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## Liquid Crystals

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# Liquid crystalline compounds in the thiophene series XIII.† Synthesis and characterization of ‘oligomeric’ liquid crystalline model compounds with vinylene units, thiophene ring systems and hexamethylene chains

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‘Oligomeric compounds’ with three, four or six mesogenic groups in the chain were synthesized by the Wittig reaction from different bis Wittig salts and various heteroaromatic aldehydes. The mesogenic groups are connected via hexamethylene moieties. All derivatives containing at each terminal position of the chain *E*-1,2-di-(2-thienyl)ethylene units and one, two or four *E,E*-2,5-bis(2-thienylvinyl)thiophene units in the chain show nematic phases while heating and/or cooling the samples (**2a**, **4** and **5**). Moreover, the oligomeric compound having the chain from **2a** and one terminal formyl group (**5**) also has a nematic phase. The derivative with four *E*-2-(2-thienylvinyl)thiophene units in the chain (**3a**) melts without forming a mesophase. Also two ‘oligomeric compounds’ with benzene and thiophene systems in the mesogenic groups were synthesized. The compounds all-*E*-1,4-bis[5-{6-[5-(2-thienylvinyl)-2-thienyl]hexamethylene}-2-thienylvinyl]benzene (**2b**) with three mesogenic groups and all-*E*-1,6-bis{4-[5-{6-[5-(2-thienylvinyl)-2-thienyl]hexamethylene}-2-thienylvinyl]phenyl}hexane (**3b**) with four mesogenic groups in the chain do not show liquid crystalline phases.

## 1. Introduction

Compounds with thiophene systems are able to form mesophases while heating and cooling [1]. Moreover, in a previous paper we have shown that ‘dimeric compounds’ with thiophene systems are also liquid crystalline [2, 3]. General ‘dimeric compounds’ are of interest because they have no rigid centre, but a flexible spacer between two rod-like mesogenic groups. For example, for all-*E*-1,6-bis{5-[5-(2-thienylvinyl)-2-thienylvinyl]-2-thienyl}hexane (**1**) with three thiophene systems and two vinylene units in each mesogenic group and a hexamethylene chain between the cores (see figure 1) we observed a nematic phase (see table 2). In the literature, recent interest in such ‘dimeric compounds’ is also evident because the similarity of ‘dimeric compounds’ to semi-flexible main chain liquid crystal polymers is obvious and should be proved [4]. Especially in the case of our given example **1**, the liquid crystallinity may suggest liquid crystalline behaviour for the corresponding polymer poly-[2,5-thienylenevinylene-2,5-thienylenevinylene-2,5-thienylenehexamethylene] (see figure 1). Surely, however, an even better approximation for comparison of

liquid crystallinity between low molecular mass model compounds and polymers would be given through the synthesis of higher ‘oligomeric compounds’ with three, four or more mesogenic groups linked by flexible spacers (see for example [5–7]). So we wish to report in this paper the synthesis and characterization of compounds with three, four or six of the mesogenic groups *E,E*-2,5-bis(2-thienylvinyl)thiophene and/or *E*-1,2-di-(2-thienyl)ethylene which are separated from each other by flexible hexamethylene spacers in the chain (see figure 1). These ‘oligomeric compounds’ are chemically similar to ‘dimeric compounds’ described previously by our group [8, 9]. In contrast to investigations presented in the literature [6, 7] a comparison between the known thermodynamic properties of the polymer (see figure 1) and the corresponding ‘oligomers’ has not been made, because a satisfactory preparation of the polymer is still unknown. In this case, the ‘oligomeric compounds’ should make it possible to obtain information about the liquid crystalline behaviour and the thermal stability of the polymer with a high degree of polymerisation of thiophene systems. Moreover, the ‘oligomeric compounds’ containing thiophene systems presented here seem to be the first liquid crystalline materials with heteroaromatic systems of this structural type.

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†For part 12 in this series [16].

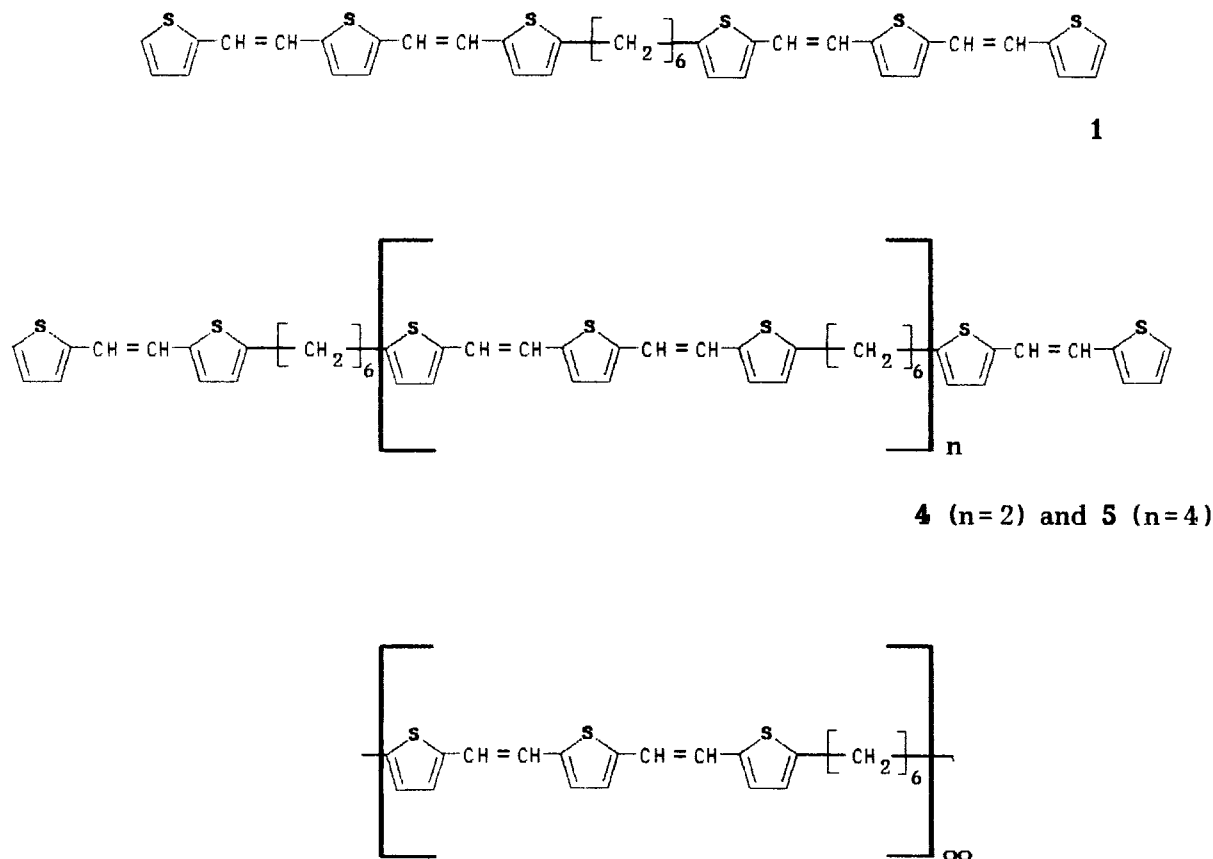


Figure 1. Structures of *E,E*-2,5-bis(2-thienylvinyl)thiophene as the mesogenic group and a hexamethylene chain as the spacer in a 'dimeric' and an 'oligomeric' compound and in a polymer.

## 2. Experimental

The IR spectra were obtained with a Perkin-Elmer 580B spectrometer. The  $^1\text{H}$  NMR spectra were recorded at 270 MHz using a Bruker WH 270 instrument; the chemical shifts are given relative to tetramethylsilane (TMS). The mass spectra were recorded with a Varian MAT 112S instrument. The elemental analyses were performed with a Perkin-Elmer Recorder 56. The phase transitions were determined by thermal analysis using a Heraeus TA 500 instrument with a scanning speed of  $10\text{ K min}^{-1}$ , and occasionally at  $5\text{ K min}^{-1}$ , for heating and cooling runs under an argon atmosphere. The first and second heating cycles were used for the determination of the phase transition temperatures and enthalpies. Optical observations were carried out with a Zeiss polarizing microscope using a Lincam heating regulation system. The *E*-isomers were confirmed by IR spectroscopy and in the case of soluble derivatives by  $^1\text{H}$  NMR spectroscopy.

### 2.1. General synthesis of the 'oligomeric compounds' with three mesogenic groups (**2a** and **2b**) (see figure 2)

One of the bis Wittig salts, 2,5-bis(triphenylphosphoniomethyl)thiophene dichloride or 1,4-bis(triphenyl-

phosphoniomethyl)benzene dichloride (prepared according to a method described by Koßmehl *et al.* [10] and Friedrich *et al.* [11]) and *E*-1-(5-formyl-2-thienyl)-6-[5-(2-thienylvinyl)-2-thienyl]hexane (synthesized by a known route [3]) were dissolved under an argon atmosphere in a 2:1 mixture of absolute DMF and ethanol. The reaction was started by the addition of lithium methanolate (1M in methanol), and the solution stirred and heated for 3 h. The end of the reaction was detected by using TLC ( $\text{CHCl}_3$  as solvent) where the product ran foremost at around  $R_f=0.5$ . In the case of incomplete reaction, more base (in 1 ml portions) had to be added to the solution. Purification was carried out by column chromatography (silica gel/ $\text{CHCl}_3$ ); the first fraction was the *E/Z*-mixture of the product. The *E/Z* mixture of isomers was transformed into pure all-*E* product by boiling the mixture with a catalytic amount of iodine in absolute toluene for about 8 h. Finally, the product was purified by extraction with absolute toluene or absolute xylene and dried over  $\text{P}_2\text{O}_5$ .

All-*E*-2,5-bis[5-{6-[5-(2-thienylvinyl)-2-thienyl]hexamethylene}-2-thienylvinyl]thiophene (**2a**) was synthesized from 4.20 g (10.88 mmol) of *E*-1-(5-formyl-2-thienyl)-6-[5-(2-thienylvinyl)-2-thienyl]hexane, 3.80 g

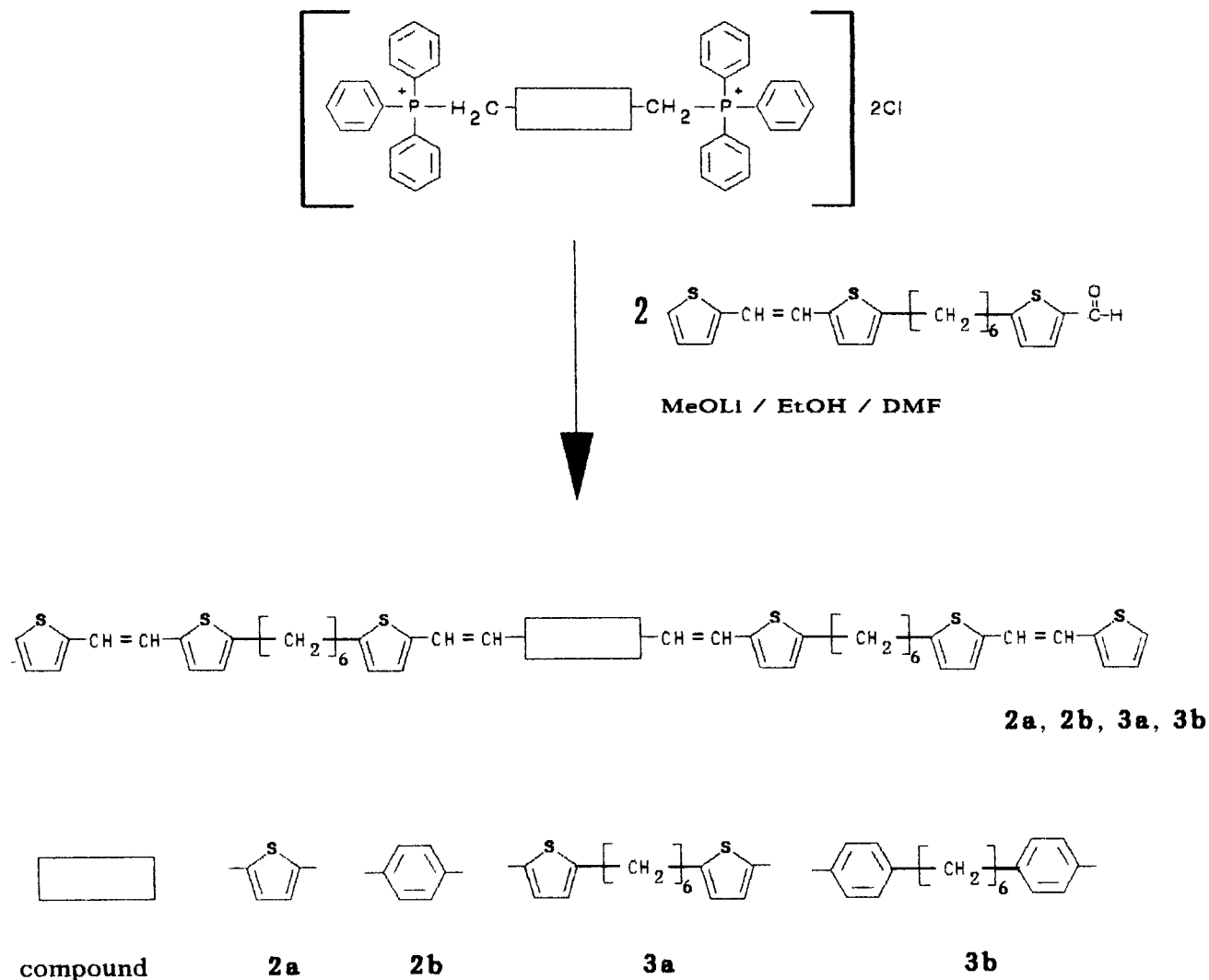


Figure 2. Synthetic routes to the 'oligomeric compounds' with three (**2a** and **2b**) and four (**3a** and **3b**) mesogenic groups.

(5.40 mmol) 2,5-bis(triphenylphosphoniomethyl)thiophene dichloride and 12 ml  $\text{CH}_3\text{OLi}$  (1M in methanol) in 20 ml of absolute ethanol and 40 ml of absolute DMF; the product was obtained as an orange coloured powder from toluene and then dry THF; m.p.  $130^\circ\text{C}$ ; yield 3.70 g (81 per cent);  $\text{C}_{48}\text{H}_{48}\text{S}_7$  (849.3): calculated C 67.88, H 5.70 per cent: found C 67.79, H 5.58 per cent. IR (KBr)  $\nu(\text{cm}^{-1}) = 3070$  (m)  $\nu(\text{C}-\text{H}_{\text{Ar,Th}})$ ; 3008 (m)  $\nu(\text{C}-\text{C}-\text{H}_{\text{trans}})$ ; 2925 (vs), 2850 (vs)  $\nu_{\text{sy}}(\text{CH}_2)$ ; 1612 (m)  $\nu(\text{C}-\text{C}_{\text{Ar-conj.}})$ ; 1462 (vs), 1430 (m)  $\delta_{\text{as}}(\text{CH}_2)$ , 1273 (m)  $\gamma(\text{C}-\text{C}-\text{H}_{\text{trans}})$ ; 990, 938 (vs)  $\omega(\text{C}-\text{C}-\text{H}_{\text{trans}})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta(\text{ppm}) = 7.15$  (d, 2H,  $J_{5m-4m} = 3.50$  Hz, Th- $\text{H}_{5m}$ ; 6.76–7.03 (m, 18H, Th- $\text{H}_3\text{H}_3'\text{H}_4$   $\text{H}_{3m}$   $\text{H}_{4m}$ , Vin- $\text{H}_1\text{H}_2\text{H}_1'\text{H}_2'$ ); 6.65 (d, 4H,  $J_{3-4} = J_{4'-3'} = 3.20$  Hz, Th- $\text{H}_{3s}$ , Th- $\text{H}_{4'}$ ); 2.79 (t, 8H,  $J = 8$  Hz,  $\text{H}_2\text{C}-\text{Th}$ ); 1.69 (m, 8H,  $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Th}$ ); 1.41 (m, 8H,  $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Th}$ ). MS ( $m/z$ ): 848 (100) ( $\text{M}^+$ ); 424 (4) ( $\text{M}^{2+}$ ); 740 (20) ( $\text{C}_{42}\text{H}_{44}\text{S}_6$ ) $^+$ ; 587 (11) ( $\text{C}_{33}\text{H}_{31}\text{S}_5$ ) $^+$ ; 574 (9) ( $\text{C}_{32}\text{H}_{20}\text{S}_5$ ) $^+$ ; 480 (24) ( $\text{C}_{27}\text{H}_{28}\text{S}_4$ ) $^+$ ;

466 (15) ( $\text{C}_{26}\text{H}_{26}\text{S}_4$ ) $^+$ ; 372 (4) ( $\text{C}_{21}\text{H}_{24}\text{S}_3$ ) $^+$ ; 327 (8) ( $\text{C}_{18}\text{H}_{15}\text{S}_3$ ) $^+$ ; 219 (22) ( $\text{C}_{12}\text{H}_{11}\text{S}_2$ ) $^+$ ; 205 (68) ( $\text{C}_{11}\text{H}_9\text{S}_2$ ) $^+$ .

Compound **2b** (a yellow powder) was synthesized by a similar method (see figure 2 and tables 1 and 2).

## 2.2. General synthesis of the 'oligomeric compounds' with four and six mesogenic groups (**3a**, **3b**, **4** and **5**) (see figure 2 and 3)

The synthesis of the oligomers **3a**, **3b**, **4** and **5** by the Wittig reaction and their purification were carried out similarly to **2a** and **2b**, as described above, except that the reactants were the bis Wittig salts 1,6-bis[4-(triphenylphosphoniomethyl)phenyl]hexane dichloride or 1,6-bis[5-(triphenylphosphoniomethyl)thienyl]hexane dichloride (prepared according to a method described previously [8]) and *E*-1-(5-formyl-2-thienyl)-6-[5-(2-thienylvinyl)-2-thienyl]hexane, *E*,*E*-1-[5-(5-formyl-2-thienylvinyl)-2-thienyl]-6-[5-(2-thienylvinyl)-2-thienyl]hexane

Table 1. Analytical data and yields for those compounds not described extensively in the Experimental section. Spectroscopic data obtained for these compounds correspond to the data for the examples given in the Experimental Section.

Compound	Formula (mol. mass)	Calculated/%		Found/%		Yield %
		C	H	C	H	
<b>2b</b>	C <sub>50</sub> H <sub>50</sub> S <sub>6</sub> (843·3)	71·21	5·98	71·18	5·75	80
<b>3a</b>	C <sub>58</sub> H <sub>62</sub> S <sub>8</sub> (1015·6)	68·59	6·15	68·38	5·88	68
<b>3b</b>	C <sub>62</sub> H <sub>66</sub> S <sub>6</sub> (1003·6)	74·20	6·63	74·07	6·46	43
<b>4</b>	C <sub>70</sub> H <sub>70</sub> S <sub>10</sub> (1232·0)	68·25	5·70	68·03	5·43	82

or **6**. The synthetic route to the first and second aldehyde is described elsewhere [3, 12]. The reaction solvent was purely absolute DMF. The transformation into the pure *E*-isomers was made by boiling the mixture with a catalytic amount of iodine in absolute xylene for about 8 h.

All-*E*-1,6-bis(5-{5-[5-(6-{5-[5-(2-thienylvinyl)-2-thienyl]hexamethylene}-2-thienylvinyl)-2-thienylvinyl]-2-thienyl}hexamethylene)-2-thienylvinyl]-2-thienylvinyl}hexane (**5**), was prepared from 200 mg (0·22 mmol) of **6**, 110 mg (0·11 mmol) of 1,6-bis[5-(triphenylphosphoniomethyl)thienyl]hexane dichloride and 2 ml of CH<sub>3</sub>OLi (1M in CH<sub>3</sub>OH) in 20 ml of absolute DMF; a red coloured powder was obtained after xylene extraction; m.p. 177°C, c.p. 196°C; yield 105 mg (49 per cent); C<sub>114</sub>H<sub>114</sub>S<sub>16</sub> (1997·2): calculated C 68·56, H 5·75 per cent: found C 66·42, H 4·83 per cent. IR (KBr)  $\nu(\text{cm}^{-1})=3083$  (m)  $\nu(\text{C-H}_{\text{Ar,Th}})$ ; 3008 (m)  $\nu(\text{C-C-H}_{\text{trans}})$ ; 2923 (vs), 2850 (s)  $\nu_{\text{sy}}(\text{CH}_2)$ ; 1610 (m)  $\nu(\text{C-C}_{\text{Ar-conj.}})$ ; 1462 (vs), 1430 (s)  $\delta_{\text{as}}(\text{CH}_2)$ , 1275 (m), 1235 (m)  $\gamma(\text{C-C-H}_{\text{trans}})$ ; 990, 935 (vs)  $\omega(\text{C-C-H}_{\text{trans}})$ . MS (*m/z*): 862 (0·40) (C<sub>49</sub>H<sub>50</sub>S<sub>7</sub>)<sup>+</sup>; 848 (0·60) (C<sub>48</sub>H<sub>48</sub>S<sub>7</sub>)<sup>+</sup>; 480 (34) (C<sub>27</sub>H<sub>28</sub>S<sub>4</sub>)<sup>+</sup>; 466 (15) (C<sub>26</sub>H<sub>26</sub>S<sub>4</sub>)<sup>+</sup>; 372 (20) (C<sub>21</sub>H<sub>24</sub>S<sub>3</sub>)<sup>+</sup>; 219 (69) (C<sub>12</sub>H<sub>11</sub>S<sub>2</sub>)<sup>+</sup>; 205 (80) (C<sub>11</sub>H<sub>9</sub>S<sub>2</sub>)<sup>+</sup>.

Compounds **3a** (light brown powder), **3b** (colourless powder) and **4** (red brown powder) were prepared analogously (see figures 2 and 3 and tables 1 and 2).

2.3. *Synthesis of all-E-2-{5-[5-(6-[5-(5-formyl-2-thienylvinyl)-2-thienyl]hexamethylene)-2-thienylvinyl]-2-thienylvinyl}-5-{5-[5-(6-[5-(2-thienylvinyl)-2-thienyl]hexamethylene)-2-thienylvinyl]-2-thienylvinyl}thiophene (**6**)*  
(see figure 3)

A mixture of 50·00 g of DMF, 1·30 g of POCl<sub>3</sub> and 1·70 g (2·00 mmol) of **2a** (suspension) was stirred for four days. During this procedure, the reaction mixture turned deep red. The resulting complex was decomposed by stirring the mixture for 1 h with a saturated aqueous solution of sodium acetate. The products formed were

separated by filtration, washed with water and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. Purification was carried out by column chromatography (silica gel/CHCl<sub>3</sub>); the first fraction was **2a** and the second fraction the *E/Z* mixture of **6**: yield 280 mg (16 per cent). The dialdehyde which is also formed cannot elute from the column; a red powder was obtained from toluene; m.p. 104°C, c.p. (dec.) 130°C; yield (unpurified) 110 mg (6 per cent). C<sub>49</sub>H<sub>48</sub>S<sub>7</sub>O (877·4): calculated C 67·08, H 5·51 per cent: found C 69·65, H 5·09 per cent. IR (KBr)  $\nu(\text{cm}^{-1})=3070$  (w)  $\nu(\text{C-H}_{\text{Ar,Th}})$ ; 3010 (m)  $\nu(\text{C-C-H}_{\text{trans}})$ ; 2920 (vs), 2850 (vs)  $\nu_{\text{sy}}(\text{CH}_2)$ ; 1660 (vs)  $\nu(\text{C-O})$ ; 1608 (s)  $\nu(\text{C-C}_{\text{Ar-conj.}})$ ; 1461 (vs), 1433 (vs)  $\delta_{\text{as}}(\text{CH}_2)$ , 1295 (m), 1235 (m)  $\gamma(\text{C-C-H}_{\text{trans}})$ ; 933 (vs)  $\omega(\text{C-C-H}_{\text{trans}})$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta(\text{ppm})=9\cdot83$  (s, 1H,  $-\text{CH}-\text{O}$ ); 7·63 (d, 1H,  $J_{4''-3''}=3\cdot50$  Hz, OHC-Th-H<sub>4''</sub>); 6·57–7·23 (m, 22H, aromatic protons); 2·78 (m, 8H,  $\text{H}_2\text{C}-\text{Th}$ ); 1·69 (m, 8H,  $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Th}$ ); 1·41 (m, 8H,  $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Th}$ ). MS (*m/z*): 876 (56) (M<sup>+</sup>); 438 (M<sup>2+</sup>); 768 (100) (C<sub>43</sub>H<sub>44</sub>S<sub>6</sub>O)<sup>+</sup>; 616 (22) (C<sub>35</sub>H<sub>36</sub>S<sub>5</sub>)<sup>+</sup>; 479 (11) (C<sub>27</sub>H<sub>27</sub>S<sub>4</sub>)<sup>+</sup>; 327 (25) (C<sub>18</sub>H<sub>15</sub>S<sub>3</sub>)<sup>+</sup>.

### 3. Results and discussion

The vinylenes were prepared by the Wittig reaction. The structures of all vinylenes were confirmed by their IR and MS data and, especially for the compounds **2a** and **6**, also by their <sup>1</sup>H NMR data. Representative examples are given in § 2. Moreover the position of the formyl (carbaldehyde) group in **6** was verified by an extensive comparison between the MS and the IR spectra of **2a**, **6** and other similar compounds which are described elsewhere [8, 12].

The 'oligomeric compound' **2a** with three mesogenic groups shows on cooling a monotropic liquid crystalline phase (see figure 4). This result is exceptional in so far as the 'monomeric compounds' containing one of the units *E,E*-2,5-bis(2-thienylvinyl)thiophene ( $\tau_3$ -unit) or *E*-1,2-bis(2-thienyl)ethylene ( $\tau_2$ -unit) do not form liquid crystalline phases. For example, *E,E*-1-(5-propyl-

Table 2. Thermodynamic properties of all-*E*-1,6-bis{5-[5-(2-thienylvinyl)-2-thienylvinyl]-2-thienyl}hexane (**1**), the 'oligomeric compounds' with three (**2a** and **2b**), four (**3a**, **3b** and **4**) and six (**5**) mesogenic groups, the aldehyde with three mesogenic groups (**6**), *E*-1-(5-propyl-2-thienyl)-2-(5-butyl-2-thienyl)ethylene (**7**), *E,E*-2,5-bis(5-butyl-2-thienylvinyl)thiophene(**8**), *E,E*-1,6-bis[5-(2-thienylvinyl)thienyl]hexane (**9**), all-*E*-1-{5-[5-(2-thienylvinyl)-2-thienylvinyl]-2-thienyl}-8-[5-(2-thienylvinyl)-2-thienyl]octane (**10**) and *E,E*-1,4-bis(5-butyl-2-thienylvinyl)benzene (**11**); on heating and cooling (in case of monotropic phases); dec. denotes decomposition.

Compound	Transition	Temperature/°C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$
<b>1</b> [9]	Cr <sub>1</sub> —Cr <sub>2</sub>	144	6.0	14.4
	Cr <sub>2</sub> —I	173	54.3	121.7
	I—N	160	2.4	5.5
	N—Cr	149		
<b>2a</b>	Cr <sub>1</sub> —Cr <sub>2</sub>	115	24.5	63.1
	Cr <sub>2</sub> —Cr <sub>3</sub>	118	8.9	22.8
	Cr <sub>3</sub> —Cr <sub>4</sub>	123	1.8	4.5
	Cr <sub>4</sub> —I	130	14.2	35.2
	I—N	127	3.3	8.3
	N—C	106		
<b>2b</b>	C—I	188	91.8	198.9
	I—C	177		
<b>3a</b>	C—I	172	110.6	248.2
	I—C	141		
<b>3b</b>	C <sub>1</sub> —C <sub>2</sub>	123	3.7	9.4
	C <sub>2</sub> —C <sub>3</sub>	146	19.6	46.8
	C <sub>3</sub> —I	161	71.9	165.3
	I—C	151		
<b>4</b>	C <sub>1</sub> —C <sub>2</sub>	127	8.0	19.9
	C <sub>2</sub> —C <sub>3</sub>	171	78.2	175.9
	C <sub>3</sub> —I	176	6.2	13.8
	I—N	166	5.4	12.3
	N—C	135		
<b>5</b>	C—N	177	75.0	166.6
	N—I	196	9.2	19.6
	I—N	196		
	N—C	163		
<b>6</b>	C—N	104	39.5	104.5
	N—I/dec	130	(4.3)	(10.6)
<b>7</b> [13]	C—I	29	20.5	67.9
<b>8</b> [13]	C—I	88	30.4	84.2
<b>9</b> [9]	C—I	129	51.3	127.3
<b>10</b> [14]	C—I	138		
<b>11</b> [13]	C—S <sub>B</sub>	91	14.8	40.7
	S <sub>B</sub> —I	180	17.7	39.1

2-thienyl)-2-(5-butyl-2-thienyl)ethylene (**7**, see figure 5, [13]) and *E,E*-2,5-bis(5-butyl-2-thienylvinyl)thiophene (**8**, see figure 5, [13]) melt directly to the isotropic phase (see table 2). Also even a 'dimerization' of the  $\tau_3$ - and the  $\tau_2$ -units does not generally induce a mesophase. Although **1** melts with a mesophase, the 'dimeric compounds' *E,E*-1,6-bis[5-(2-thienylvinyl)thienyl]hexane (**9**, see figure 5, [9]), with two  $\tau_2$ -units separated by a hexamethylene spacer, or all-*E*-1-{5-[5-(2-thienylvinyl)-2-thienylvinyl]-2-thienyl}-8-[5-(2-thienylvinyl)-2-thienyl]octane (**10**, see figure 5, [14]), with one  $\tau_2$ - and one  $\tau_3$ -

unit separated by an octamethylene spacer, do not form liquid crystalline phases (see table 2). But as we can see, in harmony with the 'oligomeric compounds' with four mesogenic groups connected by hexamethylene spacers, the compounds only have liquid crystalline phases if the  $\tau_3$ -unit is in the chain. So we observe no mesophase for **3a** with four  $\tau_2$ -units in the chain, but for **4** with two  $\tau_3$ - and two  $\tau_2$ -units a monotropic mesophase occurs (see table 2). Moreover, the mesophase of the 'oligomeric compounds' is stabilized with increasing numbers of  $\tau_3$ -units in the chain. Specifically, **2a** and **4** have a

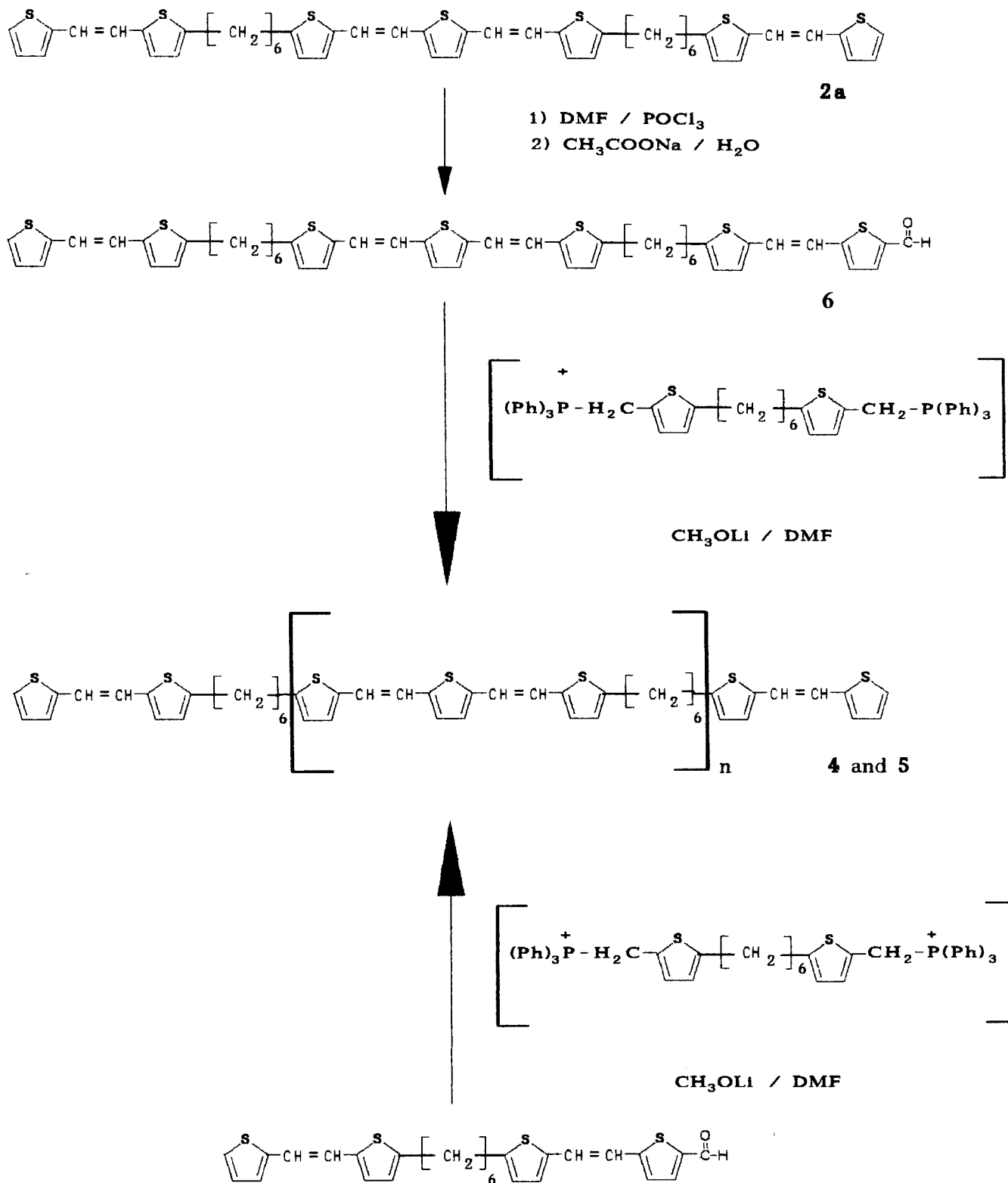


Figure 3. Synthetic routes to the 'oligomeric compound' with three mesogenic groups and a carbaldehyde group (**6**) and to the compounds with four (**4**;  $n=2$ ) and six (**5**;  $n=4$ ) mesogenic groups.

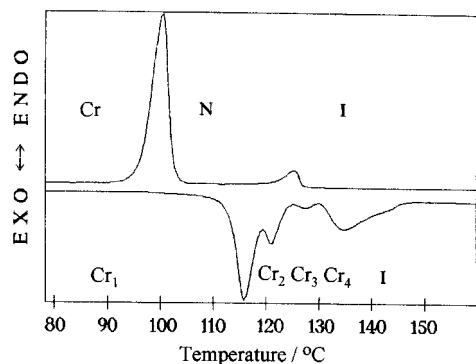


Figure 4. DSC scan of the 'oligomeric compound' **2a** (second heating cycle).

monotropic phase, and **5** has an enantiotropic liquid crystalline phase. Polarizing microscopy of the compounds indicates only a nematic phase for all the liquid crystalline compounds described here.

Comparison of the temperature and the entropy,  $\Delta S$ , at the N-I or I-N transition between the corresponding 'oligomeric compounds' **2a**, **4** and **5** shows an increase for  $\Delta S$  from **2a** to **4** to **5** (see table 2). Although these transition entropies of these compounds were sometimes detected while cooling (**2a** and **4**) and sometimes while heating (**5**), we find by normalization of the given data, 2.77 (**2a**), 3.08 (**4**) and 3.27 (**5**)  $\text{J K}^{-1} \text{mol}^{-1}$  per polymer

unit, that  $\Delta S_{\text{N-I}}$  is increasing weakly with increasing chain length of the 'oligomeric compounds'. This typical trend to a higher order in the mesophase with growing chain length is well known from the literature [5, 7]. Nevertheless, the values which were found for these 'oligomeric compounds' were small in comparison with those given in the literature.

In continuation of our previous work [8], the aim here was again to predict liquid crystalline behaviour for poly-[2,5-thienylenevinylene-2,5-thienylenevinylene-2,5-thienylenehexamethylene] (see figure 1). This prediction seems to be feasible since the members of the homologous series **2a**, **4** and **5** show nematic phases. But, as we know from our own experience, in contrast to this prediction, the corresponding polymer (see figure 1) melts without forming a mesophase because the synthesis of this polymer, which can be made by different methods, is still not satisfactory. Therefore liquid crystalline polymers from thiophene systems are known up to this moment only for side chain polymers [15, 16].

It has been shown that the possibility of formation of a mesophase by a given compound is in principle enhanced by exchanging a thiophene for a benzene ring system [8]. Quite a different result was obtained for the synthesized 'oligomeric compounds'. Neither **2b**, with three mesogenic groups and containing a benzene

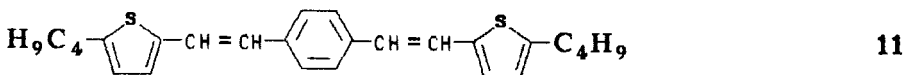
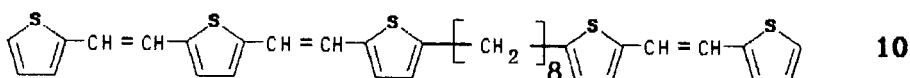
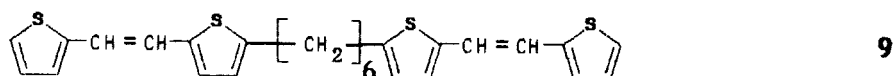
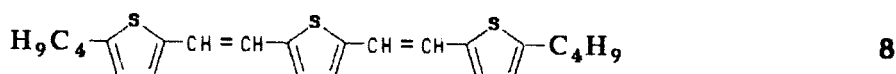
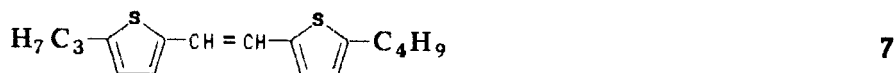


Figure 5. Reference compounds **7-11** relevant to the new compounds **1-5**.



system, nor **3b**, with four mesogenic groups and containing benzene systems, form liquid crystalline phases. In contrast with **2b**, the 'monomeric compound' *E,E*-1,4-bis(5-butyl-2-thienylvinyl)benzene (**11**, see figure 5, [13]) melts forming a broad range mesophase (see table 2). Although the structural difference between **11** and **2b** is similar to that between **8** and **2a**, the change in the thermal behaviour from **11** to **2b** is the inverse of the change in the thermal behaviour from **8** to **2a**. One reason may be the structural difference between the mesogenic groups in the chains of **2a** and **2b**. Because the structural difference between the mesogenic groups in **2a** ( $\tau_3$ -unit and  $\tau_2$ -unit) is insignificant in comparison with the structural difference between the mesogenic groups in **2b** (*E,E*-1,4-bis(2-thienylvinyl)benzene and  $\tau_2$ -unit), the formation of mesophases is more probable for **2a**. However, this higher degree of difference in the mesogenic groups in the chains causes polycrystallinity of the compounds. Therefore for some compounds we observed crystal-crystal transformations on heating the samples (see table 2 and figure 5).

Obviously, the substitution of the formyl group at the terminal position of **2a** leads to a broad range mesophase for the resulting compound **6**. A similar tendency has been shown for low molecular mass model compounds with thiophene and/or benzene ring systems in a previous paper [12]. However, the formyl group does not greatly affect the melting point of **2a**. It seems therefore that the formyl group as the end group of corresponding polymers should enhance the liquid crystalline phase

behaviour of those polymers. A comparison between the compounds shows that only **2a** and **6** contain one  $\tau_3$ -unit and form liquid crystalline phases.

### References

- [1] CAI, R., and SAMULSKI, E. T., 1991, *Liq. Cryst.*, **9**, 617.
- [2] KOBMEHL, G., HOPPE, F. D., and HIRSCH, B., 1993, *Z. Naturforsch.*, **48b**, 826.
- [3] KOBMEHL, G., and HOPPE, F. D., 1993, *Z. Naturforsch.*, **48b**, 1807.
- [4] GRIFFIN, A. C., and BRITT, T. R., 1981, *J. Am. chem. Soc.*, **103**, 4957.
- [5] FRADET, A., and HEITZ, W., 1987, *Makromol. Chem.*, **188**, 1233.
- [6] ATTARD, G. S., and IMRIE, C. T., 1989, *Liq. Cryst.*, **6**, 387.
- [7] GRIFFIN, A. C., SULLIVAN, S. L., and HUGHES, W. E., 1988, *Liq. Cryst.*, **4**, 677.
- [8] HOPPE, F. D., and KOBMEHL, G., 1996, *Liq. Cryst.*, **21**, 255.
- [9] KOBMEHL, G., and HOPPE, F. D., 1994, *Mol. Cryst. liq. Cryst.*, **257**, 169.
- [10] KOBMEHL, G., HARTEL, M., and MANECKE, G., 1970, *Makromol. Chem.*, **131**, 15.
- [11] FRIEDRICH, K., and HENNING, H. G., 1959, *Chem. Ber.*, **92**, 2756.
- [12] KOBMEHL, G., and HOPPE, F. D., 1993, *Liq. Cryst.*, **15**, 383.
- [13] KOBMEHL, G., and BUDWILL, D., 1985, *Z. Naturforsch.*, **40b**, 1199.
- [14] MOORMANN, P., 1993, Diploma Thesis, Freie Universität Berlin.
- [15] KOBMEHL, G., and PITHARDT, C., 1992, *Z. Naturforsch.*, **47b**, 567.
- [16] KOBMEHL, G., and LABAHN, B., 1996, *Z. Naturforsch.*, **51b**, 286.