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Liquid crystalline compounds in the thiophene series†

VIII. Synthesis and characterization of liquid crystalline vinylenes with thiophene moieties and carbaldehyde groups

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New thermotropic liquid crystal compounds, with one and two mesogenic groups, have been synthesized and characterized. The structural elements of the compounds consist of thiophene ring systems, vinylene units and, for some compounds, carbaldehyde groups. Mesogenic groups involving three thiophene ring systems are normally not liquid crystalline. Only in the case of *E*,*E*-5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]-2-thiophenecarbaldehyde could a monotropic nematic phase be easily observed. By replacing thiophene ring systems in the core with a benzene ring system, or by attaching one carbaldehyde group at the moieties, or by doubling the mesogenic groups via an alkylene spacer, the temperature ranges of the mesophases of the compounds with thiophene ring systems can be enlarged or liquid crystal phases induced. The small values for ΔS_{NI}, which have been observed for the low molecular weight compounds, indicate a very low order in the nematic phases.

1. Introduction

The influence of thiophene ring systems on mesomorphic behaviour has recently been the subject of some investigation [1]. Low molar mass thiophene compounds with ester, azomethine or vinylene groups were of most interest [2, 3]. The mesophase behaviour of these compounds is explained satisfactorily through geometric differences between the thiophene and benzene ring systems in the core. It is obvious that 2,5-disubstituted thiophene systems, with a bend of 30°, do not form a linear mesogenic shape and therefore a deviation from an ideal linear structure must be found. In the literature [2, 3], the influence of polarizing groups, with hetero-atoms on the formation of mesophases, has consequently been neglected for such compounds. So, for example, the compounds thiophene-2,5-dicarboxylic acid bis-4-methoxyphenyl ester [1] and thiophene-2,5-dicarboxylic acid bis-4-ethylphenyl ester [4] melt quite differently although they have the same core, and only the former substance shows (on heating and cooling) a narrow enantiotropic nematic phase (C 164 N 166 I), while the other substance, without oxygen in the terminal chains, melts directly to the isotropic phase (C 121 I). This difference between alkyl and alkoxy groups in the liquid crystallinity of the compounds is typical for other compounds, because in contrast to the methylene group, the oxygen contributes a dipole moment which normally promotes mesophases [5]. The influence of dipoles and polarizing groups, in and at the core, is usually discussed in terms of the formation of mesophases rather than of their geometrical

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† Part VII, KOßMEHL, G., and HOPPE, F. D., *Z. Nautrf.* (*b*) (submitted for publication).

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behaviour in the core. However, in order to understand the physical properties of mesophases, all influences must be considered as being of interest. This has led us to synthesize and characterize compounds without any 'functional groups', such as ester or Schiff's base groups. The chosen substances only have benzene and thiophene ring systems and vinylene units. The thermal behaviour of these compounds should be more favourable to mesophase formation by the thiophene system. For comparison, a carbonyl group with a strong dipole moment (and with a high polarizing tendency) was attached to the purely aromatic units. The differences in the thermal behaviour of the substituted and unsubstituted compounds cannot be explained solely by the different geometric structures of the compounds, and electrostatic or other interactions must be involved.

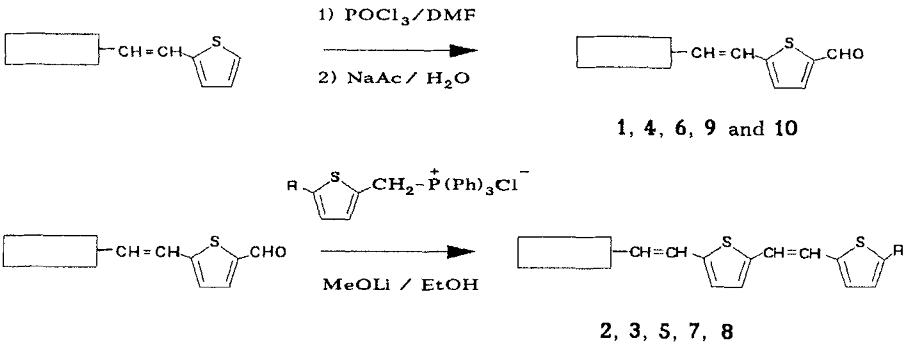
2. Experimental

The IR spectra were measured with a Perkin–Elmer 580-B spectrometer. The ^{1}H NMR spectra were measured at 270 MHz using a Bruker WH 270 instrument; the chemical shifts are given relative to tetramethylsilane (TMS). Mass spectra were obtained with a Varian MAT-112-S instrument, and elemental analyses with a Perkin–Elmer Recorder 56. The phase transitions were determined calorimetrically using a Heraeus TA 500 instrument with a scanning speed of 10°C min^{-1}, and occasionally at 5°C or 20°C min^{-1}, for heating and cooling runs in an argon atmosphere. The first and second heating cycles were used for the determination of the phase transition temperatures and enthalpies. Optical investigations were carried out with a Zeiss polarizing microscope coupled with a Lincam heating regulation system. The *E*-isomers were confirmed by IR and ^{1}H NMR spectroscopy.

2.1. *General synthesis of the aldehydes* **1**, **4**, **6**, **9** and **10** (see figure 1)

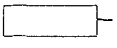
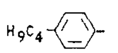
The vinylenes, *E*-4-butylstyryl-2-thiophene and *E*-5-butyl-2-thienylvinyl-2-thiophene, which had been synthesized by known routes [6], and compounds **2**, **5** or **7** also in the *E*-form (see below), were dissolved in DMF in an argon atmosphere. To the resulting solutions, $POCl_3$ was added dropwise at room temperature and the mixture heated to 60°C for 24 h. During this procedure, the reaction mixture turned deep red. The resulting complex was decomposed by stirring the mixture for 1 h with an aqueous saturated solution of sodium acetate. The products formed were separated by filtration, washed with water and dried in vacuum over P_2O_5. Intensive purification was carried out by column chromatography (silica gel/$CHCl_3$: hexane 1 : 1) where the first fraction contained starting materials and the second fraction the *E*/*Z* mixture. The all-*E*-isomer was separated by recrystallization from hexane or ethanol.

All-*E*-5-[5-(4-butylstyryl)-2-thienylvinyl]-2-thiophenecarbaldehyde, **6**, was prepared from 8·20 g (23·4 mmol) of **7** and 3·46 g (22 mmol) of $POCl_3$ in 11·0 ml of absolute DMF; orange coloured crystals, mp 135°C, cp 167°C, yield 2·70 g (31 per cent), were obtained from hexane. $C_{23}H_{22}S_2O$ (378·5), calculated C 72·98 per cent, H 5·86 per cent, found C 73·01 per cent H 5·90 per cent. IR (KBr) ν (cm^{-1}) = 3078 (w) ν(C–H$_{Ar}$); 3010 (m) ν(C=C$_{trans}$–H); 2978 (s), 2960 (m), 2930 (m), 2855 (m) ν(C–H); 1655 (vs) ν(C=O); 1218 (vs) δ(C=C$_{trans}$); 938 (m) δ(C=C$_{trans}$–H); 818 (m) δ(Th–C–H) ^{1}H NMR ($CDCl_3$) δ(ppm) = 9·84 (s, 1 H, –C$\underline{H}$=O); 7·64 (d, 1 H, J_{3-4} = 3·8 Hz, Th–H_3); 7·39 (d, 2 H, J_{2-3}=J_{6-5}=8 Hz, Bz–H_2H_6); 6·84–7·28 (m, 9 H, Bz–H_3H_5, Vin–$H_1H_2H_{1'}H_{2'}$, Th–$H_4H_{3'}H_{4'}$); 2·61 (t, 2 H, J = 7·5 Hz, $\underline{H}_2$C–Bz); 1·61 (quintet, 2 H, J = 7·5 Hz, $\underline{H}_2$C–H_2C–Bz); 1·35 (hextet, 2 H, J = 7·5 Hz, $\underline{H}_2$C–(H_2C)$_2$–Bz); 0·92 (t, 3 H, J = 7·5 Hz, –C$\underline{H}_3$). MS (*m*/*z*): 378 (100) (M$^+$);



1, 4, 6, 9 and 10

2, 3, 5, 7, 8

	compound	R
	1	–
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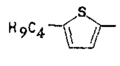	4	–
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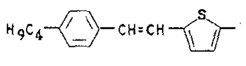	6	–
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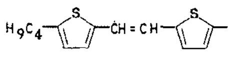
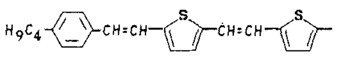
	9	–
	10	–

Figure 1. Synthetic routes to the thiophene systems with carbaldehyde groups (**1**, **4**, **6**, **9** and **10**) or without carbaldehyde groups (**2**, **3**, **5**, **7** and **8**).

189 (5) (M^{2+}); 349 (3) (M^+–CO); 335 (15) $(C_{20}H_{15}S_2O)^+$; 307 (9) $(C_{19}H_{15}S_2)^+$. UV ($CHCl_3$) (λ(nm)/log ε): 265 (3·77), 332 (4·05), 429 (4·07).

Compounds **1** (light yellow crystals), **4** (yellow crystals), **9** (red crystals) and **10** (deep red crystals) were prepared analogously (see figure 1 and tables 1 and 2).

2.2. *General synthesis of the vinylene compounds* 2, 3, 5, 7 *and* 8 (*see figure 1*)

The conversions of the aldehydes **1**, **4**, **6** or **9** with triphenyl(2-thienylmethyl) phosphonium chloride or triphenyl)5-butyl-2-thienylmethyl)phosphonium chloride to the vinylene derivatives **2**, **3**, **5**, **7** and **8** were effected in absolute ethanol or mixtures of absolute ethanol and absolute DMF in an argon atmosphere. The reaction was started by the addition of lithium methanolate (1 M in methanol), when the intermediate ylid coloured the solution with luminous colours. The reaction solutions were stirred for

Table 1. Experimental data for those compounds not described in detail in §2. Their spectroscopic data correspond to data given in §2 for specific examples.

Compound	Formula (Molecular weight)	Calculated/per cent		Found/per cent		Yield per cent
		C	H	C	H	
1	$C_{17}H_{18}SO$ (270·4)	75·50	6·71	75·50	6·71	53
2	$C_{22}H_{22}S_2$ (350·5)	75·38	6·33	75·37	6·34	84
3	$C_{26}H_{30}S_2$ (406·6)	76·80	7·44	76·83	7·44	84
4	$C_{15}H_{16}S_2O$ (276·4)	65·18	5·83	65·17	5·82	64
7	$C_{28}H_{26}S_3$ (458·7)	73·32	5·71	73·29	5·65	93
8	$C_{32}H_{34}S_3$ (514·8)	74·66	6·66	74·62	6·62	92
9	$C_{21}H_{20}S_3O$ (384·6)	65·59	5·24	65·56	5·21	57
10	$C_{29}H_{26}S_3O$ (486·7)	71·56	5·38	71·53	5·41	18
12	$C_{17}H_{18}SO$ (270·4)	75·50	6·71	75·40	6·72	17
13	$C_{32}H_{30}S_2O_2$ (510·7)	75·26	5·92	75·13	5·85	12
14	$C_{28}H_{26}S_4O_2$ (522·8)	64·33	5·01	64·33	5·02	71
15	$C_{26}H_{22}S_4O_2$ (494·7)	63·12	4·48	63·08	4·46	58

3 h. The end of the reaction was detected by using TLC and $CHCl_3$ where the product ran foremost and the precursor was 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/chloroform : hexane 1 : 1) when 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 products were further purified by recrystallization from ethanol or toluene. The crystals were dried over P_2O_5.

All-*E*-5-(5-butyl-2-thienylvinyl)-2-thienylvinyl-2-thiophene (**5**) was synthesized from 1·50 g (5·40 mmol) of **4**, 2·50 g (6·33 mmol) of triphenyl(2-thienylmethyl) phosphonium chloride and 7·0 ml of CH_3OLi (1 M in absolute methanol) in 40 ml of absolute ethanol/DMF (1 : 1); orange coloured crystals, mp 81°C; yield 1·80 g (93 per cent), were obtained from ethanol. $C_{20}H_{20}S_3$ (356·6); calculated C 67·40 per cent, H 5·65 per cent, found C 67·38 per cent, H 5·65 per cent. IR (KBr) $\nu(\mathrm{cm}^{-1}) = 3105$ (m), 3065 (m) $\nu(C–H_{Ar})$; 3018 (m) $\nu(C{=}C_{trans}–H)$; 2956 (s), 2920 (s), 2855 (s) $\nu(C–H)$; 1245 (m), 1228 (m) $\delta(C{=}C_{trans})$; 935 (vs) $\delta(C{=}C_{trans}–H)$; 815 (vs) $\delta(Th–C–H)$. ^1H NMR ($CDCl_3$) $\delta(\mathrm{ppm}) = 7·19$ (d, 1 H, $J_{5''-4''} = 4·5$ Hz, Th–$H_{5''}$); 6·8–7·1 (m, 9 H, Th–$H_3H_4H_{4'}H_{3''}H_{4''}$, Vin–$H_1H_2H_{1'}H_{2'}$); 6·67 (d, 1 H, $J_{3'-4'} = 2·8$ Hz, Th–$H_{3'}$); 2·6 (t, 2 H, $J = 7·5$ Hz, H_2C–Th); 1·67 (quintet, 2 H, $J = 7·5$ Hz, $\underline{H}_2C–H_2C$–Th); 1·42 (sextet, 2 H, $J = 7·5$, $\underline{H}_2C–(H_2C)_2$–Th); 0·95 (t, 3 H, $J = 7·5$ Hz, $–C\underline{H}_3$). MS (m/z): 356 (100) (M^+); 178 (9) (M^{2+}); 313

Table 2. Thermodynamic properties of the aldehydes **1**, **4**, **6**, **9**, **10**, **11**, **12**, **13**, **14** and **15** and 1,6-bis(4′-cyanobiphenyl-4-yloxy)hexane [15] (**16**) and *E*,*E*-1,6-bis[4-(2-thienylvinyl)phenyl] hexane [7] (**17**); on heating and cooling (in case of monotropic phases).

Compound	Transition	Temperature/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
1	C–I	70	14·2	41·3
4	C–I	65	19·3	57·0
6	C–N	135	30·7	75·1
	N–I	167	0·3	0·8
9	C_1–C_2	95	2·5	6·9
	C_2–I	119	30·3	77·2
	I–N	109	0·2	0·5
	N–C	83		
10	C–N	193	37·3	80·0
	N–I/dec.†	283	(1·4)	2·6
11	C–I	82	12·0	33·9
	I–mesophase	74	6·7	19·3
	Mesophase–C	58		
12	C–I	40	16·6	52·8
13	C–I	208	53·9	111·6
	I–N	208	5·3	11·2
	N–C	191		
14	C–I	165	56·2	128·3
15	C–I	187	52·4	113·9
16[15]	C–N	187	47·6	103·5
	N–I	221	8·17	16·5
17[7]	C–N	189	49·8	107·6

† dec. denotes decomposition.

(79) $(C_{17}H_{13}S_3)^+$; 279 (4) $(C_{17}H_{11}S_2)^+$; 247 (3) $(C_{17}H_{11}S)^+$. UV ($CHCl_3$) (λ(nm)/log ε): 263 (3·34); 312 (3·08); 323 (3·18); 400 (sh); 418 (4·28); 442 (4·03).

Compounds **2**, **3**, **7** (all orange coloured crystals) and **8** (red crystals) were synthesized by the same method (see figure 1 and tables 1 and 3).

2.3. *General synthesis of the aldehydes* 11 *and* 12 (*see figure* 2)

The synthesis of the aldehydes **11** and **12** by the Wittig reaction was carried out similarly to the previously described reaction except that the reactants were 4-formylbenzaldehyde diethyl acetal and a small excess of the phosphonium salt. The unpurified products were isolated by column chromatography (silica-gel, $CHCl_3$/hexane 1 : 1). The first fraction was the *E*/*Z*-mixture of 1,4-bis(5-butyl-2-thienylvinyl)benzene or 1,4-bis-4-butylstyryl benzene; the second fraction consisted of the acetals of the corresponding aldehydes **11** or **12**, *E*/*Z*-4-butylstyryl benzaldehyde diethyl acetal or *E*/*Z*-4-(5-butyl-2-thienylvinyl)benzaldehyde diethyl acetal; these were dissolved in a mixture of ethanol and dilute HCl (15 per cent) and heated to reflux for 1 h. Additional purification of the crude product was achieved by high pressure liquid chromatography (HPLC) using a Knauer LC-55 B (detector: UV-315 nm) system with Polygosil 60 silicagel (diameter of the grains 7 μm) in a column (32 cm long and 2·5 cm

Table 3. Thermodynamic properties of the vinylenes **2**, **3**, **5**, **7** and **8** and *E*,*E*-2,5-bis(4-butylstyryl)thiophene [13] (**18**), *E*,*E*-2,5-bis(5-butyl-2-thienylvinyl)thiophene [13] (**19**) and *E*,*E*-1,4-bis(5-butyl-2-thienylvinyl)benzene[13] (**20**); on heating and cooling (in case of monotropic phases).

Compound	Transition	Temperature/°C	ΔH/kJ mol^{-1}	ΔS/JK^{-1} mol^{-1}
2	C–I	123	26·6	67·0
3	C–I	107	20·2	53·2
	N–I	111	0·5	1·4
	N–C	68		
5	C_1–C_2	52	−2·3	−7·0
	C_2–I	81	19·5	55·1
7	C–N	198	59·2	125·7
	N–I	235	1·27	2·5
8	C_1–C_2	159	5·5	12·7
	C_2–N	188	35·4	76·8
	N–I	231	0·9	1·7
18 [13]	C–N	141	20·1	48·4
	N–I	171	0·3	0·7
19 [13]	C–I	88	30·4	84·2
20 [13]	C–S	91	14·8	40·7
	S–I	180	17·7	39·1

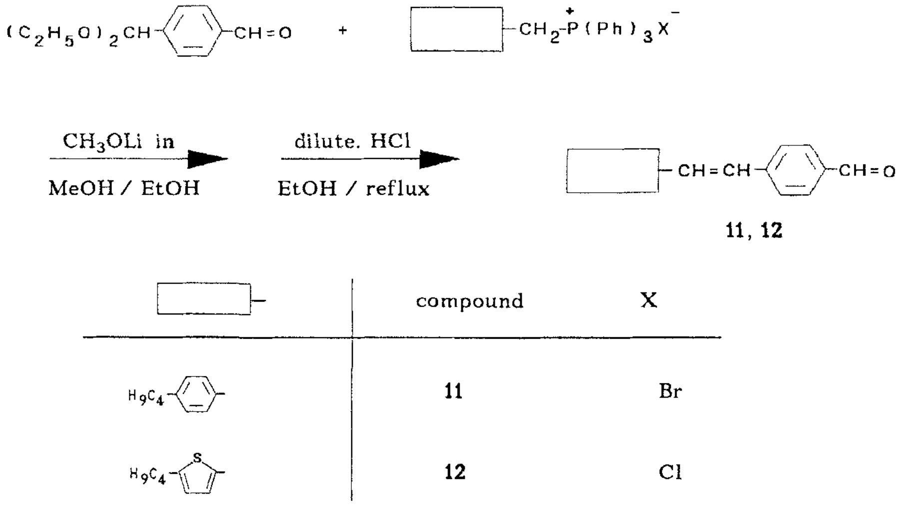
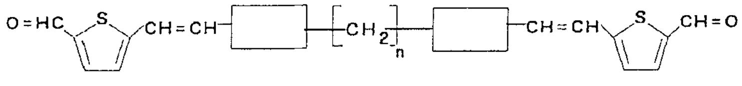


Figure 2. Synthetic route to the aldehydes **11** and **12**.

diameter) for preparative analyses (solvent: hexane/dioxane, volume ratio: 99/1; flow rate 2 ml min^{-1}; $P = 60$ bar). The first product was the '*Z*-product' which is an oil and the second was the '*E*-product' which was recrystallized under dark conditions from hexane and then from ethanol.

E-4-(4-Butylstyryl)benzaldehyde (**11**) was prepared from 5·00 g (24·0 mmol) of 4-formylbenzaldehyde diethyl acetal, 12·0 g (24·6 mmol) of triphenyl-(4-butylbenzyl)-phosphonium bromide and 30 ml of CH_3OLi (1 M in absolute methanol) in 70 ml absolute ethanol: decomposition of the acetal occurred on boiling in 30 ml of ethanol



13, 14, 15

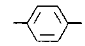
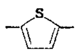
	compound	n
	**13**	6
	**14**	6
	15	4

Figure 3. Structures of *E,E*-1,6-bis[4-(5-formyl-2-thienylvinyl)phenyl]hexane (**13**), *E,E*-1,6-bis[5-(5-formyl-2-thienylvinyl)-2-thienyl]hexane (**14**), and *E,E*-1,4-bis[5-(5-formyl-2-thienylvinyl)-2-thienyl]butane (**15**), synthesized analogously to compound **6**.

and 30 ml of dilute HCl (15 per cent) for 1 h; colourless crystals were obtained from hexane and then from ethanol (in the dark); mp 82°C; yield 5·00 g (79 per cent). $C_{19}H_{20}O$ (264·4) calculated, C 86·32 per cent, H 7·63 per cent, found C 86·33 per cent, H 7·63 per cent. IR (KBr) ν(cm^{-1}) = 3073 (w), 3038 (w) ν(C–H$_{Ar}$); 3023 (m) ν(C=C$_{trans}$–H); 2955 (m), 2928 (s), 2855 (m), 2790 (w), 2730 (w) ν_{sy} (C–H); 1703 (vs) ν(C=O); 1632 (w) (C=C$_{Ar}$); 1268 (w), 1209 (m) γ(C=C–H$_{trans}$); 972 (s), 951 (m) ω(C=C–H$_{trans}$). ^{1}H NMR (CDCl$_3$) δ(ppm) = 10·00 (s, 1 H, –C$\underline{H}$=O); 7·86 (d, 2 H, J_{2-3}=J_{6-5} = 8·5 Hz, Bz–H$_2$H$_6$); 7·63 (d, 2 H, J_{3-2}=J_{5-6} = 8·5 Hz, Bz–H$_3$H$_5$); 7·46 (d, 2 H, $J_{2'-3'}$=$J_{6-5'}$ = 8·75 Hz, Bz–H$_{2'}$H$_{6'}$); 7·25 (d, 1 H, J_{2-1} = 15·8 Hz, Vin–H$_2$); 7·2 (d, 2 H, $J_{3'-2'}$=$J_{5'-6'}$ = 8·75 Hz, Bz–H$_{3'}$H$_{5'}$) 7·09 (d, 1 H, J_{1-2} = 15·8 Hz, Vin–H$_1$); 2·64 (t, 2 H, J = 8 Hz, $\underline{H}_2$C–Bz); 1·61 (quintet, 2 H, J = 8 Hz $\underline{H}_2$C–H$_2$C–Bz); 1·38 (sextet, 2 H, J = 8 Hz, $\underline{H}_2$C–H$_2$C–H$_2$C–Bz); 0·94 (t, 3 H, J = 8 Hz, $\underline{H}_3$C–). MS (*m*/*z*): 264 (90) (M$^+$); 221 (100) $(C_{16}H_{13}O)^+$; 191 (21) $(C_{15}H_{13})^+$; 178 (51·9) $(C_{14}H_{10})^+$ UV (CHCl$_3$) (λ(nm)/log ε): 243 (3·5), 343 (4·04).

Compound **12** (colourless crystals) was synthesized by the same method (see figure 2 and table 2). Additionally, we have synthesized compounds **13** (yellow crystals), **14** and **15** (yellow to orange coloured crystals) (see figure 3) as described for compound **6**. The synthetic route to the precursors *E,E*-1,6-bis[4-(2-thienylvinyl)phenyl]hexane, *E,E*-1,6-bis[5-(2-thienylvinyl)-2-thienyl]hexane and *E,E*-1,4-bis[5-(2-thienylvinyl)-2-thienyl]butane are described elsewhere [7].

3. Results and discussion

The aldehydes were prepared by Vilsmeier–Haack formylation and the vinylenes by the Wittig reaction. The structures of the aldehydes **1, 4, 6, 9, 10, 11, 12, 13, 14** and **15**, and the vinylenes **2, 3, 5, 7**, and **8** were confirmed by the IR, ^{1}H NMR and MS data. The spectra of all compounds contain the expected information on the typical structural units present. Representative examples are given in 2.

If, in the moieties of a liquid crystalline compound, benzene systems are exchanged by thiophene systems, the mesophase of the compound is destabilized or completely destroyed. For example, the compound *E,E*-2,5-bis[4-butylstyryl)thiophene with two benzene rings, shows an enantiotropic nematic phase, whereas the compound *E,E*-2,5-bis(5-butyl-2-thienylvinyl)thiophene, without any benzene rings, but having three thiophene rings in the core, has no liquid crystalline phase.

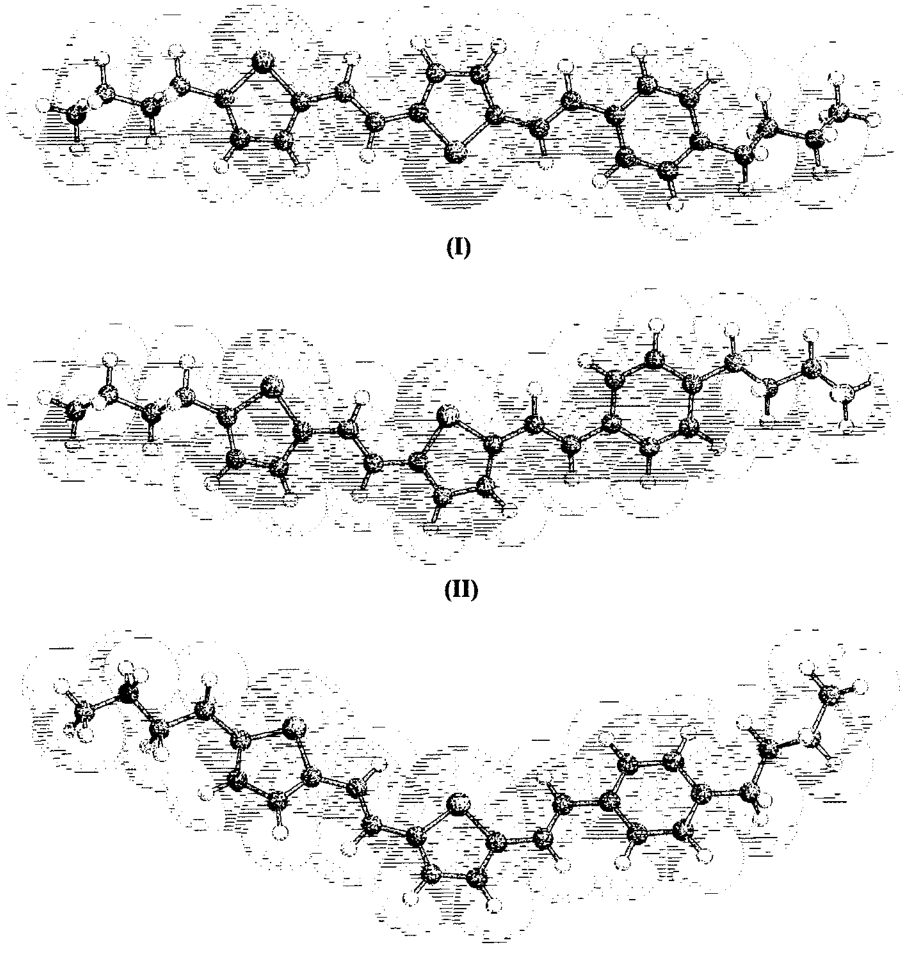


Figure 4. Different conformational isomers of the vinylene **3** in the all-*E*-form; all-*s-transoid* (**I**), *s-cisoid-s-transoid* (**II**), all-*s-cisoid* (**III**). The simulation of the isomers in the vapour phase was carried out with MOPAC 6·0, using the PM 3 method.

A comparison between the compound *E*,*E*-1,4-bis(5-butyl-2-thienylvinyl)benzene (**20**) and compound **3** shows that although both compounds have the same number of thiophene and benzene ring systems in the core, they behave quite differently on heating. In contrast to the vinylene **3**, the former compound shows a smectic phase over a wide temperature range (see table 2). This different behaviour can be explained by the different geometrical arrangements in the core; the core of **3** shows more deviation from linearity than the core of **20**, because in contrast to **20**, the thiophene system in **3** is in the centre of the core.

In contrast to benzene derivatives, compounds with thiophene ring systems are able to form different conformational isomers. In figure 4 for example, some isomers of **3** are illustrated. From the geometrical viewpoint we conclude that in the mesophase, the all-*s-trans*-conformational isomer is predominant, because in this conformer the breadth/length ratio of **3** has the best value. However, the existence of the other conformer is also probable, as the absolute entropy of the mesophase is enlarged by admixture with the other conformer.

The mesophases of the compounds with thiophene ring systems correspond to those found in the studies by Cai and Samulski [1]. They exist over a wide temperature range if more than three aromatic and/or heteroaromatic ring systems are in the core. However, if in the vinylenes, **7** and **8** there are three thiophene ring systems, they also show liquid crystallinity over a wide temperature range. It appears that the length/breadth ratio of these moieties are good for compensating the 'kinks' in the core which result from the 2,5-substitution in the thiophene system.

The aldehydes **1**, **4**, **11** and **12** are generally photosensitive, as melts and in solution; therefore determination of the real texture of the mesophase of the aldehyde **11** was not possible because, in light, the compound transformed rapidly from the *E*- to the *Z*-isomer. Measurements with the aldehydes in solution (where the solvent was dioxane and the light source a normal UV-lamp, with high and low frequency UV-light) showed approximately 80 per cent of the *Z*-form. This photo-induced equilibrium was also observed for the other three aldehydes. The equilibrium is therefore independent of the chemical structure of the four aldehydes. Only the high transition entropy determined at the clearing point for the aldehyde **11** indicated a higher ordered mesophase. X-ray studies will be done.

In tables 2 and 3, the thermodynamic properties of the vinylenes and aldehydes are listed. From the values of the transitions, it can be seen that the carbaldehyde group, attached to the mesogenic group, induces liquid crystallinity or enhances the temperature range from that of the mesophase of the corresponding vinylene. In the case of the compounds with three thiophene ring systems and two vinylene groups in the aromatic unit (**9**, **19** and **21**), only the compound with one butyl and one carbaldehyde group attached to the core has a monotropic liquid crystalline phase (see figure 6). In contrast to other liquid crystalline compounds with thiophene ring systems, the aldehydes **6** and **9** (see table 2) show very small transition entropies at the clearing point, thus indicating a low order in the nematic phases of these compounds.

Compounds such as 4-(5-butyl-2-thienylvinyl)benzoic acid and 4-(5-butyl-2-thienylcarbonylimino)benzoic acid are capable of forming mesophases over a wide temperature range [4, 8], as carboxylic acid groups dimerize by hydrogen bonding. X-ray studies show that comparable dimerizations involving carbaldehyde groups are not possible [9]; therefore the reasons for mesophase formation by carbaldehydes are

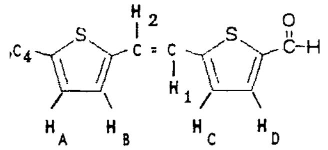
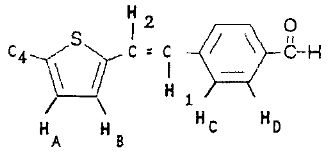
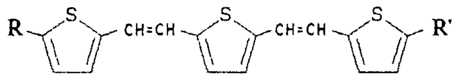
Compound		δ-values (ppm)	(coupling constants *J*/Hz)					
		H_A	H_B	H_C	H_D	H_1	H_2	CHO
	**4**	6·70 (4·0)	6·95 (4·0)	7·07 (4·0)	7·63 (4·0)	6·88 (15·5)	7·19 (15·5)	9·82
	**12**	6·70 (3·0)	6·94 (3·0)	7·57 (7·75)	7·83 (7·75)	6·84 (15·8)	7·31 (15·8)	9·96

Figure 5. ^1H NMR spectral data for the aldehydes **4** and **12** in $CDCl_3$.



Compound	R	R′	Transition	Temperature/°C
21	CH=O	CH=O	C–I	222 [12]
9	CH=O	C_4H_9	C–I	119
			I–N	109
			N–C	83
19	C_4H_9	C_4H_9	C–I	88 [13]

Figure 6. Transition temperatures of different compounds with the same core, but substituents of different polarity (see also table 2).

not the same as those for carboxylic acids. For the formation of mesophases, the polarizing and dipolar character of the carbonyl groups should be taken into consideration. As shown by the ^{1}H NMR spectra of the aldehydes **4** and **12**, on exchanging the aromatic unit from the aldehydes **4** to **12**, no difference can be seen in the shift of the protons, H_A and H_B, which are substituted at the thiophene ring system carrying the butyl group (see figure 5). The polarizing influence and dipolar character of the carbonyl group appears therefore to be concentrated at the directly bound aromatic unit. This result is important, as it is known that carbonyl groups conjugate more effectively with a thiophene system than with a benzene system [10].

It is obvious that intermolecular interactions between aldehyde groups are very low, and therefore for the nematic phases of aldehydes **6**, **9** and **10**, low order parameters are characteristic (low values for ΔS_{NI}). Consequently, the conformational preferences of thiophene-2-carbaldehydes have to be considered carefully to explain the liquid crystallinity of the aldehydes. NMR measurements show that in a nematic matrix the O,S-*cis*-conformer is the only existing conformational isomer [11]. Nevertheless, we assume that at a higher temperature, the formation of the mesophase of compound **9** is closely dependent on the fractions of O,S-*cis*- and O,S-*trans*-conformers in the mesophase. The aldehyde **9** however, is able to form a mesophase due to a well defined balance between the length/breadth ratio of the mesogenic group, the number of thiophene systems in the core and the polarizability of the compound (see figure 6).

In recent years, many investigations have been undertaken towards a better understanding of the mesophase behaviour of molecules with two mesogenic groups connected by an alkylene chain ('dimers') [14, 15]. We have also shown previously that dimers which have thiophene systems in the core are liquid crystalline [7]. In many cases, the connecting of the two moieties by an alkylene chain enhanced the probability of formation of mesophases. While the aldehyde **1** does not form a liquid crystalline phase, **13** (containing two moieties of **1** connected by a hexamethylene group) shows, upon cooling, a monotropic nematic phase. In contrast, the connecting of two aldehyde moieties of **4** via a hexamethylene spacer in compound **14** is not sufficient to induce a mesophase, because the number of thiophene ring systems in the aromatic units is too large. This means that the exchange of benzene for thiophene ring systems (**13**→**14**) is unfavourable for liquid crystallinity. Normally, the formation of mesophases is enhanced for comparable compounds with decreasing spacer length, but in the case of **15** (with a tetramethylene chain) liquid crystalline phases have also not been found. Moreover, we can see for **13** that a mesophase can only be included by attaching a carbaldehyde group at each moiety. Accordingly the compound *E*,*E*-1,6-bis[4-(2-thienylvinyl)phenyl]hexane (**17**) shows (in contrast to the corresponding dialdehyde **13**) no mesophase [7] (see table 2).

As seen in table 2, the transitional entropy from the isotropic to the nematic phase of **13** shows a higher value than, for example, that for the monomeric aldehydes **6** and **9**. Studies by Emsley and Luckhurst of α,ω-bis(4,4′-cyanobiphenyloxy)alkanes show comparable results [16]. According to these results the mesogenic groups in the dimers are more highly ordered in the nematic phases than in the case of nematogens with a rigid core and terminal chains in two separate molecules. Furthermore, the almost similar values observed for the temperature and transition entropy (see table 2) of 1,6-bis(4′-cyanobiphenyl-4-yloxy)hexane (**16**) and compound **13** indicate analogous structural behaviour for the compounds. We therefore assume that carbaldehyde and cyano groups produce similar effects in mesophases.

These compounds are also interesting with regard to their potential for further reaction in the mesophase, as the carbaldehyde group is a reactive functional group.

Summarizing the results, we can now say that the liquid crystallinity of thiophene compounds is promoted by enlarging the rigid core, by attaching a dipole or polarizing group at the end thiophene moieties or by connecting two aromatic units through an alkylene spacer to give a compound with two equal mesogenic units.

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