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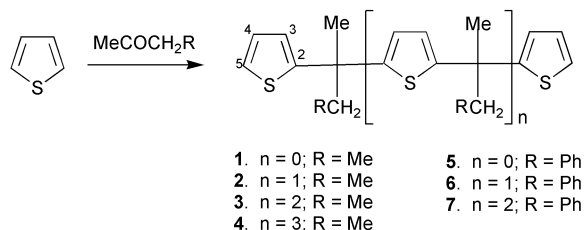
Thiophene reacts with aliphatic ketones in aqueous 75% v/v sulfuric acid to give condensation products containing up to five thiophene units. Ketones bearing phenyl substituents yield mono- and di-styrylthiophenes. All the reactions occur at the C-2 and -5 positions of thiophene. 2,5-Bis( $\alpha$ -phenylstyryl)thiophene undergoes photocyclisation to give a dinaphthothiophene.

## Introduction

The acid-catalysed condensation of thiophene with simple aliphatic ketones provides a convenient route to dithienylalkanes and related compounds.<sup>1</sup> We have now extended the range of these reactions to include ketones having phenyl substituents.

## Results and discussion

Previous investigators<sup>1</sup> employed “72%” sulfuric acid to effect such condensations but did not specify whether the concentration was v/v or w/v or w/w. We chose to use aqueous 75% v/v acid (ca. 140–145% w/v), a concentration similar to that which had proved highly effective in the condensations of ketones with the reactive benzene derivative veratrole.<sup>2</sup> In this medium thiophene and butan-2-one reacted at room temperature to give the previously described compounds **1**,<sup>3,4</sup> and **2**,<sup>3</sup> together with the analogous products of further condensation **3** and **4** (Scheme 1), which we separated by PLC. Their <sup>1</sup>H NMR spectra



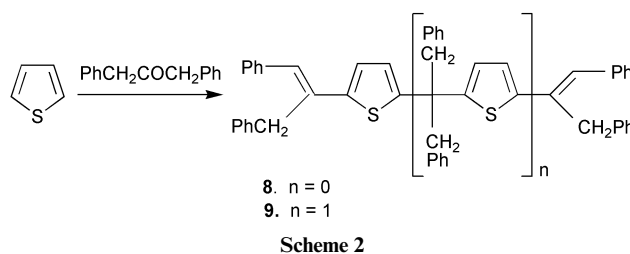
Scheme 1

established their structures with the signals in the  $\delta$  6.6–7.1 region being readily assigned to specific protons attached to the thiophene rings. Thus the signals of the protons of the mono-substituted thienyl groups exhibit a characteristic pattern of doublet, doublet-of-doublets, and doublet at ca.  $\delta$  7.1, 6.85, and 6.8 which we attribute to H-5, H-4, and H-3 respectively; the coupling between H-5 and H-3 appears to be negligible. The signals for the protons H-3 and H-4 of a symmetrical 2,5-disubstituted thiophene appear further up-field giving rise to a distinctive singlet usually at ca.  $\delta$  6.6. The mass spectra of the products show the expected repeated loss of ethyl radicals from the quaternary carbons of the molecular ions.

We next examined reactions between thiophene and ketones containing one or more phenyl groups. Phenylpropan-2-one behaved like the simple aliphatic ketones and gave the expected phenyl derivatives **5**, **6**, and **7**, each of which readily lost one or more of the quaternary benzyl groups in the mass spectrometer. The NMR signals for **5** were less easy to interpret than were

those for the simple aliphatic analogues. Models show that the thienyl and phenyl groups are close together leading to changes in the chemical shifts of both sets of protons. The signals for **6** are subject to further complications because the molecule can exist in both *meso* and *racemic* forms and the mixture of stereoisomers is responsible for the thienylene protons appearing as two singlets. Structure **7** has two *meso* and one *racemic* form and as a result its NMR signals are even more complicated.

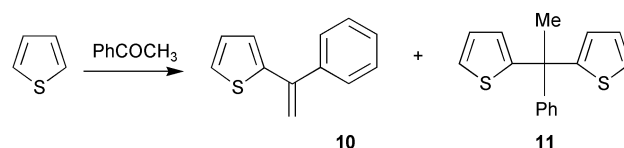
The presence of the second phenyl group in 1,3-diphenylpropan-2-one resulted in the reaction with thiophene taking a somewhat different course leading to the formation of the bis(diphenylpropenyl) derivatives **8** and **9** (Scheme 2). Here the



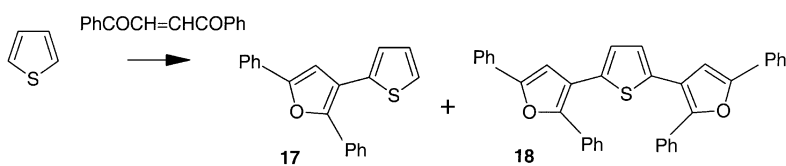
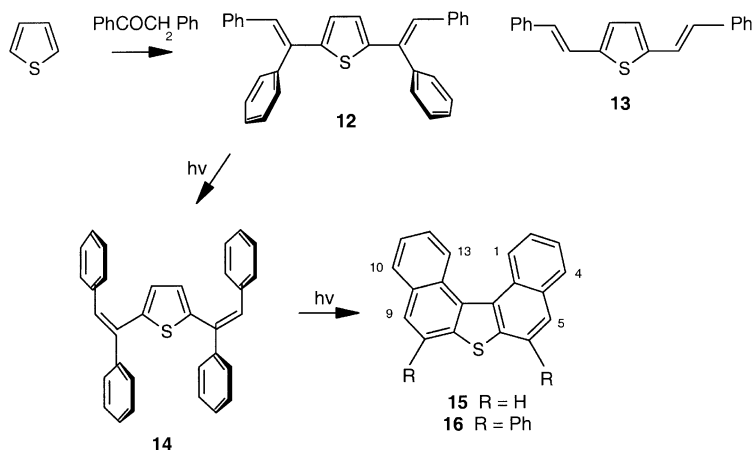
Scheme 2

intermediate tertiary alcohols undergo dehydration to form the conjugated alkenes in preference to reacting further with thiophene. The mass spectra of the products again show the ready ejection of benzyl groups from the molecular ions. The UV absorption of compound **9** resembles that<sup>5</sup> of (*E*)-2-styrylthiophene while the absorption of compound **8** at rather longer wavelengths indicates the presence of the extended conjugated system. “Catalin” molecular models strongly favour the *E,E* configuration about the double bonds and the particular conformation shown. For the conjugated system to be essentially coplanar, the two benzyl groups require to be rotated out of the plane to minimise steric interactions.

The lower reactivity of ketones having a conjugated phenyl group results in the formation of somewhat simpler products. Thus acetophenone reacted with thiophene to produce low yields of the thienylstyrene **10** and the phenyldithienylethane **11** (Scheme 3), but with an extended time of reaction the related ketone 1,2-diphenylethanone gave an acceptable yield of the



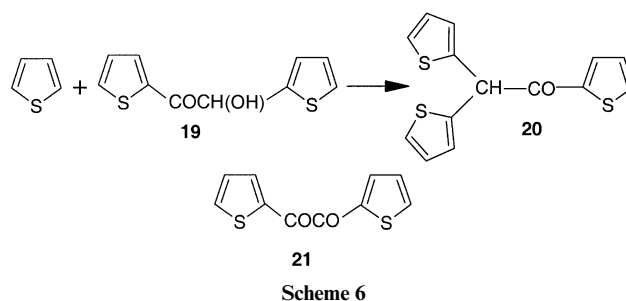
Scheme 3



sole product the bis(phenylstyryl)thiophene **12** (Scheme 4). This shows UV absorption resembling that of compound **8** and consequently has a similar structure. Models again support the *E,E* configuration and suggest that the two phenyl rings adjacent to the thiophene nucleus lie in planes nearly perpendicular to that of the main conjugated system. The UV absorption of the diene **12** provides strong support for the proposed *E,E* configuration, the spectrum resembling closely that<sup>6</sup> of (*E,E*)-2,5-distyrylthiophene **13** despite the presence of the two additional phenyl substituents adjacent to the thiophene nucleus in the former compound. These phenyl groups, being orthogonal to the main conjugated system, are effectively insulated from it. This behaviour resembles that shown by triphenylethylene<sup>7</sup> which displays UV absorption similar to that of (*E*)-stilbene. The UV absorptions of **12** and of its dibenzyl analogue **8** differ mainly in the positions of their long wavelength bands (at 378 and 354 nm respectively). The hypsochromic shift of the latter compound appears to be a consequence of the benzyl substituents on the two styryl groups; a similar shift<sup>8</sup> results from the introduction of an  $\alpha$ -methyl group into (*E*)-stilbene. Compound **12** has previously been prepared by a multi-stage synthesis<sup>9</sup> but its stereochemistry was not investigated.

Thiophene reacted with two other aromatic ketones in rather different ways. 1,2-Dibenzoyl ethylene underwent 1,4-addition to its enone system, cyclisation of the resulting 1,4-diketones giving the mono- and di-furylthiophenes **17** and **18** (Scheme 5), while 2,2'-thenoin **19** formed the trithienylethanone **20** (Scheme 6), presumably by addition of thiophene to the carbonyl group, followed by dehydration of the resulting glycol. We were able to assign the NMR signals of **20** to specific protons by comparing them with those of 2,2'-thenil **21** and 2,2'-thenoin.

The bis(phenylstyryl)thiophene **12** formally contains two (*Z*)-stilbene groupings and on irradiation with UV light<sup>10</sup> might be expected to form a diphenanthrylthiophene. However, the product, C<sub>32</sub>H<sub>20</sub>S, proved to be the diphenyldinaphthothiophene **16**. It shows UV absorption very similar to that<sup>11</sup> of the parent compound **15** (and quite different to that of phenanthrene), while the <sup>1</sup>H NMR signals are in excellent agreement with those<sup>12</sup> of the corresponding protons of **15**. The formation of the condensed thiophene **16** must involve the initial excitation of the distyrylthiophene  $\pi$ -electron system (but not, apparently, of the two orthogonal phenyl substituents). Isomerisation about the double bonds then occurs, possibly facilitated by the



development of a twisted (*E*)-stilbenyl derivative such as **14**. Electrocyclic ring closure follows between the terminal phenyl groups and the thiophene nucleus<sup>13</sup> and finally the resulting dihydro compounds undergo aerial oxidation to give **16**. The above reactions enable thiophene to be converted into the polycyclic derivative **16** in two simple steps.

## Experimental

IR spectra were recorded for KBr discs and UV absorption spectra for methanolic solutions;  $\epsilon$  values are given in units of dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> and *infl* denotes an inflexion. <sup>1</sup>H NMR spectra were measured at 220 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were obtained using electron impact at 70 eV. PLC was performed using Merck Kieselgel GF<sub>254</sub>. "Light petroleum" refers to the fraction with bp 60–80 °C. The yields of products are based on the initial weights of the ketones used and were not optimised.

### Reactions of thiophene with ketones

A mixture of the ketone, thiophene and aqueous 75% (v/v) sulfuric acid (50 ml) was stirred at room temperature usually for 4 h and then poured into water. The product was extracted with chloroform and subjected to PLC using light petroleum and light petroleum–chloroform (4 : 1). The fractions are listed in order of their mobility with the fastest-moving first.

(a) **Thiophene and butan-2-one.** Butan-2-one (3.6 g, 50 mmol) and thiophene (8.4 g, 100 mmol) produced four products as pale yellow oils. The fastest-moving was 2,2-di-thienylbutane **1** (3.08 g, 13.9 mmol, 27.7%) (Found: M<sup>+</sup>,

222.0536. Calc. for  $C_{12}H_{14}S_2$ :  $M$ , 222.0537;  $m/z$  222 (8%,  $M^+$ ), 193 (100,  $M - Et$ ), 109 (14,  $C_6H_5S$ ) and 83 (78,  $C_4H_5S$ );  $\lambda_{max}/nm$  232infl (3.88);  $\nu_{max}/cm^{-1}$  1589 (aromatic C=C);  $\delta_H$  0.86 (3H, t,  $J$  8,  $CH_2CH_3$ ), 1.76 (3H, s,  $CH_3$ ), 2.19 (2H, q,  $J$  8,  $CH_2Me$ ), 6.82 (2H, d,  $J$  3, H-3), 6.88 (2H, dd,  $J$  3 and 5, H-4), and 7.12 (2H, d,  $J$  5, H-5).

Next came 2,5-bis[2-(2-thienyl)butan-2-yl]thiophene **2** (890 mg, 2.5 mmol, 9.9%) (Found:  $M^+$ , 360.1053.  $C_{20}H_{24}S_3$  requires  $M$ , 360.1040);  $m/z$  360 (19%,  $M^+$ ), 331 (100,  $M - Et$ ), 302 (47, 331 - Et), 287 (5, 302 - Me), 218 (9,  $C_{12}H_{10}S_2$ ), 109 (27,  $C_6H_5S$ ), and 97 (15,  $C_5H_5S$ );  $\lambda_{max}/nm$  235 (log  $\epsilon$  4.26);  $\delta_H$  0.84 (6H, t,  $J$  8,  $CH_2CH_3$ ), 1.70 (6H, s,  $CH_3$ ), 2.13 (4H, q,  $J$  8,  $CH_2Me$ ), 6.60 (2H, s, thienylene  $CHCH$ ), 6.79 (2H, d,  $J$  4, H-3), 6.86 (2H, dd,  $J$  4 and 4, H-4), and 7.11 (2H, d,  $J$  4, H-5).

Then followed 2,2-bis[5-[2-(2-thienyl)butan-2-yl]-2-thienyl]butane **3** (1.59 g, 3.2 mmol, 19.2%) [Found: ( $M - C_2H_5$ ) $^+$ , 469.1145.  $C_{26}H_{29}S_4$  requires  $M$ , 469.1150];  $m/z$  498 (4%,  $M^+$ ), 469 (100,  $M - Et$ ), 440 (18, 469 - Et), 411 (53, 440 - Et), 220 (11, 440 $^{2+}$ ), 139 (19,  $C_8H_{11}S$ ), 109 (26,  $C_6H_5S$ ) and 97 (19,  $C_5H_5S$ );  $\lambda_{max}/nm$  236 (log  $\epsilon$  4.36);  $\delta_H$  0.82 (3H, t,  $J$  8,  $CH_2CH_3$ ), 0.84 (6H, t,  $J$  8,  $CH_2CH_3$ ), 1.65 (3H, s,  $CH_3$ ), 1.70 (6H, s,  $CH_3$ ), 2.07 (2H, q,  $J$  8,  $CH_2Me$ ), 2.12 (4H, q,  $J$  8,  $CH_2Me$ ), 6.57 (4H, br s, thienylene  $CHCH$ ), 6.78 (2H, d,  $J$  3, H-3), 6.86 (2H, dd,  $J$  3 and 4, H-4) and 7.11 (2H, d,  $J$  4, H-5).

The final fraction was 2,5-bis[2-(5-[2-(2-thienyl)butan-2-yl]-2-thienyl]butan-2-yl]thiophene **4** (1.90 g, 3.0 mmol, 23.9%) [Found: ( $M - Et$ ) $^+$ , 607.1655.  $C_{34}H_{39}S_5$  requires  $M$ , 607.1655];  $m/z$  636 (2%,  $M^+$ ), 607 (25,  $M - Et$ ), 578 (5, 607 - Et), 552 (11,  $M - C_4H_4S$ ), 523 (100, 552 - Et), 494 (14, 523 - Et), 469 (20, 552 -  $C_4H_4S$ ), 465 (18, 494 - Et), 436 (18, 465 - Et), 248 (21,  $C_{14}H_{16}S_2$ ) and 218 (22,  $C_{12}H_{10}S_2$ );  $\lambda_{max}/nm$  235infl (log  $\epsilon$  4.43);  $\delta_H$  0.81 and 0.83 (each 6H, t,  $J$  8,  $CH_2CH_3$ ), 1.64 and 1.69 (each 6H, s,  $CH_3$ ), 2.05 and 2.12 (each 4H, q,  $J$  8,  $CH_2Me$ ), 6.58 (6H, br s, thienylene  $CHCH$ ), 6.79 (2H, d,  $J$  3, H-3), 6.87 (2H, dd,  $J$  3 and 4, H-4), and 7.11 (2H, d,  $J$  4, H-5).

**(b) Thiophene and phenylpropan-2-one.** Phenylpropan-2-one (4.47 g, 33.3 mmol) and thiophene (2.8 g, 33.3 mmol), after 16 h, gave three products. The first, 2,2-di-2-thienyl-1-phenylpropane **5** (3.39 g, 11.9 mmol, 35.8%) crystallised from light petroleum as yellow needles, mp 84–85 °C [Found: ( $M - C_7H_7$ ) $^+$ , 193.0156.  $C_{10}H_9S_2$  requires  $M$ , 193.0145];  $m/z$  284 (1%,  $M^+$ ), 193 (100,  $M - C_7H_7$ ), 109 (20, 193 -  $C_4H_4S$ ), and 91 (9,  $C_7H_7$ );  $\lambda_{max}/nm$  237 (log  $\epsilon$  4.16);  $\nu_{max}/cm^{-1}$  1600 (aromatic C=C), 758 and 700 (5 adjacent ArH);  $\delta_H$  1.72 (3H, s,  $CH_3$ ), 3.49 (2H, s,  $CH_2$ ), 6.78–6.96 (6H, thienyl H and ArH) and 7.13–7.25 (5H, thienyl H and ArH).

The second was 2,5-bis[1-phenyl-2-(2-thienyl)propan-2-yl]thiophene **6** (0.61 g, 1.26 mmol, 7.6%) which crystallised from light petroleum as needles, mp 100–101 °C [Found: ( $M - C_7H_7$ ) $^+$ , 393.0793.  $C_{23}H_{21}S_3$  requires  $M$ , 393.0803];  $m/z$  393 (63%,  $M - C_7H_7$ ), 302 (100, 393 -  $C_7H_7$ ), 109 (11,  $C_6H_5S$ ), and 91 (21,  $C_7H_7$ );  $\lambda_{max}/nm$  239 (log  $\epsilon$  4.31) and 257infl (4.05);  $\nu_{max}/cm^{-1}$  1599 (aromatic C=C), 742 and 696 (5 adjacent ArH);  $\delta_H$  1.66 (6H, s,  $CH_3$ ), 3.42 (4H, s,  $CH_2$ ), 6.57 and 6.60 (each 1H, s, thienylene H), 6.70–6.90 (8H, m, thienyl H and ArH), and 7.05–7.21 (8H, thienyl H and ArH).

The third product was 2,2-bis[5-[2-(2-thienyl)-1-phenylpropan-2-yl]-2-thienyl]-1-phenylpropane **7** (0.27 g, 0.39 mmol, 3.5%), a viscous oil [Found: ( $M - C_7H_7$ ) $^+$ , 593.1478.  $C_{36}H_{33}S_4$  requires  $M$ , 593.1465];  $m/z$  593 (46%,  $M - C_7H_7$ ), 502 (11, 593 -  $C_7H_7$ ), 411 (100, 502 -  $C_7H_7$ ), 109 (13,  $C_6H_5S$ ) and 91 (45,  $C_7H_7$ );  $\lambda_{max}/nm$  239 (log  $\epsilon$  4.40) and 257infl (4.20);  $\nu_{max}/cm^{-1}$  1599 (aromatic C=C), 755, 743, 700 and 696 (5 adjacent ArH);  $\delta_H$  1.60 (3H, s,  $CH_3$ ), 1.67 (6H, s,  $CH_3$ ), 3.40 (2H, s,  $CH_2$ ), 3.45 (4H, s,  $CH_2$ ), 6.55–6.65 (4H, m, thienylene H), 6.77–6.95 (9H, m, thienyl H and ArH) and 7.08–7.25 (12H, m, thienyl H and ArH).

**(c) Thiophene and 1,3-diphenylpropan-2-one.** 1,3-Diphenylpropan-2-one (5.2 g, 24.8 mmol) and thiophene (4.2 g, 50 mmol) gave two major products. The faster-moving was (*E,E*)-2,5-bis(1,3-diphenylpropen-2-yl)thiophene **8** (750 mg, 1.60 mmol, 12.9%) which crystallised from acetone as yellow needles, mp 128–130 °C (Found:  $M^+$ , 468.1901.  $C_{34}H_{28}S$  requires  $M$ , 468.1912);  $m/z$  468 (100%,  $M^+$ ), 377 (30,  $M - C_7H_7$ ), 286 (6, 377 -  $C_7H_7$ ), 156 (28,  $C_{22}H_{16}S^{2+}$ ) and 91 (45,  $C_7H_7$ );  $\lambda_{max}/nm$  238 (log  $\epsilon$  4.26), 263 (4.19) and 354 (4.37);  $\nu_{max}/cm^{-1}$  1610 and 1599 (aromatic and aliphatic C=C), 758, 733, 702 and 697 (5 adjacent ArH);  $\delta_H$  4.07 (4H, s,  $CH_2$ ), 6.72 (2H, s, thienylene H), and 7.15–7.38 (22H, m, C=CH and ArH).

The second product was (*E,E*)-2,2-bis[5-(1,3-diphenylpropen-2-yl)-2-thienyl]-1,3-diphenylpropane **9** (970 mg, 1.30 mmol, 15.8%) which crystallised from acetone-methanol as yellow microcrystals, mp 134–136 °C [Found: ( $M - C_7H_7$ ) $^+$ , 653.2362.  $C_{46}H_{37}S_2$  requires  $M$ , 653.2337];  $m/z$  653 (53%,  $M - C_7H_7$ ), 563 (18, 653 -  $C_7H_6$ ) and 91 (100,  $C_7H_7$ );  $\lambda_{max}/nm$  239 (log  $\epsilon$  4.09) and 321 (4.20);  $\nu_{max}/cm^{-1}$  1598 (aromatic C=C), 751, 740, 727 and 696 (5 adjacent ArH);  $\delta_H$  3.31 and 4.11 (each 4H, s,  $CH_2$ ), 6.56 and 6.73 (each 2H, d,  $J$  4, thienylene H), 6.64–6.70 (4H, m, C=CH and ArH) and 6.97–7.46 (28H, m, ArH).

**(d) Thiophene and acetophenone.** Acetophenone (3.0 g, 25 mmol) and thiophene (3.36 g, 40 mmol) at 50 °C gave unchanged acetophenone (2.58 g) and two products. The first was *a*-(2-thienyl)styrene **10** (43 mg, 0.23 mmol, 0.9%), a pale orange oil, bp 104–106 °C (lit.,<sup>14</sup> 106 °C) (Found:  $M^+$ , 186.0502.  $C_{12}H_{10}S$  requires  $M$ , 186.0503);  $m/z$  186 (100%,  $M^+$ ), 185 (58,  $M - H$ ), 184 (24,  $M - 2H$ ), 171 (37,  $C_{11}H_7S$ ), 152 (11,  $M - H_2S$ ) and 141 (9,  $M - CHS$ );  $\lambda_{max}/nm$  216 (log  $\epsilon$  4.48), 236infl (3.92) and 280infl (3.64);  $\nu_{max}/cm^{-1}$  1605 (C=C), 774 and 700 (5 adjacent ArH);  $\delta_H$  5.22 and 5.56 (each 1H, br s, = $CH_2$ ), 6.86 (1H, d,  $J$  3, H-3), 6.94 (1H, dd,  $J$  3 and 5, H-4), 7.18 (1H, d,  $J$  5, H-5) and 7.28–7.58 (5H, m, ArH).

The second was 1,1-di-2-thienylthylbenzene **11**, a pale yellow oil (36 mg, 0.13 mmol, 0.5%) (Found:  $M^+$ , 270.0526.  $C_{16}H_{14}S_2$  requires  $M$ , 270.0536);  $m/z$  270 (29%,  $M^+$ ), 255 (100,  $M - Me$ ), 221 (8, 255 -  $H_2S$ ), 193 (25,  $M - Ph$ ), 171 (14,  $C_{11}H_7S$ ) and 109 (10,  $C_6H_5S$ );  $\lambda_{max}/nm$  236infl (log  $\epsilon$  4.20);  $\nu_{max}/cm^{-1}$  1599 (aromatic C=C), 746 and 700 (5 adjacent ArH);  $\delta_H$  2.28 (3H, s,  $CH_3$ ), 6.70 (2H, d,  $J$  2, H-3), 6.90 (2H, dd,  $J$  3 and 5, H-4), 7.17 (2H, d,  $J$  5, H-5) and 7.20–7.35 (5H, m, ArH).

**(e) Thiophene and 1,2-diphenylethanone.** 1,2-Diphenylethanone (4.9 g, 25 mmol) and thiophene (2.1 g, 25 mmol) gave, after 18 h, (*E,E*)-2,5-bis( $\alpha$ -phenylstyryl)thiophene **12** (0.98 g, 2.2 mmol, 17.8%) which crystallised from acetone-methanol as yellow needles, mp 141–142 °C (lit.,<sup>8</sup> 142 °C) (Found:  $M^+$ , 440.1592.  $C_{32}H_{24}S$  requires  $M$ , 440.1599);  $m/z$  440 (100%,  $M^+$ ), 220 (7,  $M^{2+}$ ) and 178 (8,  $C_{14}H_{10}$ );  $\lambda_{max}/nm$  241 (log  $\epsilon$  4.31), 274 (4.18), 308 (4.17), 352infl (4.32) and 378 (4.42);  $\nu_{max}/cm^{-1}$  1594 (aromatic C=C), 715 and 692 (5 adjacent ArH);  $\delta_H$  6.52 (2H, s, thienylene H), and 6.90–7.47 (22H, m, C=CH and ArH).

**(f) Thiophene and (*E*)-1,2-dibenzoylthiophene.** 1,2-Dibenzoylthiophene (2.36 g, 10 mmol) and thiophene (1.68 g, 20 mmol) gave two products. The first, 2,5-diphenyl-3-(2-thienyl)furan **17** (830 mg, 2.75 mmol, 27.5%) crystallised from diethyl ether-light petroleum as needles, mp 185–187 °C (Found:  $M^+$ , 302.0759.  $C_{20}H_{14}OS$  requires  $M$ , 302.0765);  $m/z$  302 (100%,  $M^+$ ), 273 (6,  $M - CHO$ ), 197 (22,  $M - PhCO$ ), 105 (44,  $PhCO$ ) and 77 (20,  $Ph$ );  $\lambda_{max}/nm$  230infl (log  $\epsilon$  4.25), 235infl (4.20), 276 (4.23), 310infl (4.28), 323 (4.31), 332infl (4.25) and 342infl (4.12);  $\nu_{max}/cm^{-1}$  1596 (aromatic C=C), 766 and 691 (5 adjacent ArH);  $\delta_H$  6.80 (1H, s, furyl H), 7.01–7.16 (2H, m, thienyl H) and 7.25–7.82 (11H, m, thienyl H and ArH).

The second was 2,5-bis(2,5-diphenyl-3-furyl)thiophene **18** (460 mg, 0.88 mmol, 17.7%) which crystallised from diethyl ether-light petroleum as needles, mp 218–220 °C (Found:  $M^+$ ,

520.1500.  $C_{36}H_{24}O_2S$  requires  $M$ , 520.1497;  $m/z$  520 (100%,  $M^+$ ), 415 (7,  $M - PhCO$ ), 260 (18,  $M^{2+}$ ) and 105 (30,  $PhCO$ );  $\lambda_{max}/nm$  230 (log  $\epsilon$  4.42), 306infl (4.62), 315 (4.62), 329infl (4.55) and 343infl (4.36);  $\nu_{max}/cm^{-1}$  1597 (aromatic C=C), 767 and 697 (5 adjacent ArH);  $\delta_H$  6.84 (2H, s, furyl H), 7.09 (2H, s, thienylene H), 7.25–7.52 (12H, m, ArH) and 7.71–7.86 (8H, m, ArH).

(g) **Thiophene and 2,2'-thenoin 19**. 2,2'-Thenoin<sup>15</sup> (2.24 g, 10 mmol) and thiophene (1.68 g, 20 mmol) gave, after 24 h, 1,2,2-tri-2-thienylethanone **20** (1.32 g, 4.55 mmol, 45.5%) which crystallised from diethyl ether as needles, mp 82–83 °C (Found:  $M^+$ , 289.9897.  $C_{14}H_{10}OS_3$  requires  $M$ , 289.9894);  $m/z$  290 (2%,  $M^+$ ), 179 (100,  $M - C_4H_3SCO$ ) and 45 (11, CHS);  $\lambda_{max}/nm$  240 (log  $\epsilon$  4.16) and 293 (3.94);  $\nu_{max}/cm^{-1}$  1638 (C=O);  $\delta_H$  6.28 (1H, s, CHCO), 6.94 (2H, dd,  $J$  5 and 6, thienyl H-4), 7.03 (2H, d,  $J$  5, thienyl H-3), 7.11 (1H, dd,  $J$  5 and 6, thenoyl H-4), 7.22 (2H, d,  $J$  6, thienyl H-5), 7.65 (1H, d,  $J$  6, thenoyl H-3) and 7.83 (1H, d,  $J$  5, thenoyl H-5).

2,2'-Thenoin **19**. This compound<sup>15</sup> showed  $\delta_H$  4.40 (1H, br s, OH), 6.03 (1H, s, CHOH), 6.93–7.01 (1H, m, thienyl H), 7.07–7.16 (2H, m, thienyl H), 7.29 (1H, dd,  $J$  5 and 6, thenoyl H-4), 7.69 (1H, d,  $J$  6, thenoyl H-3) and 7.75 (1H, d,  $J$  5, thenoyl H-5).

2,2'-Thenil **21**. This compound<sup>15</sup> showed thenoyl proton signals at  $\delta_H$  7.20 (2H, dd,  $J$  4 and 7, H-4), 7.83 (2H, d,  $J$  7, H-5) and 8.06 (2H, d,  $J$  4, H-3).

#### Photocyclisation of (*E,E*)-2,5-bis( $\alpha$ -phenylstyryl)thiophene **12**

A solution of the bis(phenylstyryl)thiophene (50 mg, 0.11 mmol) in acetonitrile (50 ml) was irradiated at 40 °C for 8 h using a medium-pressure mercury lamp (120 W,  $\lambda = 253.7$  nm) with free access to air. Evaporation of the solvent and PLC of the residual solid gave 6,8-diphenyldinaphtho[2,1-*b*:1',2'-*d*]thiophene **16** (5 mg, 0.01 mmol, 10%), mp 197–198 °C (Found:  $M^+$ , 436.1290.  $C_{32}H_{20}S$  requires  $M$ , 436.1286);  $m/z$  436

(100%,  $M^+$ ), 434 (27,  $M - 2H$ ), 388 (29, 434 –  $CH_2S$ ), 359 (17,  $M - Ph$ ) and 179 (12,  $C_{14}H_{11}$ );  $\lambda_{max}/nm$  247infl (log  $\epsilon$  4.54), 287 (4.38), 320 (3.95), 341 (3.94) and 356 (3.93);  $\nu_{max}/cm^{-1}$  1600 (aromatic C=C), 762 (4 adjacent ArH), 749 and 697 (5 adjacent ArH);  $\delta_H$  7.10–7.85 (14H, m, ArH), 7.88 (2H, s, H-5 and -9), 8.00–8.15 (2H, m, H-4 and -10) and 8.85–8.99 (2H, m, H-1 and -13).

#### Dinaphtho[2,1-*b*:1',2'-*d*]thiophene **15**

This compound<sup>16</sup> had  $\lambda_{max}/nm$  236 (log  $\epsilon$  4.61), 276 (4.46), 300 (4.02), 312 (4.21), 336 (4.19) and 352 (4.19);  $\delta_H$  7.50–7.62 (4H, m, H-2, -3, -11 and -12), 7.92 (4H, br s, H-5, -6, -8 and -9), 7.96–8.06 (2H, m, H-4 and -10) and 8.80–8.90 (2H, m, H-1 and -13).

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