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Liquid Crystals

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Liquid crystalline compounds in the thiophene series†

X. Synthesis and characterization of liquid crystalline vinylenes with thiophene and benzene moieties

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Compounds with two mesogenic groups connected by a hexamethylene chain and terminal butyl groups were synthesized by the Wittig reaction from the newly described bis-Wittig salts 1,6-bis[4-(triphenylphosphoniomethyl)benzyl]hexane dichloride (**1**) or 1,6-bis[5-(triphenylphosphoniomethyl)-2-thienyl]hexane dibromide (**2**) and various aromatic aldehydes. All derivatives containing two or three vinylenes and three or four aromatic rings in each mesogenic group have liquid crystalline phases. These aromatic rings are 1,4-disubstituted benzene and/or 2,5-disubstituted thiophene rings. The transition temperatures of these compounds increase with increasing numbers of benzene rings in each core. All-*E*-1,6-bis{4-[4-(4-butylstyryl)styryl]phenyl}hexane (**3**) (which is one of the few examples of conventional rod-like liquid crystalline materials without any hetero-atoms) has the highest transition temperatures compared to all the other substances. The formation of smectic phases of a high order is dependent on the number of thiophene rings in each core. Therefore compounds with two thiophene rings and one benzene system in each core (**8**, **14**, **15** and **16**) normally have only nematic phases. The only exception is all-*E*-1,6-bis{4-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]phenyl}hexane (**7**) which shows a smectic phase both on heating and cooling the sample. Most of the compounds with two benzene rings and one thiophene ring form smectic phases. It is obvious that the formation of a smectic phase is more probable if the mesogenic group is connected to the hexamethylene spacer by a benzene than by a thiophene system (see for example **4** and **7**). For compounds **3** and **6**, X-ray studies have been made. The compounds with four aromatic rings in each core show only nematic phases. They decompose either in the mesophase or the isotropic phase.

1. Introduction

The synthesis and characterization of liquid crystalline compounds with two mesogenic groups attached at the ends to a flexible group ('dimeric compounds', see figure 1) have been the subject of several publications [1–3]. In most cases the aromatic system in the mesogenic groups has been the benzene ring. Previously, we have demonstrated that such compounds with thiophene

rings in the core also have liquid crystalline phases [4–6]. For example, all-*E*-1,6-bis{5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]-2-thienyl}hexane (**9**) [6] with three thiophene rings in each core melts without decomposition to a nematic phase (see table 1). Nevertheless, the problem in designing thermotropic compounds with thiophene rings is that the liquid crystalline phases of these compounds are often narrow and normally of only low order. Moreover, compounds with two mesogenic groups are often in danger of decomposing in the mesophase or isotropic phase. Their melting points are usually higher than those with only one core. For example all-*E*-1,6-bis{5-[5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]-2-thienyl]hexane (**13**) [6] with two mesogenic groups and four thiophene rings in each core (i.e. eight thiophene rings in all) decomposes in the mesophase, in contrast to 2-(5-butyl-2-thienylvinyl)-5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]thiophene (**20**, see table 2) with only one mesogenic group. Also, the compounds tend to decompose more with an

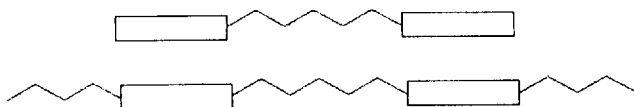


Figure 1. Schematic formulae for compounds containing two mesogenic groups with or without terminal alkyl chains (dimeric compounds).

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† Part 9, ref. [6].

increasing number of thiophene rings in the cores independent of transition temperature. Therefore only the liquid crystalline substance **13** decomposes in the mesophase (see tables 1 and 2) although the melting points of **9** (with three thiophene rings in each core) and **13** (with four thiophene systems in each core) are comparable.

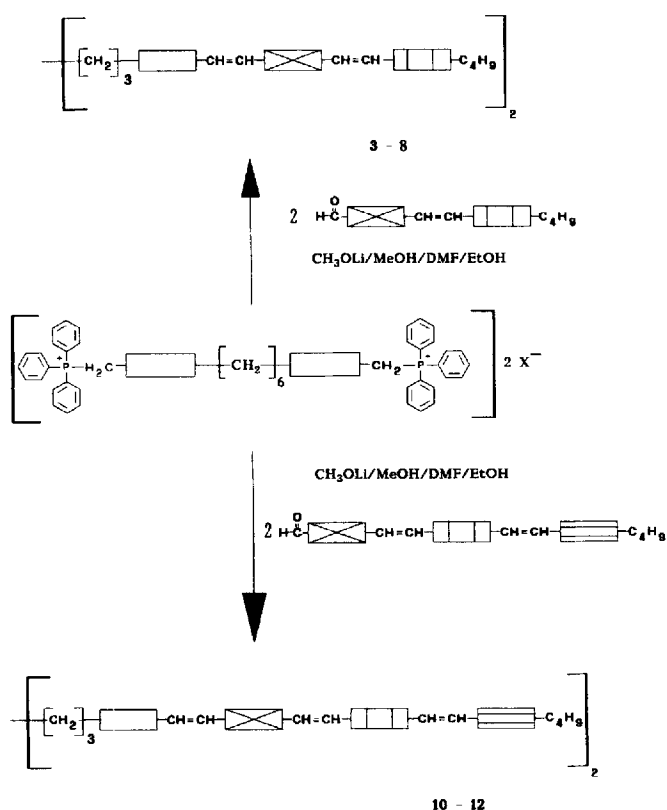
In this paper we wish to give a more systematic report of compounds with two mesogenic groups, linked by a spacer, which have both thiophene *and* benzene rings in the cores. Our studies started with all-*E*-1,6-bis{4-[4-(4-styryl)-4-styryl]-4-phenyl}hexane (**3**) with no thiophene rings. The benzene rings were replaced one by one by thiophene rings. We have also varied the relative position of the aromatic rings in each core (see figure 2) for compounds with a given combination of thiophene and benzene rings in each core. Moreover, we report on some compounds with four aromatic rings in each core.

2. Synthesis

The vinylenes compounds ('dimeric compounds') were prepared by the Wittig reaction with triphenyl(4-butylbenzyl)phosphonium bromide [7] or the bis-Wittig salts **1** or **2** and various aromatic monoaldehydes or the dialdehydes 1,6-bis(5-formyl-2-thienyl)hexane or α,ω -bis[5-(5-formyl-2-thienylvinyl)-2-thienyl]hexane (see figures 2 and 3). As shown in figure 4 the bis-Wittig salts 1,6-bis[4-(triphenylphosphoniomethyl)phenyl]hexane dichloride (**1**) and 1,6-bis[5-(triphenylphosphoniomethyl)-2-thienyl]hexane dibromide (**2**) were formed during the reaction of 1,6-bis(4-chloromethylphenyl)hexane or 1,6-bis(5-bromomethyl-2-thienyl)hexane with triphenylphosphane in absolute toluene. The synthesis of 1,6-bis(5-bromomethyl-2-thienyl)hexane from the corresponding dihydroxy compound (see figure 4) follows a method described by Koßmehl *et al.* [8]. 1,6-Bis(5-hydroxymethyl-2-thienyl)hexane

Table 1. Thermodynamic properties of the compounds **3–8** and all-*E*-1,6-bis{5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]-2-thienyl}hexane (**9**) on heating and cooling; ^a=verified by cooling; ^b=verified by microscopy; ^c=verified by gauss-fit of the DSC curve; dec.=decomposition.

Compound	Transition	Temperature/°C	$\Delta H_h/\text{kJ mol}^{-1}$	$\Delta S_h/\text{JK}^{-1} \text{mol}^{-1}$
3	C ₃ -C ₂	200	4.8	10.2
			2.2 ^a	3.6 ^a
	C ₂ -C ₁	241	2.7	5.3
	C ₁ -S ₁	331	22.7	37.5
	S ₁ -S _A	338	28.9	47.2
	S _A -N	354 ^b		
	N-I/dec.	387	2.6 ^a	5.2 ^a
4	C ₂ -C ₁	181	2.5	5.4
	C ₁ -N	263	31.1	57.0
	N-I/dec.	293	(4.8)	(15.8)
5	C ₃ -C ₂	236	0.9	1.8
	C ₂ -C ₁	282	9.6	17.3
	C ₁ -S ₃	291	3.6	6.4
	S ₃ -S ₂	302	16.7	29.0
	S ₂ -S ₁	315	(5.0) ^c	(8.5) ^c
	S ₁ -N	335	(6.0) ^c	(9.9) ^c
	N-I/dec.	346		
6	C ₂ -C ₁	193	4.0	8.6
	C ₁ -S _A	203	44.8	94.1
	S _A -N	212		
	N-I	282	7.0	12.6
7	C ₂ -C ₁	145	21.5	51.4
	C ₁ -S ₁	156	32.6	76.0
	S ₁ -N	186 ^b		
	N-I/dec.	225	(6.2)	(2.4)
8	C ₂ -C ₁	201	7.28	15.4
	C ₁ -N	229	43.92	87.5
	N-I	250	1.91	3.7
9 [6]	C-N	154	68.19	159.7
	N-I	169	3.3	7.5



was prepared by a known method [9]. 1,6-Bis(4-chloromethylphenyl)hexane was synthesized from 1,6-diphenylhexane according to Jaunin and Baer [10]. The synthesis of the starting aldehydes has been described extensively in previous papers or by Baldwin *et al.* [4–6 or 11].

The structures of the vinylenes 3–8, 10–12 and 14–16 were confirmed by the ^1H NMR, IR, UV and MS data. The spectra of all compounds contained the expected information on the typical structural units present. Representative examples are given in the experimental section; see also table 3.

3. Results and discussion

The thermal behaviour of the compounds as determined by DSC and polarizing microscopy is given in tables 1 and 2. Independently of the number of thiophene rings in each core, all derivatives are liquid crystalline. The temperature ranges of the mesophases decrease with increasing numbers of thiophene rings in each core (see table 1). Therefore in the substance-class with three aromatic rings in each core, 3, with exclusively benzene rings, shows, upon cooling the sample, extended mesophases, whereas 9, with exclusively thiophene rings, has only a short range nematic phase. In contrast to the low molecular weight model compounds with only one core and similar mesogenic groups, the ‘dimeric compounds’

compound				
3				—
4				—
5				—
6				—
7				—
8				—
9 [6]				—
10				
11				
12				
13 [6]				

Figure 2. Synthetic routes for the vinylene compounds 3–8 and 10–12.

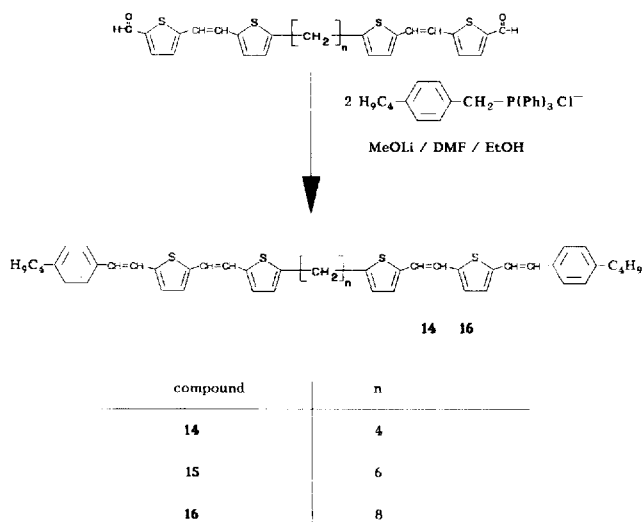


Figure 3. Synthetic route for the compounds 14–16.

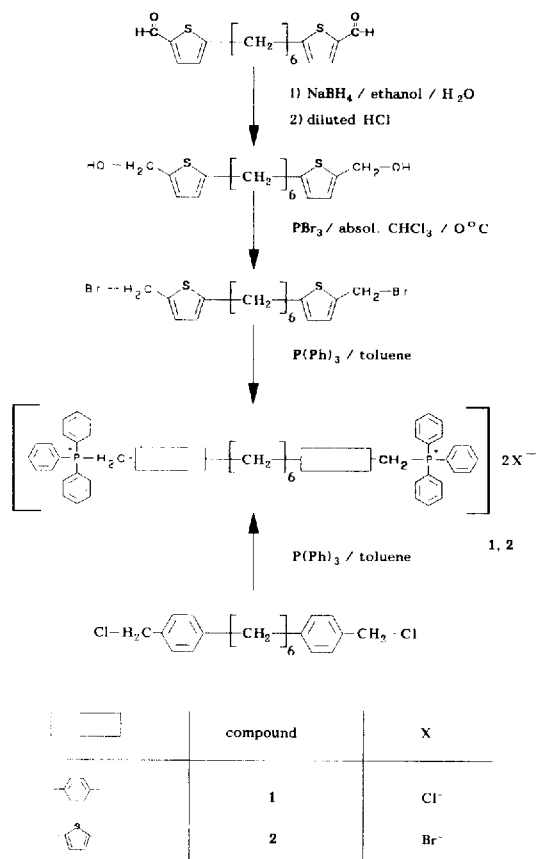


Figure 4. Synthetic routes for the bis-Wittig salts 1 and 2.

often decompose in the isotropic liquid or the meso-phase. Therefore the temperature range of the meso-phases is often limited by the decomposition temperature of the compounds (see 3, 4, 5 and 7 in table 1). Moreover,

the decomposition temperatures are to some degree dependent on the position of the benzene and thiophene rings in the cores and the transition temperatures of the compound. Therefore, on heating the samples, 6 and 12 are thermally stable over a wide temperature range because here the butyl group and hexamethylene chain are not directly bound to thiophene rings and the numbers of thiophene rings in the cores are low. In particular, a comparison between compounds 6–8 and 10–13 shows that the compounds with thiophene rings have higher thermal stabilities if, in the cores, the thiophene ring, which is an electron rich aromatic ring, is directly bound via a vinylene group to a benzene ring, which is an electron-deficient aromatic ring. Therefore compounds having regions with a high degree of electron excess in the cores decompose at even lower temperatures. Areas with an electron excess are more probable if one thiophene ring is directly bound via a vinylene group to a second thiophene rings and to an alkyl or alkylene group. Those conditions are found in 7, 10, 11 and 13, and, for example 7 decomposes quite soon above its isotropic transition point, although the isotropization temperature of this compound is low in comparison to the transitions points for compounds 6 and 8.

Only 9, 14, 15 and 16 melt without decomposition due to a well defined balance between the areas of electron excess in the mesogenic groups and the comparable low transition temperatures. Nevertheless, not all compounds are thermally stable on prolonged heating. Most of the compounds decompose rapidly in the heating stage of the microscope if they are heated to a temperature higher than 250°C. Therefore the transition temperatures which are listed in tables 1 and 2 were taken direct from the DSC curves of the substances.

The melting points of these compounds are depressed by increasing numbers of thiophene rings in the cores. In particular, 3 (with no hetero-atoms in the core!) melts far above 300°C, in contrast to all the other compounds, whereas 9 shows all its transition temperatures far below 200°C. The relative positioning of the aromatic rings in each core is most important in determining the liquid crystalline behaviour of the compounds. Therefore compounds have a high tendency to form smectic phases on heating the samples when the hexamethylene moiety is directly bound to the mesogenic groups via benzene rings. (3 and 5–7). Similar results for 'dimeric compounds' do not exist in the literature because most systematic studies of 'dimeric compounds' have been made by variations of the alkylene spacer [12] or substituent alkyl groups [13]. A short comparison between 'dimeric and monomeric compounds' with the same core elucidates the results described. The 'dimeric compound' 6 and the 'monomeric compound' 18 have the same core, namely 2,5-distyrylthiophene. But as

Table 2. Thermodynamic properties of the compounds **10**, **11**, **12**, all-*E*-1,6-bis{5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]-2-thienylvinyl}{-2-thienyl}hexane (**13**), **14**, **15**, **16**, all-*E*-1,4-bis(5-butyl-2-thienylvinyl)benzene (**17**), all-*E*-2,5-bis(4-butylstyryl)thiophene (**18**) and all-*E*-2-(2-butyl-5-thienylvinyl)-5-(4-butylstyryl)thiophene (**19**); 2-(5-butyl-2-thienylvinyl)-5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]thiophene (**20**) on heating and cooling; ^a=verified by cooling; ^b=verified by microscopy; dec. = decomposition.

Compound	Transition	Temperature/°C	$\Delta H_h/\text{kJ mol}^{-1}$	$\Delta S_h/\text{JK}^{-1} \text{mol}^{-1}$
10	C-N/dec.	244	72.9	141.0
11	C ₂ -C ₁	176	4.4	9.8
	C ₁ -N/dec.	221	47.3	95.7
12	C-N	279	86.1	156.0
	N-I/dec.	349	9.5	15.3
13 [6]	C ₂ -C ₁	164	3.1	7.0
	C ₁ -N/dec.	197	60.5	128.6
14	C-N	171	51.3	115.5
	N-I	240	2.8	5.5
15	C ₂ -C ₁	164	43.5	99.5
	C ₁ -N	172	21.4	48.1
	N-I	195	2.7	5.8
16	C-N	198	90.21	191.5
	N-I	203 ^b	5.1 ^a	10.7 ^a
17 [18]	C-S ₁	91	14.8	40.7
	S ₁ -I	180	17.7	39.1
18 [18]	C-N	141	20.1	48.4
	N-I	171	0.4	0.9
19 [5]	C-I	107	20.2	53.2
20 [17]			0.54 ^a	1.4 ^a
	C-N	158	30.2	70.1
	N-I	199	0.4	0.9

shown in tables 1 and 2, although **18** melts at a lower temperature, only **6** has a smectic phase. This phenomenon must surely be explained by the fact that, in contrast to **18**, in **6** two cores are associated via an alkylene chain. As shown by Buglione *et al.* [14] this combination of two mesogenic groups normally enhances the probability of formation of higher ordered phases. Hence, the dimerization of two cores seems also to be the reason for the formation of the more extended nematic phase of **6** than that of **18**. But a comparison between the 'dimeric and monomeric compounds' **8** and **17** having the same core [1,4-bis(2-thienylvinyl)benzene] leads to a more expanded view. Thus, **8** (with two cores) in contrast to **17** (with one core) shows a nematic phase only over a small temperature range on heating the sample. Moreover, in disagreement with the results reported for **6** and **18**, only the 'monomeric compound' **17** has a smectic phase over a wide temperature range. A comparison between the structures of compounds **6**, **8**, **17** and **18** therefore leads to the following general conclusion. The liquid crystalline behaviour of 'dimeric compounds' with thiophene rings is mostly influenced by the inner aromatic ring which is directly bound to

the alkylene spacer. The liquid crystalline behaviour of 'monomeric compounds' with thiophene rings is more dependent on the aromatic ring which is in the centre of the mesogenic group.

Compounds **18** and **19** with a thiophene ring in the centre of the core melt to form exclusively nematic phases, whereas **17** with a benzene ring in the middle of the core melts to yield an extended smectic phase. Moreover, the thermal behaviour of the series **3-6** can also be easily explained in the same way. The replacement of one benzene ring or one thiophene ring in **3** changes mainly the mesophases formed by **4** (see figure 2). In contrast to all the other compounds described, **5** (see figure 2) melts in a similar way to **3**. In **4** the thiophene ring in each core is nearest to the hexamethylene chain, whereas in **5** the thiophene ring in each core is furthest from the chain. The liquid crystalline behaviour of **6** is therefore of an intermediate nature between those of **4** and **5** because the thiophene ring is in the middle of each core (see figure 2 and table 1). Replacing one thiophene ring in **9** by a benzene ring in each core leads to the compounds **7**, **15** and **8**. A comparison between the thermal behaviour of these

compounds is in good agreement with the results reported above. For example, within the series **9**, **7**, **15** and **8**, the compounds **7** and **9** (on heating) show the most different thermal behaviour, because the benzene rings in **7** are in the most central position (see figure 2).

A second replacement of a benzene (thiophene) by a thiophene (benzene) ring also affects the thermal behaviour of the compounds significantly if the substitution of the aromatic ring is made near to the hexamethylene central linkage. For example, by replacing a benzene ring by a thiophene ring in **5**, the thermal behaviour is more influenced for the resulting compound **8** than for **7** (see figure 2 and table 1). Especially for **7**, a comparison between the 'dimeric compounds' **7** and **15** and the 'monomeric compound' **19** is important. In contrast to **15** and **19**, only in **7** is the arrangement of thiophene and benzene rings in the 'dimeric compound' well suited for melting with formation of extended mesophases. Moreover in the series **7**, **15** and **19**, only **7** shows a smectic phase on heating and cooling the sample.

The tendencies in the thermal behaviour of the compounds reported above often agree with those observed for 'dimeric compounds' described in the literature [15]. For example, it is well known that the transition entropies ΔS_{N-I} at the transition from the nematic to the isotropic phase increase from monomeric to dimeric compound. As shown for a few examples in table 4, the dimerisation of the cores drastically increases the transition entropies, and the 'dimeric compounds' **6** and **7**

have high ΔS_{N-I} values. Therefore, consistent with the foregoing results, these 'dimeric compounds' which are of the highest order in their nematic phases have the cores connected directly via a benzene ring to the alkylene central linkage. On the other hand, the small ΔS_{N-I} value found for **15** is consistent with the relatively small temperature range of the nematic phase.

In accordance with studies done by Griffin and Britt [16], Emsley *et al.* [3] and our own measurements [4] for similar derivatives, the temperature ranges of the mesophases of the 'dimeric compounds' **14**, **15** and **16** increase with decreasing numbers of methylene groups in the spacer (see table 2) because the intramolecular coupling strength decreases with increasing chain length.

The results from X-ray measurements (Kratky camera/CuK α) of **3** at different temperatures up to 295°C are listed in table 5. The X-ray diffraction patterns show different orders ($n=1, 2, 3, 4$) of one reflection (orthogonal layer structure) at each temperature. The layer distance which is detected at 40°C (see table 5) is similar to the molecular length of **3** in its fully stretched conformation. The decrease in the layer distance with increasing temperature of the sample is caused by the changing angle between the mesogenic groups and the director of the phase. Moreover, this X-ray analysis at different temperatures shows a hysteresis effect during heating and cooling of the sample of **3**. Similar patterns are detected at 200°C during heating and at 100°C during cooling. These data (together with the results

Table 3. Analytical data and yields for the compounds not described extensively in the Exp. Part. Their spectroscopic data correspond to those for the examples given in the Exp. Part.

Compound	Formula (molecular weight)	Calculated/per cent		Found/per cent		Yield/per cent
		C	H	C	H	
4	C ₅₄ H ₅₈ S ₂ (771.2)	84.10	7.58	84.05	7.63	65
5	C ₅₄ H ₅₈ S ₂ (771.2)	84.10	7.58	84.13	7.55	33
6	C ₅₄ H ₅₈ S ₂ (771.2)	84.10	7.58	83.92	7.66	88
7	C ₅₀ H ₅₄ S ₄ (783.2)	76.68	6.95	76.71	6.99	98
8	C ₅₀ H ₅₄ S ₄ (783.2)	76.68	6.95	76.75	6.99	46
10	C ₆₂ H ₆₂ S ₆ (999.6)	74.50	6.25	74.60	6.31	46
11	C ₆₂ H ₆₂ S ₆ (999.6)	74.50	6.25	74.39	6.18	60
12	C ₆₆ H ₆₆ S ₄ (987.5)	80.28	6.74	80.31	6.70	73
15	C ₅₀ H ₅₄ S ₄ (783.2)	76.68	6.95	76.73	6.73	70
16	C ₅₂ H ₅₈ S ₄ (811.3)	76.99	7.21	76.87	7.21	88

Table 4. ΔS_{N-I} -values for the monomeric compounds **18**, **19** and all-*E*-1,2-bis[5-(4-butylstyryl)-2-thienyl]ethylene (**21**) and the dimeric compounds **6**, **7**, **15** and **12**; in parenthesis the ΔS_{N-I} -values for each half of the dimeric compound.

Monomeric compounds	$\Delta S_{N-I}/JK^{-1} \text{ mol}^{-1}$	Dimeric compounds	$\Delta S_{N-I}/JK^{-1} \text{ mol}^{-1}$
18	0.7	6	12.6 (6.3)
19	0.54	7	12.4 (6.2)
		15	5.8 (2.9)
21 [17]	0.7	12	15.3 (7.65)

Table 5. Layer distance in **3** at different temperatures (Kratky camera/CuK α /detector: proportional counter).

Temperature/ $^{\circ}\text{C}$	Layer distance/ \AA	Orders
40	48.2	4
200	46.1	4
295	43.6	4
200	43.9	5
100	47.0	4
30	48.2	4

from microscopy) confirm that at 137 $^{\circ}\text{C}$ a very highly ordered mesophase changes on cooling to the crystalline phase. But the transformation of the layer distance on cooling the sample from 100 $^{\circ}\text{C}$ to 30 $^{\circ}\text{C}$ (see table 5) can only be verified by X-ray measurements. Although the layer distances change drastically from 100 to 30 $^{\circ}\text{C}$, no usual behaviour can be observed by DSC and microscopy.

Finally, we compared the X-ray diffraction patterns observed at 40 $^{\circ}\text{C}$ for compounds **3** and **6**. The X-ray diffraction pattern of **6** at 40 $^{\circ}\text{C}$ also shows different orders of one reflection and the layer distances of both compounds differ only marginally (for **6** 47.2 \AA). Nevertheless, the different intensities of the reflections of both patterns indicate different structures for the mesogenic groups, the flexible central linkage and the flexible end groups in the crystals.

4. Experimental

4.1. Analyses

The IR spectra were measured using a Perkin-Elmer 580B spectrometer. The ^1H NMR spectra were measured at 270 MHz using a Bruker WH 270 instrument and the chemical shifts are given relative to tetramethylsilane (TMS). The mass spectra were measured with a Varian MAT-112-S instrument. The elemental analyses (table 1) were carried out using a Perkin-Elmer Recorder 56. The phase transitions were determined using a Heraeus TA 500 instrument with a scanning speed of $10 \text{ K} \times \text{min}^{-1}$ and sometimes $5 \text{ K} \times \text{min}^{-1}$ 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 and by ^1H NMR spectra in the case of soluble derivatives.

4.2. Synthesis of

1,6-bis[4-(triphenylphosphoniomethyl)phenyl]hexane dichloride (**1**)

1,6-Bis(4-chloromethylphenyl)hexane (25.0 g, 0.075 mol) and triphenylphosphane (44 g, 0.17 mol) were dissolved under an argon atmosphere in absolute toluene (400 ml). For the formation of **1**, the reaction mixture was heated under reflux for 24 h. The precipitated products from the (cooled) reaction mixtures were filtered off, washed with cooled diethyl ether, recrystallized from ethanol and dried over P_2O_5 for one week. Yield 27.30 g (56 per cent); m.p. 345 $^{\circ}\text{C}$; $\text{C}_{56}\text{H}_{54}\text{P}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (877.9) calculated, C 76.61, H 6.43; found C 76.72, H 6.70 per cent; IR (KBr) $\nu(\text{cm}^{-1})$ = 3050 (m), 3010 (m) $\nu(\text{Ar}-\text{C}-\text{H})$; 2925 (s), 2855 (s), 2777 (m) $\nu(\text{C}-\text{H})$; 1435 (vs) $\nu(\text{P}-\text{Ar})$; ^1H NMR (CDCl_3) $\delta(\text{ppm})$ = 7.50–7.83 (m, 30H, $\text{P}(\text{Ph}-\text{H}_2\text{H}_3\text{H}_4\text{H}_5\text{H}_6)$); 6.97 (d, 4H, $J_{3,2} = J_{5,6} = 6.20 \text{ Hz}$, $\text{Ar}-\text{H}_3\text{H}_5$); 6.83 (d, 4H, $J_{2,3} = J_{6,5} = 6.20 \text{ Hz}$, $\text{Ar}-\text{H}_2\text{H}_6$); 5.38 (d, 4H, $J_{\text{P-H}} = 15.70 \text{ Hz}$, $\text{Ar}-\text{CH}_2-\text{P}(\text{Ph})_3$); 2.47 (t, 4H, $J = 5.40 \text{ Hz}$, $\text{H}_2\text{C}-\text{Ar}$); 1.48 (m, 4H, $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Ar}$); 1.19 (m, 4H, $\text{H}_2\text{C}-(\text{H}_2\text{C})_2-\text{Ar}$); MS-FAB (DMSO/glycerine/xenon) (m/z): 823 (0.10) ($\text{C}_{56}\text{H}_{54}\text{P}_2\text{Cl}$) $^+$; 712 (29), ($\text{C}_{50}\text{H}_{50}\text{P}_2$) $^+$; 279 (9) ($\text{C}_{18}\text{H}_{16}\text{PO}$) $^+$; 183 (21) ($\text{C}_{12}\text{H}_8\text{P}_2$) $^+$; UV (CHCl_3) (λ (nm)/log ϵ): 212 (sh), 268 (3.27), 274 (3.17).

4.3. Synthesis of 1,6-bis[5-(triphenylphosphoniomethyl)-2-thienyl]hexane dibromide (**2**)

A solution of PBr_3 (1.73 g, 6.40 mmol) in absolute chloroform (2 ml) was added dropwise to a stirred suspension of 1,6-bis[5-(hydroxymethyl)-2-thienyl]hexane (1.50 g, 4.80 mmol) in cooled absolute chloroform (10 ml at -10°C to -5°C). The solution was stirred for 1 h at -5°C and the resulting complex was then hydrolysed on ice. The crude light brown product was dissolved in diethyl ether. The extract was washed with water and dried briefly over CaCl_2 . The solvent was removed under reduced pressure. This crude product was dissolved in a solution of triphenylphosphane (2.8 g, 10.6 mmol) in absolute toluene (40 ml). The reaction mixture was stirred for 1 h at room temperature, and then for 48 h at 40 $^{\circ}\text{C}$. The precipitated products from

the reaction mixture were filtered off, recrystallized from ethanol/diethyl ether (1:10) and dried over P_2O_5 for one week. Yield 3.70 g (80 per cent related to the starting materials); m.p. 125°C/dec; $C_{52}H_{50}S_2P_2Br_2 \cdot 2H_2O$ (980.87) calculated, C 62.65, H 5.66; found C 61.02, H 5.43 per cent; IR (KBr), $\nu(\text{cm}^{-1}) = 3050$ (m) $\nu(\text{Ar}-\text{C}-\text{H})$; 2925 (s), 2850 (s), 2775 (m) $\nu(\text{C}-\text{H})$; 1510 (m) $\nu(\text{Ar}-\text{C}=\text{C})$; 1435 (vs) $\nu(\text{C}-\text{P})$; 845 (vs) $\delta(\text{ArC}-\text{H})$; $^1\text{H-NMR}$ (CDCl_3) $\delta(\text{ppm}) = 7.53-7.88$ (m, 30H, $\text{P}(\text{Bz}-\text{H}_2\text{H}_3\text{H}_4\text{H}_5\text{H}_6)_3$); 6.86 (d, 2H, $J_{4,3} = 3.80$ Hz, $\text{Th}-\text{H}_4$); 6.46 (d, 2H, $J_{3,4} = 3.80$ Hz, $\text{Th}-\text{H}_3$); 5.60 (d, 4H, $J = 14$ Hz, $\text{Th}-\text{CH}_2-\text{P}$); 2.60 (t, 4H, $J = 6.80$ Hz, $\text{H}_2\text{C}-\text{Th}$); 1.50 (quintet, 4H, $J = 6.80$ Hz, $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Th}$); 1.20 (m, 4H, $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Th}$); MS (m/z) (DMSO/glycerine-FAB): 879 (1) ($C_{52}H_{50}S_2P_2Br$) $^+$; 799 (1) ($C_{52}H_{50}S_2P_2$) $^+$; 723 (2) ($C_{46}H_{45}S_2P_2$) $^+$; 262 (26) ($\text{OP}(\text{Ph})_3$); 183 (23) (C_6H_7P) $^+$; UV (EtOH) (λ (nm)/log ϵ): 223 (4.39), 260 (sh), 275 (3.57).

4.4. Synthesis of compounds 3-8 and 10-12

To a solution of **1** or **2** and 4-(4-butylstyryl)benzaldehyde or 4-(5-butyl-2-thienylvinyl)benzaldehyde [5] or 5-(4-butylstyryl)-2-thiophenecarboxaldehyde [5] or 5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]-2-thiophenecarboxaldehyde [5] or 5-[5-(4-butylstyryl)-2-thienylvinyl]thiophenecarboxaldehyde [5] in absolute DMF was added lithium methanolate (1M in absolute methanol) under an argon atmosphere. While stirring the reaction mixture for 12 h at room temperature the products were precipitated. The products were purified by column chromatography (silica gel 60, CHCl_3). The first fraction, which was the desired product, was transformed to the pure *E*-product by heating the isomeric mixtures under reflux with a catalytic amount of iodine in absolute toluene for about 8 h. Further purification was effected by recrystallization from toluene. All-*E*-1,6-Bis{4-[4-(4-butylstyryl)styryl]phenyl}hexane (**3**) was synthesized from 4-(4-butylstyryl)benzaldehyde (620.0 mg, 2.35 mmol), **1** (1.00 g, 1.17 mmol) and CH_3OLi (3 ml, 1M in CH_3OH) in absolute DMF (30 ml); light yellow powder and crystals from toluene. Yield 426 mg (48 per cent); m.p. 331°C, c.p./dec. 387°C; $C_{58}H_{62}$ (759.1) calculated C 91.77, H 8.23; found C 91.81, H 8.20 per cent; IR (KBr) $\nu(\text{cm}^{-1}) = 3090$ (w) $\nu(\text{C}-\text{H}_{\text{Ar,Th}})$; 3022 (m) $\nu(\text{C}=\text{C}_{\text{trans}})$; 2955 (s), 2930 (vs), 2850 (vs) $\nu_{\text{sy}}(\text{CH}_2)$; 1465 (s), 1425 (s) $\delta_{\text{as}}(\text{CH}_2)$, 1280 (m) 1270 (m), 1250 (m) $\gamma(\text{C}=\text{C}-\text{H}_{\text{trans}})$; 965 (vs) $\omega(\text{C}=\text{C}-\text{H}_{\text{trans}})$. MS (m/z): 758 (100) (M^+); 379 (13) (M^{2+}); 351 (11) ($\text{C}_{27}\text{H}_{27}$) $^+$; 309 (14) ($\text{C}_{24}\text{H}_{21}$) $^+$. UV (KBr) (λ (nm)/log ϵ): 202, 243, 256 (sh), 322 (sh), 334, 349 (sh), 370 (sh).

Compounds **4-8** and **10-12** were synthesized by the same method (see figure 4). The analytical data were comparable to those of **3**.

4.5. Synthesis of compounds 14-16

The synthesis, *E/Z*-transformation and purification of the compounds **14-16** was carried out as described for **3-8** starting from 1,4-bis[5-(5-formyl-2-thienylvinyl)-2-thienyl]butane [5] or 1,6-bis[5-(5-formyl-2-thienylvinyl)-2-thienyl]hexane [5] or 1,8-bis[5-(5-formyl-2-thienylvinyl)-2-thienyl]octane [5] and triphenyl(4-butylbenzyl)phosphonium bromide [7] (see figure 3). All-*E*-1,4-bis{5-[5-(4-butylstyryl)-2-thienylvinyl]-2-thienyl}butane (**14**) was prepared from 1,4-bis(5-(5-formyl-2-thienylvinyl)-2-thienyl)butane (400 mg, 0.81 mmol), triphenyl(4-butylbenzyl)phosphonium bromide (920 mg, 1.68 mmol) and CH_3OLi (3 ml, 1M in CH_3OH) in absolute DMF (30 ml) and absolute EtOH (15 ml); orange coloured crystals from CHCl_3 . Yield 592 mg (97 per cent); m.p. 171°C; c.p. 240°C; $C_{48}H_{50}S_4$ (755.2) calculated, C 76.34, H 6.67; found, C 76.27, H 6.57 per cent; $^1\text{H-NMR}$ (CDCl_3) $\delta(\text{ppm}) = 7.37$ (d, 4H, $J_{2,3} = J_{6,5} = 8.10$ Hz, $\text{Ar}-\text{H}_2\text{H}_6$); 7.16 (d, 4H, $J_{3,2} = J_{5,6} = 8.10$ Hz, $\text{Ar}-\text{H}_3\text{H}_5$); 7.12 (d, 2H, $J_{1,2} = 15.70$ Hz, $\text{Vin}-\text{H}_1$); 6.77-7.00 (m, 12H, $\text{Th}-\text{H}_4\text{H}_3\text{H}_4$, $\text{Vin}-\text{H}_2\text{H}_1\text{H}_2$); 6.66 (d, 2H, $J_{3,4} = 3.50$ Hz, $\text{Th}-\text{H}_3$); 2.84 (m, 4H, $\text{H}_2\text{C}-\text{Th}$); 2.61 (t, 4H, $J = 7.40$ Hz, $\text{H}_2\text{C}-\text{Ar}$); 1.78 (m, 4H, $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Th}$); 1.60 (quintet, 4H, $J = 7.40$ Hz, $\text{H}_2\text{C}-\text{H}_2\text{C}-\text{Ar}$); 1.35 (sextet, 4H, $J = 7.40$ Hz, $\text{H}_2\text{C}-(\text{H}_2\text{C})_2-\text{Ar}$); 0.91 (t, 6H, $J = 7.40$ Hz, H_3C). IR (KBr) $\nu(\text{cm}^{-1}) = 3070$ (m) $\nu(\text{C}-\text{H}_{\text{Ar,Th}})$; 3020 (m) $\nu(\text{C}=\text{C}-\text{H}_{\text{trans}})$; 2958 (s), 2920 (vs), 2855 (vs) $\nu_{\text{sy}}(\text{CH}_2)$; 1480 (m), 1460 (s), 1435 (m) $\delta_{\text{as}}(\text{CH}_2)$ or thiophene absorption, 1270 (m), $\gamma(\text{C}-\text{C}-\text{H}_{\text{trans}})$; 945 (vs), 935 (vs) $\omega(\text{C}=\text{C}-\text{H}_{\text{trans}})$. MS (m/z): 754 (100) (M^+); 377 (4) (M^{2+}); 363 (9) ($\text{C}_{23}\text{H}_{23}\text{S}_2$) $^+$; 321 (4) ($\text{C}_{20}\text{H}_{17}\text{S}_2$) $^+$. UV (CHCl_3) (λ (nm)/log ϵ): 253 (3.94), 313 (3.63), 392 (4.44), 411 (4.60), 432 (4.36).

Compounds **15** and **16** were prepared analogously (see figure 2 and table 3). The analytical data were comparable to those for **14**.

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