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Liquid Crystalline Compounds in the Thiophene Series, Part 9*

Synthesis and Characterization of Liquid Crystalline Vinylenes with Two Mesogenic Groups Containing Exclusively Thiophene System

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The first examples of compounds with two mesogenic groups connected by an alkylene chain and containing mesogenic groups with exclusively two, three or four thiophene rings and one, two or three vinylene groups in each moiety are reported. Only the materials with three or four thiophene rings in each core have nematic phases. For example all-E-1.6-bis{5-[5-(2-thienylvinyl)-2-thienylvinyl]-2-thienyl}hexane shows a monotropic nematic phase while cooling the sample, but E,E-2-(5-butyl-2-thienylvinyl)-5-(thienylvinyl)thiophene has no mesophases. The liquid crystalline behaviour of the various compounds is dependent on the length of the flexible inner chain. Compounds with terminal alkyl groups show nematic phases in a broader temperature range than those without substituents. The temperature range of a mesophase is enhanced by substituting thiophene rings in the described compounds for benzene rings. The thermal behaviour of the compounds has been studied by DSC and polarizing microscopy.

Keywords: Thiophene derivatives, liquid crystallinity, model compounds for polyvinylenes, dimeric molecules.

1. INTRODUCTION

The majority of thermotropic liquid crystals are composed of molecules with benzene rings connected by groups with heteroatoms like the ester, azo, Schiff base or other groups.[1] A few papers have been published on liquid crystalline compounds with thiophene rings.[2–6,16,17] It has been found that the incorporation of a thiophene ring, which is bound at the 2.5-position in the core, has resulted in a reduction of the liquid crystalline phase range, or even its disappearance. This fact is usually explained by the deviation from the linearity of the core, caused by the thiophene ring which introduces a 30° bend into the molecular shape. However, as already shown by Nash and Gray,[4] the influence of electron pairs, polarizability, dipolarity and π-bond interaction within the thiophene rings is important for the mesophase behaviour of the compounds. So, e.g., analogous compounds with thiophene, pyridine or furan rings having more or less

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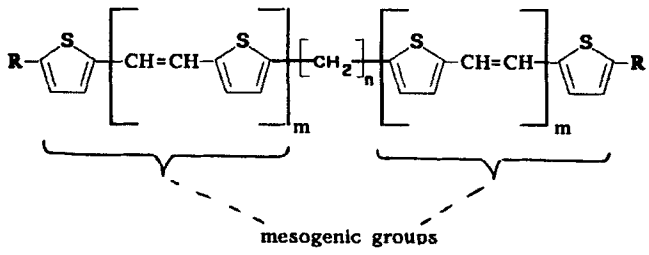


FIGURE 1 General formula of the described compounds.

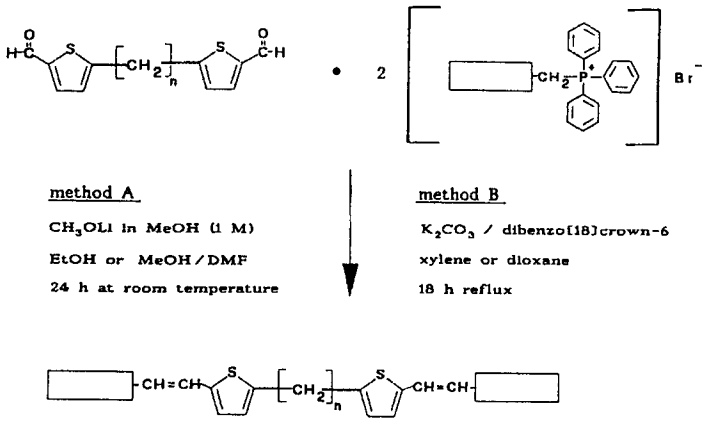
the same geometrical arrangements in the molecules to each other, show quite a different thermal behaviour during heating and cooling of the samples. Yet, a comparison between the known compounds with one mesogenic group containing thiophene rings which have been reported[5,6] leads to the following comprehensive phenomenal results:

Replacing the benzene rings with thiophene rings in the core of a two benzene ring system lowers the melting and clearing points of the resulting compound. Compounds with one thiophene and one benzene ring in the core normally have no liquid crystalline phases. The possibility of the formation of mesophases is high for compounds with three thiophene and/or benzene rings in the core and decreases with increasing numbers of thiophene rings. Therefore liquid crystalline compounds with three thiophene rings, and one or two terminal alkyl chains, have not yet been described in the literature. Compounds with four heteroaromatic and/or aromatic rings shows exclusively nematic phases but sometimes decompose in the mesophase temperature range. Vinylene units connecting heteroaromatic or heteroaromatic-aromatic rings in the mesogenic group more readily promote the formation of mesophases, than units with azo, ester or azomethine groups in the linkage.

In a previous paper, it was shown that compounds with two mesogenic groups and an alkylene chain ("dimeric molecules") also have liquid crystalline phases if one thiophene and two benzene rings are in each mesogenic group of the compounds.[7] In this paper, interest has been focused on compounds with a large number of thiophene rings in each mesogenic group, and so only compounds with the general chemical structure shown in Figure 1 have been synthesized and characterised: with $m = 1 - 3$ and R = H, CH_3 or C_4H_9. The thermal behaviour of these compounds has been compared with those materials which have the same core but only one mesogenic group. For better comparison, and in expectation of some compounds having mesophases over a wide temperature range, thiophene rings were substituted for benzene rings.

2. EXPERIMENTAL

IR spectra were measured with a Perkin–Elmer-580-B spectrometer, ^{1}H NMR spectra were obtained at 270 MHz using a Bruker WH 270 instrument using TMS as the internal standard and mass spectra were measured with a Varian MAT-112-S instrument. Elemental analyses were performed with a Perkin–Elmer-Recorder 56. Phase



1, 2, 3, 4, 5, 6, 7, 8, 9, 10

compound	1	2	3	4	5	6	7	8	9	10
n	4	6	7	8	12	4	7	8	12	4
method	A	A	A	A	A	B	B	B	B	A

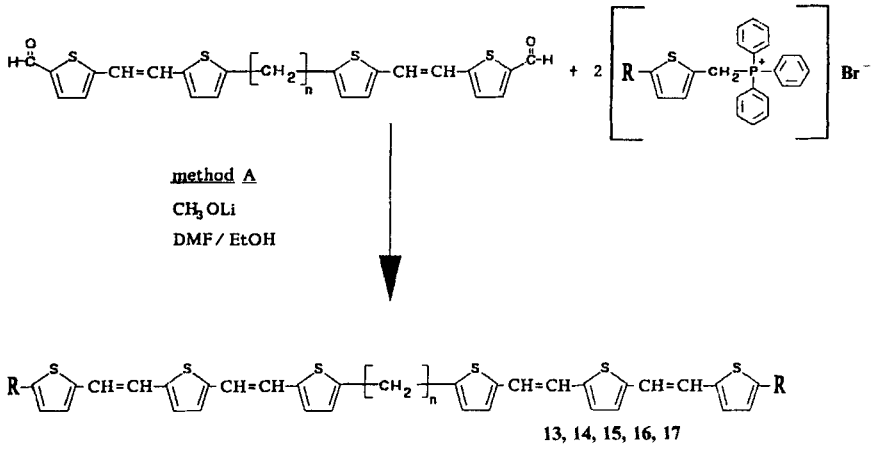
FIGURE 2 Synthetic routes of the compounds $\alpha\cdot\omega$-bis[5-(2-thienylvinyl)-2-thienyl]alkanes (1, 2, 3, 4, 5), $\alpha\cdot\omega$-bis{5-[4-(2-thienylviny)styryl]-2-thienyl]alkanes (6, 7, 8, 9) and $\alpha\cdot\omega$-bis[5-(4-methylstyryl)-2-thienyl] butane (10).

transitions (°C) were determined using a Heraeus TA 500° instrument with a scanning speed of 5–20 °C/min for heating and cooling runs under an argon atmosphere. The first and second heating cycle was used for the determination of the phase transition temperatures and enthalpies. Optical investigations were carried out with a Zeiss polarization microscope using a Lincam heating regulation system. Confirmation of the E-isomers was obtained from IR- and ^{1}H NMR-spectra.

General synthesis of the vinylenes **1–10** and **13–17** (see Figures 2 and 3): The vinylenes were obtained by Wittig reaction (method A or B). A typical example is given

Method A

all-E-1.6-Bis{5-[5-(2-thienylvinyl)-2-thienylvinyl]-2-thienyl}dodecane (**14**): 300 mg (0.50 mmol) 1.6-bis[5-(5-formyl-2-thienylvinyl)-2-thienyl]dodecane[7] and 400 mg (1.00 mmol) triphenyl(2-thienylmethyl)phosphonium chloride[8] were dissolved in a mixture of 30 ml absolute DMF and 15 ml absolute EtOH under an argon atmosphere. After the dropwise addition of 2 ml lithium methanolate (1 M in absol. methanol)



R	H		CH_3		
compound	13	14	15	16	17
n	6	12	6	7	12

FIGURE 3 Synthetic route of the compounds $\alpha.\omega$-bis{5-[5-(2-thienylvinyl)-2-thienylvinyl]-2-thienyl}alkanes (**13,14**) and $\alpha.\omega$-bis{5-[5-(5-methyl-2-thienylvinyl)-2-thienylvinyl]-2-thienyl}alkanes (**15,16,17**).

to the reaction mixture and 24 h standing at room temperature the product precipitated. The precipitate was filtered off by means of a vacuum. The E/Z isomers were transformed to the all E-form with a catalytic amount of iodine by refluxing in dry toluene for about 8 h. Recrystallization from toluene gave orange arched crystals, m.p. 148°C; yield: 370 mg (97%). Calcd. for $C_{44}H_{46}S_6$ (767.20): C 68.88, H 6.04; Found. C 68.87, H 6.02; IR (KBr) $\nu(cm^{-1}) = 3070$ (m) $\nu(C{-}H_{Ar,Th})$; 3010 (m) $\nu(C{=}C{-}H_{trans})$, 2920 (vs), 2850 (vs) $\nu_{sy}(CH_2)$; 1605 (w) $\nu(C{=}C_{Ar-conj})$, 1470 (m), 1445 (m) $\delta_{as}(CH_2)$, 1275 (w) $\gamma(C{=}C{-}H_{trans})$, 940, 920 (vs) $\omega(C{=}C{-}H_{trans})$, ^{1}H NMR ($CDCl_3$) δ(ppm) = 7.19 (d, 2H, $J_{5''-4''} = 4.90$ Hz, Th—$H_{5''}$), 6.81–7.07 (m, 9H, Th—$H_4H_{3'}H_{4'}H_{3''}H_{4''}$, Vin-$H_1H_2H_{1'}H_{2'}$), 6.60 (d, 2H, $J_{3-4} = 4.10$ Hz, Th—H_3), 2.79 (t, 4H, J = 8 Hz, H_2C—Th), 1.69 (m, 4H, $H_2C{-}H_2C$—Th), 1.32 (m, 8H, $(H_2C)_4{-}(H_2C)_2$—Th); MS (m/z): 766 (56) (M^+), 383 (6) (M^{2+}), 313 (100) $(C_{17}H_{13}S_3)^+$, 279 (5) $(C_{17}H_{11}S_2)^+$; 247 (3) $(C_{17}H_{11}S)^+$; 205 (11) $(C_{11}H_9S_2)^+$ and UV ($CHCl_3$) (λ(nm)/log ε): 262 (3.57), 312 (3.31), 323 (3.41), 400 (sh), 418 (4.45), 442 (4.23).

The compounds **1–5** and **10** (all colourless crystals) and **13, 15, 16** and **17** (all orange coloured crystals) were synthezised in the same manner (see Table I).

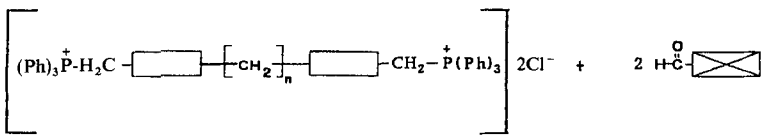
TABLE I

Experimental Data for the Compounds not Described Extensively in the Exp. Part.

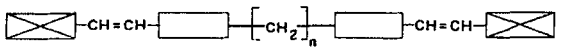
Compound	Formula (mol weight)	Calculated C	Calculated H	Found C	Found H	Yield (%)
1	$C_{24}H_{22}S_4$ (438.7)	65.71	5.05	65.65	5.00	90
2	$C_{26}H_{26}S_4$ (466.7)	66.91	5.61	66.83	5.55	81
3	$C_{27}H_{28}S_4$ (480.8)	67.45	5.87	67.39	5.83	85
4	$C_{28}H_{30}S_4$ (494.8)	67.97	6.11	67.88	6.04	85
5	$C_{32}H_{38}S_4$ (550.9)	69.77	6.95	69.67	6.90	82
6	$C_{40}H_{34}S_4$ (642.9)	74.72	5.33	74.69	5.38	39
8	$C_{44}H_{42}S_4$ (699.1)	75.60	6.06	75.58	6.03	62
9	$C_{48}H_{50}S_4$ (755.2)	76.34	6.67	76.41	6.65	48
10	$C_{30}H_{30}S_2$ (454.7)	79.25	6.65	79.23	6.63	81
13	$C_{38}H_{34}S_6$ (683.0)	66.82	5.02	66.79	5.00	42
15	$C_{40}H_{38}S_6$ (711.1)	67.56	5.39	67.53	5.43	90
16	$C_{41}H_{40}S_6$ (725.2)	67.11	5.56	66.97	5.49	85
17	$C_{46}H_{50}S_6$ (795.3)	69.47	6.34	69.39	6.38	84
18	$C_{36}H_{38}$ (470.7)	91.86	8.14	91.82	8.18	24
19	$C_{30}H_{30}S_2$ (454.7)	79.25	6.65	79.24	6.65	78
21	$C_{58}H_{58}S_8$ (1011.6)	68.86	5.78	68.83	5.73	78

Method B[14]

All-E-1.7-Bis{5-[4-(2-thienylvinyl)styryl]-2-thienyl}heptane (**7**): 320 mg (1.00 mmol) 1.7-bis(5-formyl-2-thienyl)heptane[7] and 1.08 g (2.00 mmol) *E*-triphenyl[4-(2-thienylvinyl)benzyl]phosphonium bromide were dissolved in 30 ml dry xylene under an argon atmosphere. While refluxing the reaction mixture with 2.80 g (20.00 mmol) K_2CO_3 and 7 mg (0.02 mmol) dibenzo[18]crown-6 for 18 h, the product was precipitated. The reaction mixure was allowed to cool down to room temperature and the precipitate was filtered off by means of a vacuum. The E/Z isomers were transformed to the all-E-isomer in dry toluene with a catalytic amount of iodine. Recrystallisation from toluene gave yellow crystals; m.p. 253°C, cl.p. 267°C; yield: 0.438 g (64%). Calcd. for $C_{43}H_{40}S_4$ (685.00): C 75.39, H 5.89; Found. C 75.36, H 5.83; IR (KBr) $\nu(cm^{-1}) = 3070$ (m) $\nu(C—H_{Ar,Th})$; 3020 (m) $\nu(C—C—H_{trans})$; 2920 (s), 2850 (s) $\nu_{sy}(CH_2)$, 1625 (m) $\nu(C—C_{Ar-conj})$, 1465 (m), 1430 (m), 1415 (m) $\delta_{as}(CH_2)$, 1275 (m) $\gamma(C—C—H_{trans})$, 995 (vs) $\omega(C—C—H_{trans})$; MS (m/z): 684 (100) (M); 342 (13) (M); 307 (90) $(C_{19}H_{15}S_2)^+$; 273



method A
CH_3OLi
MeOH / DMF / EtOH
24 h stirring at
roomtemperature



18, 19, 20, 21

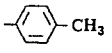
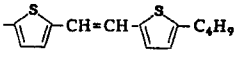
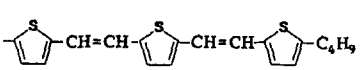
conmpound	n		
18	6		
19	6		
20	6		
21	6		

FIGURE 4 Synthetic route of the compounds 1.6-bis(4-styrylphenyl)hexane (18), 1.6-bis[4-(2-thienylvinyl)phenyl]hexane (19), 1.6-bis{5-[5-(butyl-2-thienylvinyl)-2-thienylvinyl]-2-thienyl}hexane (20) and 1.6-bis(5-{5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl]-2-thienylvinyl}-2-thienyl)hexane (21).

(15) $(C_{19}H_{13}S)^+$; 241 (8) $(C_{19}H_{13})^+$ and UV (KBr) (λ(nm)/log ε): 255, 331 (sh), *353*, 372 (sh), 395, 426.

The compounds **6**, **8** and **9** (all yellow crystals) were synthesized in the same manner. The Wittig salt, *E*-triphenyl[4-(2-thienylvinyl)benzyl)phosphonium bromide, was synthesized according to a method described by Ko—mehl and Härtel.[8]

Generally synthesis of the vinylenes **18–21** (see Figure 4). The vinylenes were obtained by a Wittig-reaction according to method A. A typical example is given below:

all-E-1.6-Bis{5-[5-(5-butyl-2-thienylvinyl)-2-thienylvinyl)-2-thineyl}hexane (**20**):

500 mg (0.52 mmol) 1.6-bis[5-(triphenylposphoniomethyl)-2-thienyl]hexane dibromide, 300 mg (1.09 mmol) 5-(butyl-2-thienylvinyl)-2-thiophenecarbaldehyde[11] and 2 ml lithiummethanolate (1 M in absol. methanol) in 20 ml dry DMF and 15 ml dry EtOH

were stirred 12 h under an argon atmosphere. The precipitate was filtered off by means of a vacuum. The E/Z-isomers were transformed in the all-E-product with a catalytic amount of iodine by refluxing in dry toluene for about 8 h. Recrystallization from toluene gave an orange coloured powder; m.p. 154°C; clp. 169°C; Yield: 389 mg (94%). Calcd. for $C_{46}H_{50}S_6$ (795.30) C 69.47, H 6.34; Found. C 69.45, H 6.36; IR(KBr) $\nu(cm^{-1})$ 3065 (w) ν(C—H_{Ar}), 3010 (w) ν(C—C—H_{trans}), 2958 (m), 2925 (s) 2850 (s) $\nu_{sy}(CH_2)$, 1610 (m) ν(C—$C_{Ar-conj}$), 1460 (s), 1430 (m) $\delta_{as}(CH_2)$ or thiophene absorption, 1245 (m) γ(C—C—H_{trans}), 930 (vs) ω(C—C—H_{trans}). ^{1}H NMR ($CDCl_3$) δ(ppm) = 6.50–7.00 (m, 20H, aromatic protons), 2.79 (m, 8H, H_2C—Th), 1.66 (m, 8H, H_2C—H_2C—Th), 1.40 (m, 8H, H_2C—(H_2C)$_2$—Th), 0.93 (t, 6H, J = 8 Hz, H_3C—); MS (m/z); 794 (100) (M^+); 397 (18) (M^{2+}); 751 (3) (M^+—C_3H_7), 369 (73) $(C_{21}H_{21}S_3)^+$ and UV ($CHCl_3$) (λ(nm)/log ε): 265 (3.76), 315 (3.49), 327 (3.61), 403 (4.43), *422* (4.71), 447 (4.47).

The compounds **18** (colourless crystals), **19** (light brown crystals) and **21** (deep red crystals) were synthesized in the same manner. The synthesis of the bis Wittig salt is described in the literature.[15]

Further details of the synthesis are described in a previous paper.[9] The spectroscopic data of the compounds not described here are in agreement with the given spectroscopic data.

RESULTS AND DISCUSSION

The thermal behaviour of the compounds determined by DSC and polarizing microscopy is listed in Table I and II. The DSC-curve of **20** is shown in Figure 5. The derivatives with two thiophene rings (**1–5**) or one thiophene and one benzene ring (**10, 19** and **22**) in each core show also by variation of the inner chain length no liquid crystalline phases (Table II and III). Only compound **18** having two stilbene systems (each two benzene rings) connected by a hexamethylene chain shows an enantiotropic nematic phase. The minimum number of aromatic rings in each mesogenic group at which the compounds with thiophene rings or thiophene and benzene rings melt to give liquid crystalline phases is therefore three (compound **6–9**, **11–13**, **15–17** and **20**). Herein the formation of mesophases is mostly independent of the degree of thiophene rings in the core. Only compound **14** with three thiophene rings in each core and 12 methylene groups has no liquid crystalline phases. Moreover, we noticed that the mesogenic group E,E-bis(2-thienylvinyl)thiophene melts to mesophases only when two of these are connected via an alkylene spacer (see compound **20** and **23**). Nevertheless a comparison between the compounds **12**, **9** and **14** which all have a dodecamethylene chain and no terminal groups shows that with the increasing number of thiophene rings (one, two, three) in each core, the temperature range of the liquid crystalline phase decreases. Additionally, the transition temperatures of the compounds decrease with increasing numbers of thiophene rings (**12**, **9** and **14**).

The tendency of the formation of a more highly ordered smectic mesophases decreases with increasing numbers of thiophene rings in the cores. It is an open question why subtituting thiophene for benzene rings promotes nematic phases. Neither are smectic phases formed by increasing the inner chain length of the

TABLE II

Thermodynamic Properties of the Compounds **1–10** and all-E-1.4-bis[5-(4-styrylstyryl)-2-thienyl]butane (**11**), all-E-1.12-bis[5-(4-styrylstyryl)-2-thienyl]dodecane (**12**) from DSC Studies; on Heating and Cooling (* = in case of monotropic phases) and Polarizing Microscopy; ** = Veryfied only by Microscopy; dec. = Decomposition

Compound	n	Transition	Temperature °C	ΔH kJ/mol	ΔS J/°C.mol
1	4	C–I	136	0.1	122.2
2	6	C–I	129	51.3	127.3
3	7	C–I	99	27.7	74.4
4	8	C–I	126	55.6	139.0
5	12	C_1–C_2	113	2.0	5.1
		C–I	117	67.1	171.2
6	4	C–N	283	33.6	60.3
		N–I(dec.)	289	(3.2)	(5.7)
7	7	C–N	253	57.2	108.6
		N–I	265	2.5	4.6
8	8	C–N	246	61.3	118.1
		N–I	260	2.4	4.5
9	12	C–N	235	70.4	138.4
		N–I	241		
		I–N	241	3.6*	7.0*
		N–S_A**	228		
		S_A–C**	219		
10	4	C–I	152	34.1	80.1
11[11]	4	C–N	288	52.5	93.4
		N–I	316	(3.1)	(5.3)
12[11]	12	C–S_2	238	7.1	13.4
		S_2–S_A	240	36.1	73.1
		S_A–N	242	8.4	16.4
		N–I	247	5.4	10.4

compounds (**13**, **14** or **15–17**). Only compound 9 with 12 methylene groups in the connecting chain and two thiophene rings and one benzene ring in the core shows a monotropic smectic A phase.

Compound **21** (with four thiophene rings in each core) has a nematic phase. But in contrast to compound **24** (with only one core), **21** decomposes shortly above the melting point. As to the design of segment-chain liquid crystalline polymers, these results lead to the assumption that mesogenic groups with three thiophene rings is particularly suitable because they are mesogenic and melt without decomposition in the mesophase.

As shown by a few examples, the transition temperatures of the compounds are quite dependent on the positions of the thiophene rings in the cores. Normally, the melting points of the compounds are depressed by attaching the cores directly at the alkylene chain via a thiophene ring and not a benzene ring. The following example may illustrate this. The compounds **2** and **22** (cores are bound via the thiophene ring) have a lower melting point that **19** (cores are bound via the benzene ring). Substituting the thiophene rings at the terminal positions of the compounds causes only a small effect of the transition temperatures. So for example the melting point of **2** [with the 5(2-thienyl-

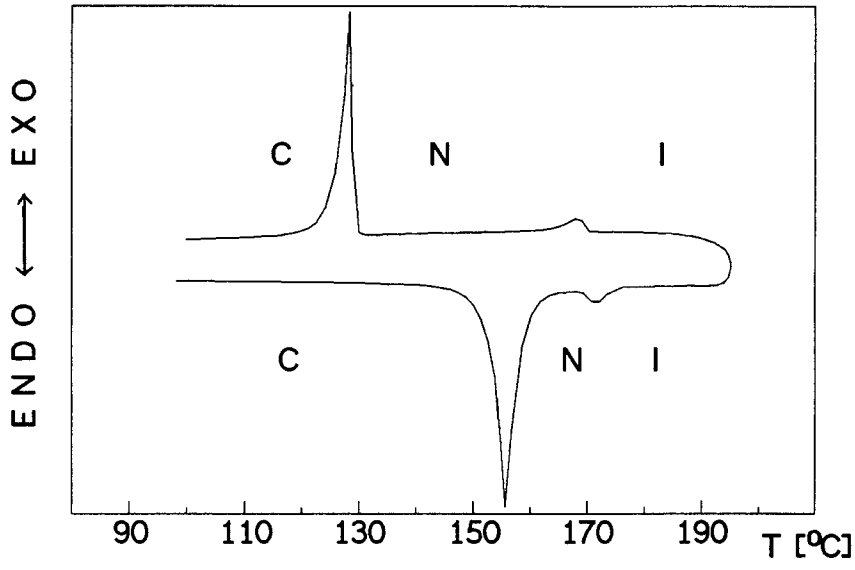


FIGURE 5 DSC curve of **20** (6 methylene groups)—heating and cooling rate 10°C/min.

TABLE III

Thermodynamic Properties of the Compounds **13–21**, E,E-1.6-bis(5-styryl-2-thienyl)-hexane (**22**) and E,E-2.5-bis(5-butyl-2-thienylvinyl)thiophene (**23**), all-E-1.2-bis[5-(5-butyl-2-thienylvinyl)-2-thienyl]ethylene (24); on Heating and Cooling (* = in case of Monotropic Phases); dec. = Decomposition

Compound	n	Transition	Temperature °C	ΔH kJ/mol	ΔS J/°C.mol
13	6	C_1–C_2	144	6.0	14.4
		C_2–I	173	54.3	121.7
		I–N	160	2.4	5.5
		N–C	149		
14	12	C–I	148	74.8	177.2
15	6	C–N	186	62.98	137.2
		N–I	209	2.2	4.6
16	7	C–N	106	27.3	71.9
		N–I	154	4.0	9.3
17	12	C–N	138	68.95	167.8
		N–I	160	4.0	9.2
18	6	C–N	206	26.0	54.2
		N–I	226	1.7	3.4
19	6	C_1–C_2	134	5.2	12.7
		C_2–I	189	49.8	107.6
20	6	C–N	154	68.19	159.7
		N–I	169	3.3	7.5
21	6	C_1–C_2	164	3.1	7.0
		C_2–N (dec.)	197	(60.5)	(128.6)
22[12]	6	C–I	129		
23[3]		C–I	88	30.4	84.2
24[13]		C–N	158	30.2	70.1
		N–I	199	0.4	0.9

vinyl)-2-thienyl unit] and **22** (with the 5-styryl-2-thienyl unit) are equal and the deviation of the transition points of **6** {with the 5-[4-(*2-thienyl*vinyl)stryryl]-2-thienyl unit) and **11** [with 5-(*4-styryl*styryl)-2-thienyl unit] or **9** (with the same core as **6**) and **12** (with the same core as 11) are small. One reason for this thermal behaviour may be the different geometrical arrangements by the thiophene and benzene rings. In contrast to the 1.4 disubstitution of the benzene ring by the 2.5 disubstitution of the thiophene rings a bend is introduced in the molecule shape (see above). This indicates, e.g., for the compounds **19** and **22** different angles between the mesogenic group E-2-styryl-thiophene and the hexamethylene spacer in both positions.

The stability of the mesophases normally is enhanced by attaching terminal groups ($R \neq H$, see Figure 1) at each core. Compound **13** shows only a monotropic nematic phase while compounds **15** ($R = CH_3$, see Figure 3) and **20** ($R = C_4H_9$, see Figure 4) have enantiotropic nematic phases. Herein compound **15** has the mesophase with the most extended temperature range. Moreover, a comparison between **14** and **17** shows that only **17** with terminal methyl groups has a liquid crystalline phase. It is obvious that the nematic–isotropic transition temperature increases markedly with the substitution of the terminal methyl groups at the cores. These results which agree with studies done by Hogan *et al.*[10] may be reasonable by the fact that in contrast to alkylene chains with more than one C-atom, the methyl group is a rigid segment. The substitution of the methyl group at the mesogenic group should therefore enhance the length/breadth ratio of the rigid moieties. The larger value for this ratio causes the higher transition temperatures.

SUMMARY

Compounds which have two mesogenic groups with and without terminal alkyl chains containing thiophene or benzene rings (see Figure 1), were prepared from various dialdehydes and bis Wittig salts (see Figures 2–4). Mesogenic groups involving two thiophene rings do not have liquid crystalline phases. Only the compounds with three or four aromatic rings in each mesogen show mostly enantiotropic nematic phases. But those compounds with four aromatic rings decompose rapidly in the mesophase. The formation of mesophases of the compounds is enhanced by substituting the thiophene ring for benzene rings or by attaching terminal methyl or butyl groups at the mesogens. This phenomenon can be explained by geometrical arrangements in the compounds. The compounds show no high tendency to melt in smectic phases.

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