per cent), mp 81°C. (Found: C, 63·5; H, 7·7; Br, 20·1 per cent. $C_{21}H_{31}BrO_2$ requires C, 63·8; H, 7·9; Br, 20·2 per cent.)

#### 5.3.2. *Preparation of diketones by the Stetter reaction* [19]

(i) A mixture of butanal (3·47 g, 48·2 mmol) and 4-bromophenyl vinyl ketone (12·2 g, 57·8 mmol) in dry ethanol (50 ml) in the presence of 3-benzyl-5-(2′-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (1·30 g, 4·82 mmol) and sodium acetate (1·58 g, 19·3 mmol) was stirred under nitrogen at 80°C for 90 min. The reaction was cooled to room temperature and the suspension so obtained was poured into dichloromethane (110 ml), washed successively with 1 per cent aqueous sulphuric acid (2 × 50 ml), saturated aqueous sodium hydrogen carbonate (110 ml) and water (100 ml), dried and evaporated to dryness. Column chromatography of the crude product using light

† Here and elsewhere where higher homologues are under consideration, IR and NMR spectroscopic data entirely consistent with the required structures were obtained.

petroleum (bp 60–80°C)–dichloromethane (2 : 1) as eluant and subsequent recrystallization from 95 per cent ethanol gave 1-(4-bromophenyl)heptane-1,4-dione (10·9 g, 80 per cent), mp 80°C. (Found: C, 55·3; H, 5·3; Br, 28·4 per cent. $C_{13}H_{15}BrO_2$ requires C, 55·1; H, 5·3; Br, 28·2 per cent). $\nu_{max}$ 1705 (CO) and 1670 $cm^{-1}$ (conj. CO); $\delta_H$ 7·85 and 7·61 (each 2H, $A_2X_2$ system $J_{AX}$ 8, $BrC_6H_4$–), 3·24 and 2·86 (each 2H, m, $COCH_2CH_2CO$), 2·51 (2H, t, $COCH_2CH_2CH_3$), 1·65 (2H, m, $COCH_2CH_2CH_3$), 0·94 (3H, t, $CH_3$); $\delta_C$ 209·3, 197·6, 135·5, 131·8, 129·5, 128·2, 44·8, 36·1, 32·2, 17·3, 13·7. Similarly prepared were:

(ii) *1-(4-Bromophenyl)octane-1,4-dione* (76 per cent), mp 86°C. (Found: C, 56·5; H, 5·9; Br, 26·8 per cent. $C_{14}H_{17}BrO_2$ requires C, 56·6; H, 5·8; Br, 26·9 per cent.)

(iii) *1-(4-Bromophenyl)nonane-1,4-dione* (87 per cent) [see § 5.3.1 (i)].

(iv) *1-(4-Bromophenyl)decane-1,4-dione* (83 per cent) mp 75°C. (Found: C, 59·1; H, 6·3; Br, 24·5 per cent. $C_{16}H_{21}BrO_2$ requires C, 59·1; H, 6·5; Br, 24·6 per cent.)

(v) *1-(4-Bromophenyl)undecane-1,4-dione* (78 per cent) [see § 5.3.1 (ii)].

(vi) *1-(4-Bromophenyl)dodecane-1,4-dione* (87 per cent), mp. 75·5°C. (Found C, 60·9; H, 6·9; Br, 22·8 per cent, $C_{18}H_{25}BrO_2$ requires C, 61·2; H, 7·1; Br, 22·6 per cent.)

(vii) 1-(4-Bromophenyl)tetradecane-1,4-dione (82 per cent) mp 80°C. (Found C, 62·8; H, 7·5; Br, 20·9 per cent. $C_{20}H_{29}BrO_2$ requires C, 63·0; H, 7·7; Br, 20·9 per cent.)

(viii) *1-(4-Bromobiphenyl-4-yl)octane-1,4-dione* (58 per cent). (Found: *C*, 64·2; H, 5·7; Br, 21·2 per cent. $C_{20}H_{21}BrO_2$ requires C, 64·3; H, 5·7; Br, 21·4 per cent.) $\nu_{max}$ 1710 and 1675 $cm^{-1}$; $\delta_H$ 8·05 and 7·64 (each 2H, $A_2X_2$ system $J_{AX}$ 8, $BrC_6H_4$–), 7·60 and 7·49 (each 2H, $A'_2X'_2$ system, $J_{AX}$ 8, $-C_6H_4CO-$), 3·31 and 2·89 (each 2H, m, $COCH_2CH_2CH_2CO$), 2·54 (2H, t, *J* 7, $COCH_2CH_2CH_2CH_3$), 1·61 (2H, m, $COCH_2CH_2CH_2CH_3$), 1·36 (2H, m, $COCH_2CH_2CH_2CH_3$), 0·93 (3H, t, $CH_3$); $\delta_C$ 209·5, 198·1, 144·5, 138·9, 132·1, 128·8, 128·7, 127·0, 122·6, 42·7, 36·3, 32·4, 22·4, 13·8.

(ix) *1-(4-Bromobiphenyl-4-yl)nonane-1,4-dione* (76 per cent). (Found: C, 65·2; H, 6·1; Br, 20·6 per cent. $C_{21}H_{23}BrO_2$ requires C, 65·1; H, 6·0; Br, 20·6 per cent.)

(x) *1-(4)-Bromobiphenyl-4-yl)decane-1,4-dione* (81 per cent) (Found: C, 65·6; H, 6·15; Br, 20·0 per cent. $C_{22}H_{25}BrO_2$ requires C, 65·8; H, 6·3; Br, 19·9 per cent.)

### 5.4. *Bromo-substituted thiophenes*

(i) 1-(4-Bromophenyl)heptane-1,4-dione (4 g, 14·0 mmol) and Lawesson's reagent (6·87 g, 17·0 mmol) in toluene were stirred at reflux temperature under nitrogen. After 4 h the reaction mixture was cooled to room temperature and the solvent evaporated under reduced pressure. The crude product was adsorbed on silica gel and eluted though a column of silica gel using light petroleum (60–80°C). Two crystallizations from 95 per cent ethanol afforded 2-propyl-5-(4-bromophenyl)thiophene (2·16 g, 54 per cent). Found, C, 55·3; H, 4·6; Br, 28·2; S, 11·15 per cent. $C_{13}H_{13}BrS$ requires C, 55·3; H, 4·7; Br, 28·4; S, 11·4 per cent); $\nu_{max}$ 1495 and 1465 $cm^{-1}$; $\delta_H$ 7·44 (4H, m, $C_6H_4$) 7·11 (1H, d, *J* 3·5, thienyl) 6·74 (1H, dt, *J* 3·5, 1, thienyl), 2·79 (2H, td, *J* 7, 1, $CH_2CH_2CH_3$), 1·72 (2H, m, $CH_2CH_2CH_3$), 1·00 (3H, t, $CH_3$); $\delta_C$ (62·9 MHz) 1460·0, 140·3, 133·7, 131·8, 126·9, 125·2, 123·1, 120·6, 32·3, 24·8, 13·7. Similarly prepared were

(i) *2-Butyl-5-(4-bromophenyl)thiophene* (46 per cent). (Found: C, 57·1; H, 5·1; Br, 27·2; S, 10·7 per cent. $C_{14}H_{15}BrS$ requires C, 57·0, H, 5·1; Br, 27·1, S, 10·7.)

(iii) *2-Pentyl-5-(4-bromophenyl)thiophene* (46 per cent). (Found: C, 58·0; H, 5·4; Br, 26·1; S, 10·3 per cent. $C_{15}H_{17}BrS$ requires C, 58·3; H, 5·5; Br, 25·8; S, 10·4 per cent.)

(iv) *2-Hexyl-5-(4-bromophenyl)thiophene* (52 per cent). (Found: C, 59·3; H, 5·9; Br.

24·9; S, 9·8 per cent. $C_{16}H_{19}BrS$ requires C, 59·45; H, 5·9; Br, 24·7; S, 9·9 per cent.)

(v) *2-Heptyl-5-(4-bromophenyl)thiophene* (45 per cent). (Found: C, 60·7; H, 6·1; Br, 23·85; S, 9·4 per cent. $C_{17}H_{21}BrS$ requires C, 60·5; H, 6·3; Br, 23·7; S, 9·5 per cent.)

(vi) *2-Octyl-5-(4-bromophenyl)thiophene* (42 per cent). (Found: C, 61·6; H, 6·5; Br, 22·8, S, 9·2 per cent. $C_{18}H_{23}BrS$ requires C, 61·5; H, 6·6; Br, 22·7; S, 9·1 per cent.)

(vii) *2-Nonyl-5-(4-bromophenyl)thiophene* (67 per cent). (Found: C, 62·25; H, 6·9; Br, 21·7; S, 8·7 per cent. $C_{19}H_{25}BrS$ requires (C, 62·5; H, 6·9; Br, 21·9, S 8·8.)

(viii) *2-Decyl-5-(4-bromophenyl)thiophene* (50 per cent). (Found: C, 63·1; H, 6·9; Br, 21·15; S, 8·5 per cent. $C_{20}H_{27}BrS$ requires C, 63·3; H, 7·2; Br, 21·1; S, 8·45 per cent.)

(ix) *2-Undecyl-5-(4-bromophenyl)thiophene* (72 per cent). (Found: C, 63·8; H, 7·3; Br, 20·6; S, 8·4 per cent. $C_{21}H_{29}BrS$ requires C, 64·1; H, 7·4; Br, 20·3; S, 8·1 per cent.)

(x) *2-Butyl-5-(4-bromobiphenyl-4-yl)thiophene* (45 per cent). (Found: C, 64·9; H, 5·2; Br, 21·4; S, 8·6 per cent. $C_{20}H_{19}BrS$ requires C, 64·7; H, 5·2; Br, 21·5; S, 8·6 per cent.) $\nu_{max}$ 1490 and 1470 $cm^{-1}$; $\delta_H$ 7·53 (8 H, m, biphenylyl), 7·17 (1 H, d, *J* 3·5, thienyl), 6·77 (1 H, dt, *J*3·5, 1, thienyl), 2·84 (2 H, m, $C\underline{H}_2CH_2CH_2CH_3$), 1·70 (2 H, m, $CH_2C\underline{H}_2$, $CH_2CH_3$), 1·43 (2 H, m, $CH_2CH_2C\underline{H}_2CH_3$), 0·95 (3H, t, $CH_3$); $\delta_C$ (62·9 MHz) 146·0, 140·9, 139·5, 138·3, 134·1, 131·9, 128·4, 127·2, 125·8, 125·1, 122·9, 121·5, 33·7, 30·0, 22·2, 13·9.

(xi) *2-Pentyl-5-(4-bromobiphenyl-4-yl)thiophene* (59 per cent). (Found: C, 65·6; H, 5·4; Br, 20·9; S, 8·1 per cent; $M^+$, 384, 386 (1 : 1). $C_{21}H_{21}BrS$ requires C, 65·45; H, 5·5; Br, 20·7; S, 8·3 per cent.)

(xii) *2-Hexyl-5-(4-bromobiphenyl-4-yl)thiophene* (53 per cent). (Found: C, 66·2; H, 5·7; Br, 19·9; S, 7·9 per cent. $C_{22}H_{23}BrS$ requires C, 66·2; H, 5·8; Br, 20·0; S, 8·0 per cent.)

### 5.5. *Cyano-substituted thiophenes*

(i) A suspension of 2-propyl-5-(4-bromophenyl)thiophene (1·00 g, 3·58 mmol) and copper(I) cyanide (0·38 g, 4·27 mmol) in *N*,*N*-dimethylformamide (2 ml) was stirred at 190°C (bath temperature) for 6 h. The hot suspension was poured into a solution of iron(III) chloride (1·8 g) and 10 M hydrochloric acid (0·6 ml) in water (2·7 ml) and stirred at 60–70°C for 20 min. The hot mixture was then shaken with toluene (3 × 10 ml). The combined extracts were washed with 6 M hydrochloric acid (10 ml), 10 per cent aqueous sodium hydroxide (10 ml) and water (10 ml), dried and evaporated. The crude product was purified by column chromatography using hexane–dichloromethane (4 : 1) as eluant, followed by sublimation under vacuum and recrystallization from 95 per cent ethanol, to yield 2-propyl-5-(4-cyanophenyl)thiophene (0·39 g, 49 per cent.) (Found: C, 73·9; H, 5·7; N, 6·0; S, 13·8 per cent. $C_{14}H_{13}NS$ requires C, 74·0; H, 5·8; N, 6·2; S, 14·1 per cent.) $\nu_{max}$ 2240 $cm^{-1}$ (CN); $\delta_H$ 7·62 (4 H, s, $-C_6\underline{H}_4-$), 7·25 (1 H, d, *J* 3·5, thienyl), 6·80 (1 H, dt, *J* 3·5, 1, thienyl), 2·82 (2H, td, *J* 7·1, $C\underline{H}_2CH_2CH_3$), 1·73 (2 H, m, $CH_2C\underline{H}_2$ $CH_3$), 1·00 (3H, t, $CH_3$); $\delta_C$ (62·9 MHz) 148·1, 139·2, 138·9, 132·6, 125·7, 125·4, 124·9, 118·9, 109·8, 32·3, 24·8, 13·6. Similarly prepared were:

(ii) *2-Butyl-5-(4-cyanophenyl)thiophene* (56 per cent). (Found: C.,74·4; H, 6·45; N, 5·8; S, 13·1 per cent. $C_{15}H_{15}NS$ requires C, 74·65; H, 6·3; N, 5·8; S, 13·3 per cent.)

(iii) *2-Pentyl-5-(4-cyanophenyl)thiophene* (65 per cent). (Found: C, 75·1; H, 6·5; N, 5·2; S, 12·5 per cent) $C_{16}H_{17}NS$ requires C, 75·25; H, 6·7; N, 5·5; S, 12·55 per cent.)

(iv) *2-Hexyl-5-(4-cyanophenyl)thiophene* (61 per cent). (Found: C, 75·6; H, 7·3; N, 5·2; S, 11·6 per cent. $C_{17}H_{19}NS$ requires C, 75·8; H, 7·1; N, 5·2; S, 11·9 per cent.)

(v) *2-Heptyl-5-(4-cyanophenyl)thiophene* (50 per cent). (Found: C, 76·3; H, 7·4; N, 4·9; S, 11·3 per cent. $C_{18}H_{21}NS$ requires C, 76·3; H, 7·5; N, 4·9; S, 11·3 per cent.)

(vi) *2-Octyl-5-(4-cyanophenyl)thiophene* (58 per cent). (Found: C, 76·95; H, 7·8; N, 4·5;

S, 10·55 per cent. $C_{19}H_{23}NS$ requires C, 76·7; H, 7·8; N, 4·7; S, 10·8 per cent.)

(vii) *2-Nonyl-5-(4-cyanophenyl)thiophene* (79 per cent). (Found; C, 77·0; H, 8·0; N, 4·5; S, 10·4 per cent. $C_{20}H_{25}NS$ requires C, 77·1; H, 8·1; N, 4·5; S, 10·3 per cent.)

(viii) *2-Decyl-5-(4-cyanophenyl)thiophene* (69 per cent). (Found: C, 77·55; H 8·4; N, 4·3; S, 9·7 per cent. $C_{21}H_{27}NS$ requires C, 77·5; H, 8·4; N, 4·3; S 9·8 per cent.)

(ix) *2-Undecyl-5-(4-cyanophenyl)thiophene* (84 per cent). (Found: C, 78·0; H, 8·5; N, 4·4; S, 9·65 per cent. $C_{22}H_{29}NS$ requires C, 77·8; H, 8·5; N, 4·1; S, 9·4 per cent.)

(x) *2-Butyl-5-(4'-cyanobiphenyl-4-yl)thiophene* (79 per cent). (Found: C, 79·6; H, 5·9; N, 4·5; S 9·8 per cent. $C_{21}H_{19}NS$ requires C, 79·5; 6·0; N, 4·4; S, 10·1 per cent.) $\nu_{max}$ 2240 $cm^{-1}$; $\delta_H$ 7·62 (8 H, m, biphenyl), 7·19 (1 H, d, *J* 3·5, thienyl), 6·67 (1 H, dt, *J* 3·5, 1, thienyl), 2·84 (2 H, m, $C\underline{H}_2CH_2CH_2CH_3$), 1·70 (2 H, m, $CH_2C\underline{H}_2CH_2CH_3$), 1·42 (2H, m, $CH_2CH_2C\underline{H}_2CH_3$), 0·95 (3H, t, $CH_3$); $\delta_C$ 146·5, 145·0, 140·6, 137·3, 135·2, 132·6, 127·5, 127·3, 126·0, 125·2, 123·3, 118·8, 110·85, 33·7, 20·9, 22·1, 13·7.

(xi) *2-Pentyl-5-(4'-cyanobiphenyl-4-yl)thiophene* (49 per cent). (Found: C, 79·9; H, 6·2; N, 4·2; S, 9·4 per cent. S, 9·4 per cent.) $C_{22}H_{21}NS$ requires C, 79·7; H, 6·4; N, 4·2; S, 9·7 per cent.)

(xii) *2-Hexyl-5-(4'-cyanobiphenyl-4-yl)thiophene* (69 per cent). (Found: C, 80·0; H, 6·4; N, 3·9; S, 9·1 per cent. $C_{23}H_{23}NS$ requires C, 80·0; H, 6·7; N, 4·05; S, 9·3 per cent.)



## 5.6. *Thiophene esters*

### 5.6.1. *Preparation of β-chloro-3-(4-substituted)cinnamaldehydes*

(i) Phosphorus oxychloride (11·1 ml, 0·12 mol) was added dropwise with stirring under nitrogen to ice cold, dry, *N*,*N*-dimethylformamide (10·9 ml, 0·14 mmol) and the mixture was stirred for 30 min at 20°C. The solution was then cooled to 0°C and 4-cyanoacetophenone (7·0 g, 0·05 mol) added in dry *N*,*N*-dimethylformamide (7 ml). After stirring at 35°C for 3 h, the mixture was cooled to 0°C and 10 per cent aqueous sodium acetate (180 ml) was added with stirring. The resultant mixture was then heated at 40°C for 30 min, cooled to room temperature and shaken with dichloromethane (3 × 100 ml); the combined extracts were washed with water, dried and evaporated. Chromatography with dichloromethane as eluant gave 3-chloro-3-(4-cyanophenyl)propenal (4·8 g, 52 per cent) as a mixture of (*Z*)- and (*E*)-isomers (*Z*/*E* 90:10); $\delta_H$ (220 MHz) (*Z*)-isomer: 10·18 (1H, d, CHO, 7·86 and 7·76 (each 2 H, m, $-C_6H_4-$), 6·69 (1 H, d, =CH), (*E*)-isomer: 9·42 (1H, d, CHO), 7·75 and 7·62 (each 2H, m, $-C_6H_4-$), 6·59 (1H, d, =CH). Fractional crystallization from cyclohexane gave (*Z*)-3-chloro-3-(4-cyanophenyl)propenal, mp 96–98°C. (Found: C, 62·6; H, 3·1; N, 7·0; Cl, 18·4 per cent. $C_{10}H_6ClNO$ requires C, 62·7; H, 3·2; N, 7·3; Cl, 18·5 per cent.) $\nu_{max}$ 2230 (CN) and 1680 $cm^{-1}$ (CO); $\delta_C$ 190·5, 149·2, 139·7, 132·5, 127·7, 126·4, 117·6, 115·2.

(ii) *3-Chloro-3-(4-hexyloxyphenyl)propenal* (38 per cent) was similarly prepared as an inseparable mixture of (*Z*)- and (*E*)-isomers (*Z*/*E* 84:16); (Found C, 67·3, H, 7·4, Cl, 13·1 per cent. $C_{15}H_{19}ClO_2$ requires C, 67·5; H, 7·2; Cl, 13·3 per cent.) $\nu_{max}$ (neat) 1680 $cm^{-1}$ (CO); $\delta_H$ (220 MHz) (*Z*)-isomer: 10·15 (1 H, d, CHO), 7·69 and 6·93 (each 2H, m, $-C_6H_4-$), 6·59 (1 H, d, =CH), 3·99 (2H, t, $-OCH_2-$), 1·78 (2 H, m, $-OCH_2CH_2-$), 1·55–1·20 (6 H, m, $CH_3(C\underline{H}_2)_3-$), 0·86 (3 H, t, $CH_3$), (*E*)-isomer: 9·46 (1 H, d, CHO), 7·44 and 6·91 (2 H, m, $-C_6H_4-$), 6·44 (1 H, d, =CH), 3·99 (2 H, t, $OCH_2-$), 1·78 (2 H, m, $-OCH_2CH_2-$), 1·55–1·20 (6 H, m, $CH_3(CH_2-$), 1·55–1·20 (6 H, m, $CH_3(C\underline{H}_2)_3-$), 0·86 (3 H, t, $CH_3$).

5.6.3. *Preparation of thiophene esters*

(i) Ethyl thioglycolate (0·27 ml, 2·6 mmol) was added to a stirred solution of sodium ethoxide (prepared from sodium (0·066 g, 2·87 mmol) in dry ethanol) under nitrogen at 0°C. 3-Chloro-3-(4- cyanophenyl)propenal (0·5 g, 2·6 mmol), in dry ethanol (15 ml) was added dropwise, and stirring was continued at 0°C for 1 h. The mixture was kept at 20°C for 12 h, then poured into water, and the resultant suspension was shaken with dichloromethane (3 × 25 ml). The combined extracts were washed with water, dried and evaporated. Chromatography on silica gel with chloroform–hexane (9 : 1) as the eluant, and recrystallization from cyclohexane gave ethyl 5-(4-cyanophenyl)thiophene-2-carboxylate (0·3 g, 45 per cent). (Found; C, 65·15; H, 4·2; N, 5·4; S, 12·2 per cent; $M^+$, 257. $C_{14}H_{11}NO_2S$ requires C, 65·35; H, 4·3; N, 5·4; S, 12·45 per cent. $M^+$, 257.) $\nu_{max}$ 2240 (CN), 1695 $cm^{-1}$ (CO); $\delta_H$ 7·79 and 7·38 (each 1 H, d, *J* 4, thienyl), 7·71 (4 H, m, $-C_6H_4-$), 4·38 (2H, q, *J* 7, $CO_2C\underline{H}_2CH_3$), 1·36 (3H, t, $CH_3$); $\delta_C$ 161·7, 148·0, 137·7, 134·8, 134·1, 132·8, 126·5, 125·3, 118·3, 112·0, 61·4, 14·3. Similarly prepared was:

(ii) *Ethyl 5-(4-hexyloxyphenyl)thiophene-2-carboxylate* (36 per cent) (from pentane). (Found: C, 68·5; H 7·0; S, 9·6 per cent. $C_{19}H_{24}O_3S$ requires C, 68·6; H, 7·3; S, 6·9 per cent.)

(iii) Hexyl thioglycolate (1·83 g, 10 mmol) [28] was added to a stirred solution of sodium metal (0·26 g, 11 mmol) in hexan-1-ol (26 ml) under nitrogen at 0°C. 3-Chloro-3-(4-cyanophenyl)propenal (2·0 g, 10 mmol) in hexan-1-ol (60 ml) was added dropwise and stirring was contained at 0°C for 1 h. The mixture was kept at 20°C for 17 h, then poured into water (200 ml) and the resultant suspension shaken with dichloromethane (3 × 100 ml). The combined extracts were washed successively with 10 per cent aqueous potassium hydroxide, water and brine, dried and evaporated. Chromatography with hexane–ethyl acetate (9 : 1) as eluant and recrystallization from pentane gave hexyl 5-(4-cyanophenyl)thiophene-2-carboxylate (0·5 g, 15 per cent). (Found: C, 69·1; H, 6·1; N, 4·3; S, 10·05 per cent. $C_{18}H_{19}NO_2S$ requires C, 69·0; H, 6·1; N, 4·5; S, 10·2 per cent.) $\nu_{max}$ 2240 (CN) and 1705 $cm^{-1}$ (CO); $\delta_H$ 7·75 and 7·35 (each 1 H, d, *J* 5, thienyl), 7·68 (4 H, m, $-C_6H_4-$), 4·29 (2 H, t, $CO_2CH_2-$), 1·75 (2 H, m, $CO_2CH_2C\underline{H}_2-$), 1·34 (6 H, m, $CH_3(C\underline{H}_2)_3-$), 0·88 (3 H, m, $CH_3$); $\delta_C$ 161·9, 148·0, 137·6, 134·1, 132·8, 126·5, 125·3, 118·4, 111·9, 65·6, 31·4, 28·6, 25·6, 22·5, 14·0.



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