Liquid Crystalline Compounds in the Thiophene Series, Part 6*
Synthesis and Characterization of Azomethines and Vinylenes with Two Mesogenic Groups and Different Alkylene Spacer Lengths

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Liquid Crystalline Thiophene Compounds, Azomethines, Azomethines with LC-Phases, Vinylenes with LC-Phases, Mesogenic Groups

Compounds which have two mesogenic groups with and without terminal alkyl chains containing thiophene systems, were prepared from \( \alpha,\omega \)-bis(5-formyl-2-thienyl)alkanes (\( 3a \sim 3n \)) and various aromatic amines or 2-fluorenyl-Wittig-salt (10). The liquid crystalline properties of these compounds were characterized by differential scanning calorimetry (DSC) and polarizing microscopy. Only the series of \( \alpha,\omega \)-bis[5-\( \left( 1,1 \right) \)-butyloxybiphenyl-4-yl]-iminoformyl-2-thienyl]alkanes (\( 7a \sim 7l \)) showed enantiotropic smectic and nematic mesophases. The series of E.E-\( \alpha,\omega \)-bis(2-fluorenylvinyl)-2-thienyl]alkanes (\( 8a \sim 8l \)) showed enantiotropic nematic mesophases for the compounds with 4 and 6 methylene groups, monotropic nematic mesophases for the compounds with 7–12 methylene groups and no liquid crystalline phases for compounds with 3, 5, 16 methylene groups in the connecting alkylene chain. In contrast to the compounds \( 8a \sim 8l \), E-1-(5-butyl-2-thienyl)-2-(2-fluorenyl)ethene has a smectic mesophase.

Introduction

The majority of thermotropic liquid crystalline compounds are molecules with a rigid core attached to which are one or more alkyl chains. These flexible groups are appended to lower the melting point and so enhance the range of the mesophase. In addition, there are molecules which have two rigid cores connected by an alkylene chain with differing numbers of methylene groups. They can additionally be attached by terminal alkyl chains (see Scheme 1). These types of compounds were first investigated by D. Vorländer [1] and his co-workers. Further theoretical and experimental investigations were first carried out at the beginning of the eighties [2–4]. Sometimes these compounds are named “dimers”. In our group, such compounds with thiophene systems were synthesized, characterized and studied for their thermal behaviour, but they were still not liquid crystalline [5]. In this paper liquid crystalline compounds are reported with two mesogenic groups containing thiophene systems which seem to be the first liquid crystalline materials with heteroaromatic systems of this structural type.

Synthesis

The synthesis of the \( \alpha,\omega \)-bis(2-thienyl)alkanes (\( 2a \sim 2l \)) is well known by the reduction of the corresponding \( \alpha,\omega \)-bis(2-thienyl)alkane-\( \alpha,\omega \)-diones [16] (\( 1a \sim 1j \)) (Wolf-Kishner-reduction – see Scheme 2) [6, 7]. This reaction is only possible for compounds with more than three methylene groups between the carbonyl units. So for example this can be illustrated for 1,4-bis(2-thienyl)butane-1,4-dione (1b), where the pyridazine-derivative has been isolated (see Scheme 2, compound 9) [14, 15]. The alkanes \( 2a \sim 2h \) are also available by a direct step reacting freshly distilled thiophene with butyllithium and \( \alpha,\omega \)-dibromoalkanes (with 3 to 10 methylene groups) in absolute tetrahydrofurane (see Scheme 2).

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Scheme 1. Schematic formula of compounds containing one mesogenic group or two mesogenic groups with or without terminal alkyl chains.


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In contrast to the Wolf-Kishner-reduction, this last mentioned synthesis leads easily to the \( \alpha,\omega \)-bis(2-thienyl)alkanes with three or four methylene groups in the connecting alkylene chain (2a and 2b). The higher homologous compounds with 5–10 methylene groups were also available in good yields. For the reaction of the \( \alpha,\omega \)-dibromomalkanes with 1, 2 and 16 methylene groups this way was not successful. The compounds with 11, 12 and 16 methylene groups, were prepared by the Wolf-Kishner-reduction of the corresponding diones (1g, 1h and 1j). The purification of the resulting \( \alpha,\omega \)-bis(2-thienyl)alkanes was carried out either by liquid chromatography (neutral Al\(_2\)O\(_3\)/hexane) or vacuum distillation.

The \( \alpha,\omega \)-bis(5-formyl-2-thienyl)alkanes (3a–3n) were synthesized from \( \alpha,\omega \)-di(2-thienyl)alkanes (2a–2l) by dilithiation in their \( \alpha \)-positions and through reaction with dimethylformamide (see Scheme 2) [8]. The dialdehydes 3a, 3c or 3e with 3, 5 or 7 methylene groups, are available very pure by hydrolysis of the corresponding bis(azomethine)s 4a, 4b or 4c (see below) with dilute HCl.

In order to transform the dialdehydes 3c–3n into the azomethines 4a–4d, 5a and 5b, 6a–6d, 7a–7l, the educts 3c–3n (see Scheme 3) and aromatic amines were refluxed for about eight hours in absolute xylene or ethanol. The products precipitated and were to be purified by recrystallization from absolute THF and absolute ethanol. The aromatic amines required for the preparation of Schiff’s bases were either commercially available or were prepared using standard methods. 4-amino-4′-butyloxy-biphenyl was synthesized by the method of Young et al. [17].

The homologous series of the divenylenes 8a–8l were synthesized from the dialdehydes 3c–3n and 2-fluorenymethyltriphenylphosphonium bromide (10) [18] in absolute ethanol, methanol, DMF of their mixtures with the base Li-methanolate or K-tert-butanolate (see Scheme 3). Mostly the yields of the compounds 8a–8l are achieved irrespective of the chosen base and solvent. K-tert-butanolate is not a favourable agent for the preparation of 8a–8l in contrast to the base Li-methanolate traces of fluorenone derivatives were formed as can be seen from the MS-spectrum of the unpurified products 8a–8l. However this fluorenone derivative also can be separated from the product by liquid chromatography.

The E/Z-isomers arising from the synthesis were transformed to pure E,E-products by refluxing the mixture of the isomers with a catalytic amount of iodine in absolute toluene. More purification was reached by recrystallization from CHCl\(_3\)/ethanol-mixtures.
Scheme 3. Synthesis of the \( \alpha,\omega \)-bis\{5-\([N-(phenyl)imino]formyl\)-2-thienyl\}alkanes \( 4a-4d \), the \( \alpha,\omega \)-bis\{5-\([N-(4-buty lphenyl)imino]formyl\)-2-thienyl\}alkanes \( 5a, 5b \), the \( \alpha,\omega \)-bis\{5-\([N-(2-fluorenyl)imino]formyl\)-2-thienyl\}alkanes \( 6a-6c \), the \( \alpha,\omega \)-bis\{5-\([N-(4'-butylo xybiphenyl-4-yl)imino]formyl\)-2-thienyl\}alkanes \( 7a-7l \) and the \( \alpha,\omega \)-bis\{5-(2-fluorenylviny l)-2-thienyl\}alkanes \( 8a-8l \).

Results

The melting points of the dialdehydes \( 3a-3n \) are listed in Table I and are shown in Fig. 1. It can be seen that as the numbers of methylene groups in the connecting alkylene chain increase, the melting points (m.p.) show an “even-odd effect”; so the m.p. for odd numbers of methylene groups in the alkylene chain is low and for even numbers high. Comparable 5-alkyl-2-formyl-thiophenes are fluid at room temperature \([10-12]\).

The Bis(azomethines) \( 4a-4d, 5a, 5b \) and \( 6a-6c \) melt while heating normally from the solid to the isotropic state, or they decompose \( 6a \) with

Fig. 1. Phase diagram of the \( \alpha,\omega \)-bis(5-formyl-2-thienyl)alkanes \( 3a-3n \) with different chain lengths \( n, \gamma = \text{transition temperature crystal} \rightarrow \text{isotropic}; \) the m.p. of the homologous compounds with 1 and 2 methylene groups in the chain are taken from literature \([8, 9]\).
Table I. Thermal transitions of the α,ω-bis(5-formyl-2-thienyl)alkanes (3a–3n) with different chain lengths n.

| Comp. | n  | t.t.h. [°C] | t.t.c. [°C] | ΔH$_h$ [kJ/mol] | ΔS$_h$ [J/K mol] | A  
|-------|----|-------------|-------------|----------------|----------------|------
| 3a    | 8  | 1 C 95 I    |             |                |                |      
| 3b    | 9  | 2 C 137 I   |             |                |                |      
| 3c    | 10 | 3 C 32 I    |             |                |                |      
| 3d    | 11 | 4 C 161 C   |             |                |                |      
| 3e    | 12 | 5 C 192 I   |             |                |                |      
| 3f    | 13 | 6 C 186 I   |             |                |                |      
| 3g    | 14 | 7 C 411 I   |             |                |                |      
| 3h    | 15 | 8 C 49 I    |             |                |                |      
| 3i    | 16 | 9 C 551 I   |             |                |                |      
| 3k    | 17 | 10 C 1041 I |             |                |                |      
| 3l    | 18 | 11 C 551 I  |             |                |                |      
| 3m    | 19 | 12 C 1061 I |             |                |                |      
| 3n    | 20 | 13 C 861 I  |             |                |                |      

4 methylene groups). The solidification point which is the temperature where the sample solidified from the isotropic or nematic phase to the solid state (cooling rate 10 K/min), is mostly lower than the m.p. For the diazomethine 6b with 10 methylene groups, it is possible (while rapidly cooling the substance - cooling rate 20 K/min) to induce a monotropic nematic phase (see Table II). The mesophases of 6b were observed through a microscope. Generally, the melting enthalpies and entropies for the compounds 3a–3n, 4a–4d, 5a, 5b and 6a–6c rise with increasing length of the alkylene chains between the aromatic units and show “even-odd effects” for the compounds which possess an even-length spacer of a higher value.

The varying phase behaviour of 7a–7l and 8a–8l is shown in Fig. 2 and 3. The diazomethines 7a–7l form enantiotropic nematic phases and smectic phases (odd members with 7, 9 and 11 methylene groups). The monotropic smectic phases arise while “supercooling” the sample (see Table III). The divinylene 8b and 8d (with 4 and 6 methylene groups) are enantiotropic nematic, 8e–8k (with 7–12 methylene groups) monotropic nematic and 8a, 8c and 8l (with 3, 5 and 16 methylene groups) not liquid crystalline (see Table IV). The nematic phases were assigned from their schlieren optical texture. While in the 7 series the

Table II. Thermal transitions of the α,ω-bis{5-[N-(phenyl)iminio]formyl-2-thienyl}alkanes (4a–4d), the α,ω-bis{5-[N-(4-butylphenyl)iminio]formyl-2-thienyl}alkanes (5a and 5b) and the α,ω-bis{5-[N-(2-fluorenyl)iminio]formyl-2-thienyl}alkanes (6a–6c) with different chain lengths n and the model compounds 4-(5-alkyl-2-thienylmethylideneamino)butylbenzenes and 2-(5-pentyl-2-thienyl-methylideneamino)fluorenes.

<table>
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<th>Comp.</th>
<th>n</th>
<th>t.t.h. [°C]</th>
<th>t.t.c. [°C]</th>
<th>ΔH$_h$ [kJ/mol]</th>
<th>ΔS$_h$ [J/K mol]</th>
<th>t.t.h. of the model compounds</th>
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<td></td>
<td></td>
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<td>11.3</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>I 150 C'</td>
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<td></td>
<td></td>
<td>C'2 136 C'</td>
<td></td>
<td>162.1</td>
<td></td>
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<th>ΔH$_h$ [kJ/mol]</th>
<th>ΔS$_h$ [J/K mol]</th>
<th>t.t.h. of the model compounds</th>
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Table III. Thermal transitions of the $\alpha, \omega$-bis[5-[(4'-alkyloxybiphenyl-4-yl)imino]formyl-2-thienyl]alkanes (7a–7l) with different chain lengths $n$ and the model compounds 5-[N-(4'-alkyloxybiphenyl-4-yl)imino]formyl-2-methylthiophenes.

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<th>Comp.</th>
<th>$n$</th>
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<td>165.8</td>
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<td></td>
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<td>I 232 N</td>
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<td>7j</td>
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<td>I 220 N</td>
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<td>N 221 I</td>
<td>I 220 N</td>
<td>5.2</td>
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<tr>
<td>7l</td>
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<td></td>
<td></td>
<td>N 195 I</td>
<td>I 194 N</td>
<td>5.8</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N 165 C</td>
<td></td>
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</tr>
</tbody>
</table>

t.t.$_h$ = transition temperature while heating, t.t.$_c$ = transition temperature while cooling, $\Delta H_h$ = transition enthalpy while heating, $\Delta S_h$ = transition entropy while heating, C = crystal, I = isotropic, N = nematic, S = smectic, dec. = decomposition, * = only verified by microscopy, ** = verified by gauss-fit of the DSC curve.
number of methylene groups increases, the m.p. and the nematic-isotropic transition temperatures decrease with alteration (see Fig. 2). In the 8 series, the m.p. decreases continuously and the isotropic-nematic transition temperatures for the compounds with 4 to 11 methylene groups in the chain have an "even-odd effect". The homologous compounds with short alkylene chains decomposed rapidly (7a and 7b with 3 and 4 methylene groups and 8a with 3 methylene groups). All compounds of the series 7 and 8 are not thermally stable over longer heating times.

**Discussion**

As shown for the compounds with two mesogenic groups (compounds 8a-8l) and E-1-(5-butyl-2-thienyl)-2-(2-fluorenyl)ethylene (11), the thermal behaviour is quite different. In contrast to compound 11 which melts only with a smectic mesophase, the compounds of the series 8 are generally nematic liquid crystalline. Although the coupling between the mesogenic cores in this series decreases by increasing chain lengths, no tendency for the mesogenic groups to form higher ordered mesophases was observed. Moreover, for 8a-8l, the effect of the alkylene spacer on the mesophase is more dramatic for shorter alkylene chains. By small, odd members of the series 8 (8a and 8c with 3 and 5 methylene groups) no liquid crystalline mesophase was observed, while for small even members (8b and 8d with 4 and 6 methylene groups) the nematic enantiotropic phases exist over a wide temperature range. This fact could be explained schematically by different arrangements of the cores caused by different chain lengths in the

**Table IV. Thermal transitions of the E,E-ω,ω-bis[5-(2-fluorenyl)vinyl]-2-thienylalkanes (8a-8l) with different chain lengths n and the model compound E-1-(5-butyl-2-thienyl)-2-(2-fluorenyl)ethylene.**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>n</th>
<th>t.t.h [°C]</th>
<th>t.t.c [°C]</th>
<th>ΔH_b [kJ/mol]</th>
<th>ΔS_b [J/°C·mol]</th>
<th>t.t.h of the model compounds</th>
</tr>
</thead>
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<tr>
<td>8a</td>
<td>3</td>
<td>C 276 I (dec.)</td>
<td></td>
<td>(50.5)</td>
<td>(92.0)</td>
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<tr>
<td>8b</td>
<td>4</td>
<td>C 249 N</td>
<td>N 226 C</td>
<td>45.0</td>
<td>86.2</td>
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<tr>
<td></td>
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<td>N 276 I</td>
<td></td>
<td>3.0</td>
<td>5.5</td>
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</tr>
<tr>
<td>8c</td>
<td>5</td>
<td>C 240 I</td>
<td>I 232 C</td>
<td>51.1</td>
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</tr>
<tr>
<td>8d</td>
<td>6</td>
<td>C 227 N</td>
<td>N 234 I</td>
<td>48.2</td>
<td>96.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 207 C</td>
<td></td>
<td>1.5</td>
<td>3.0</td>
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</tr>
<tr>
<td>8e</td>
<td>7</td>
<td>C 223 I</td>
<td>I 218 N</td>
<td>54.2</td>
<td>109.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 208 C</td>
<td></td>
<td>2.5*</td>
<td>5.1*</td>
<td></td>
</tr>
<tr>
<td>8f</td>
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<td>C 222 I</td>
<td>I 230 N</td>
<td>51.7</td>
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<tr>
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<td>I 209 N</td>
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<td></td>
<td>N 195 C</td>
<td></td>
<td>2.9*</td>
<td>6.0*</td>
<td></td>
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<tr>
<td>8h</td>
<td>10</td>
<td>C 213 I</td>
<td>I 214 N</td>
<td>61.4</td>
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<tr>
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<td>N 195 C</td>
<td></td>
<td>4.4*</td>
<td>9.0*</td>
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<tr>
<td>8j</td>
<td>11</td>
<td>C 206 I</td>
<td>I 203 N</td>
<td>61.1</td>
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<td></td>
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<td>N 193 C</td>
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<td>2.5*</td>
<td>5.3*</td>
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<td>12</td>
<td>C 201 I</td>
<td>I 195 N</td>
<td>48.1</td>
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<tr>
<td></td>
<td></td>
<td>N 189 C</td>
<td></td>
<td>3.1*</td>
<td>6.6*</td>
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<td>8l</td>
<td>16</td>
<td>C 196 I</td>
<td>I 189 C</td>
<td>66.8</td>
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</table>

* t.t.h = transition temperature while heating, t.t.c = transition temperature while cooling, ΔH_b = transition enthalpy while heating (* = while cooling), ΔS_b = transition entropy while heating (* = while cooling), C = crystal, I = isotropic, N = nematic, S = smectic, dec. = decomposition.
alkylene spacer. Scheme 4 illustrates the structures of 8a and 8b where the mesogenic core possesses the most linear structure in the case of s-trans-conformation. It could be argued that from the stereochemical point of view, the two cores in 8b have a higher tendency of parallel orientation of the molecules because of an approximative linear structure than in the case of 8a. This view of argumentation therefore predicts that the majority of C—C—C bonds in the chain are anti-co-planar, which is the most stable conformation. This assumption though, cannot be regarded as being wrong, as can be seen by Kloczikowski’s theoretical studies [23] and Bartolino’s X-ray and optical studies [24] where in the mesophase of compounds with free rotating alkyl chains at the core, the effective chain length is statistically, on the whole, to the all-anti-co-planar conformation. The formation of liquid crystalline phases by the compounds 8e, 8g and 8j is possible because the intramolecular coupling strength decreases with increasing chain length. However, all compounds of the series 8 are good examples of a significant influence of the alkylene spacer on the mesophase of those compounds with two mesogenic groups. Nevertheless, in the series 7, a notable influence by the alkylene chain was also detected, so only the compounds with longer alkylene chains and odd numbers of methylene groups (7e, 7g and 7j with 7, 9 and 11 methylene groups) are able to form while cooling the sample monotropic smectic mesophases. This is particularly the case for 7g with 9 methylene groups where the ratio of the lengths of the spacer and the core is good for the formation of higher ordered mesophases over a wide temperature range. It is obvious that only the homologous compounds with odd members of methylene groups show smectic mesophases. If in compounds there are only benzene systems in the mesogenic group the appearance of smectic phases is promoted by spacers with even chain length [25]. All these results agree with care out the studies done by Griffin et al. [2] or Emsley and Luckhurst [3]. They concluded that the mesophase behaviour of liquid crystalline compounds is more influenced by the alkylene spacer than by terminal groups attached at one core.

The “even-odd effect”, which is evidently for the transition temperatures of the series 7 and 8, can not be observed for the transition enthalpies or entropies. So in contrast to the transition enthalpies \( \Delta H_{C\rightarrow N} \) which is to be observed by the transition from the crystal to the nematic phase, the enthalpies \( \Delta H_{N\rightarrow I} \), which can be measured by the transition from the nematic to the isotropic phase show for the series 7 and 8 no pattern of behaviour (see Fig. 4). So the enthalpies \( \Delta H_{N\rightarrow I} \) are more constant for 7a–7l (around 5 kJ/mol) independent of the number of the methylene groups and for 8a–8l they are without any regularity. This result has to be questioned because investigations described in literature for compounds with two mesogenic groups, but without thiophene systems principally demonstrated an “even-odd effect” for the \( \Delta H_{N\rightarrow I} \) values [13]. So the influence of thiophene systems on the mesophase seems to be more
evident than differences caused by even or odd numbers of methylene groups in the inner chain.

Generally the liquid crystallinity of a compound is provided by the length to breadth ratio of the core. So we can observe for bis(azomethine)s in the series 5 with one thiophene and one benzene system in the core no mesophase, in the series 7 with one thiophene and one biphenyl system in the core for all homologous compounds enantiotropic mesophases. Moreover in the series 7 in contrast to the series 5 polarizing groups like the oxygen-bonds in the terminal chains could stabilize the mesophase of the compounds.

Experimental Part

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). The mass spectra were measured with a Varian MAT-112-S instrument. The elemental analysis were performed with a Perkin-Elmer-580-B instrument. The determination of the phase transition temperatures and enthalpies. Optical investigations were carried out with a Zeiss polarization microscope using a Linca heating regulation system.

General synthesis of the α,ω-di(2-thienyl)alkanes (2a-21) by nucleophile substitution

20.00 g (0.24 mol) thiophene were dissolved in 100 ml absol. tetrahydrofurane under an argon atmosphere. After the addition of 145 ml 15% butyllithium in hexane (0.24 mol) the resulting mixture was refluxed for 1 h (the solution turned to orange). After cooling to $-56 \, ^\circ \text{C}$ with an acetone-dry ice-mixture a solution of 0.096 mol of the corresponding freshly distilled α,ω-dibromoalkane was added dropwise to the reaction mixture. During the reaction the solution became colourless, the alkanes 2a-21 precipitated, also LiBr is separated. For completing the reaction the mixture was stirred for additional 2 h at $-56 \, ^\circ \text{C}$, then 0.5 h at room temperature and at least 1 h at 50 $^\circ \text{C}$. The reaction solution was poured onto ice (500 ml), neutralized with diluted HCl and extracted three times with diethylether. The combined organic layers were washed with water and dried over Na$_2$SO$_4$. After evaporating the solvent the residue was distilled under vacuum.

1.3-Di(2-thienyl)propane (2a)

After distillation (b.p. 162 $^\circ \text{C}$/18 mm) colourless oil ($n_D^{20} = 1.5828$); yield: 14.00 g (70%).

**C$_{11}$H$_{12}$S$_{2}$** (208.3)  
Calcd C 63.41 H 5.80%,  
Found C 63.39 H 5.80%.

IR (KBr) $\nu$(cm$^{-1}$) = 3100 (w), 3075 (w) $\nu$(C–H Ar); 2930 (s), 2860 (s) $\nu$(C–H); 1535 (w) $\nu$(Ar–C = C); 1460 (m), 1440 (m) $\nu$(Th-aromat); 850 (m) $\delta$(C–H$_{th}$)$_{oop}$.

These absorptions are also typical for 2b-21.

$^1$H NMR (CDCl$_3$) $\delta$(ppm) = 7.07 (d, d, 2H, $J_{5-4} = 6$ Hz, $J_{5-3} = 1$ Hz, Th–H$_5$); 6.89 (d, d, 2H, $J_{5-4} = 6$ Hz, $J_{4-3} = 4$ Hz, Th–H$_4$); 6.75 (d, d, 2H, $J_{5-4} = 4$ Hz, $J_{3-5} = 1$ Hz, Th–H$_3$); 2.86 (t, 4H, $J_{1-2} = 8$ Hz, Th–CH$_2$); 2.03 (quintett, 2H, $J$ = 8 Hz, Th–CH$_2$–CH$_2$). – MS ($m/z$): 208 (34) (M$^+$); 124 (7) (C$_6$H$_5$S)$^+$; 111 (17) (C$_8$H$_7$S)$^+$; 98 (100) (C$_9$H$_6$S)$^+$.

1.4-Di(2-thienyl)butane (2b)

After distillation (b.p. 178 $^\circ \text{C}$/18 mm) colourless oil ($n_D^{20} = 1.5695$); yield: 10.20 g (48%).

**C$_{12}$H$_{14}$S$_{2}$** (224.4)  
Calcd C 64.82 H 6.35%,  
Found C 64.84 H 6.38%.

$^1$H NMR (CDCl$_3$) $\delta$(ppm) = 7.07 (d, d, 2H, $J_{5-4} = 6$ Hz, $J_{5-3} = 1$ Hz, Th–H$_5$); 6.89 (d, d, 2H, $J_{5-4} = 6$ Hz, $J_{4-3} = 4$ Hz, Th–H$_4$); 6.75 (d, d, 2H, $J_{5-4} = 4$ Hz, $J_{3-5} = 1$ Hz, Th–H$_3$); 2.86 (t, 4H, $J = 8$ Hz, Th–CH$_2$); 1.98 (m, 4H, Th–CH$_2$–CH$_2$). – MS ($m/z$): 222 (50) (M$^+$); 124 (26) (C$_6$H$_5$S)$^+$; 111 (21) (C$_8$H$_7$S)$^+$; 97 (100) (C$_9$H$_6$S)$^+$.

1.5-Di(2-thienyl)pentane (2c)

After distillation (b.p. 192 $^\circ \text{C}$/18 mm) colourless oil ($n_D^{20} = 1.5642$); yield: 14.00 g (62%).

**C$_{13}$H$_{16}$S$_{2}$** (236.4)  
Calcd C 66.05 H 6.82%,  
Found C 66.04 H 6.79%.

$^1$H NMR (CDCl$_3$) $\delta$(ppm) = 7.07 (d, d, 2H, $J_{5-4} = 6$ Hz, $J_{5-3} = 1$ Hz, Th–H$_5$); 6.89 (d, d, 2H, $J_{5-4} = 6$ Hz, $J_{4-3} = 4$ Hz, Th–H$_4$); 6.75 (d, d, 2H, $J_{5-4} = 4$ Hz, $J_{3-5} = 1$ Hz, Th–H$_3$); 2.86 (t, 4H, $J = 8$ Hz, Th–CH$_2$); 1.78 (m, 4H, Th–CH$_2$–CH$_2$). 1.34 (m, 6H, Th–(CH$_2$)$_2$–CH$_3$). This spectrum is simi-
lar to these of 2d–2h (contains six to ten methylenegroups). – MS (m/z): 236 (17) (M+); 123 (5) (C_{6}H_{7}S); 111 (17) (C_{5}H_{5}S); 97 (100) (C_{5}H_{5}S).

1.6-Di(2-thienyl)hexane (2d)

After distillation (b.p. 198–203 °C/18 mm) colourless oil (n_{D}^{20} = 1.5589); yield: 15.10 g (63%).

C_{14}H_{28}S_{2} (250.4)
Calcd C 67.15 H 7.24%
Found C 67.16 H 7.26%

MS (m/z): 250 (17) (M+); 123 (3) (C_{7}H_{7}S); 111 (15) (C_{6}H_{7}S); 97 (100) (C_{5}H_{5}S).

1.7-Di(2-thienyl)heptane (2e)

After distillation (b.p. 248 °C/9 mm) colourless oil (n_{D}^{20} = 1.5534); yield: 16.20 g (64%).

C_{16}H_{30}S_{2} (264.4)
Calcd C 68.13 H 7.62%
Found C 68.14 H 7.59%

MS (m/z): 264 (41) (M+); 123 (3) (C_{7}H_{7}S); 111 (24) (C_{6}H_{7}S); 97 (100) (C_{5}H_{5}S).

1.8-Di(2-thienyl)octane (2f)

After distillation (b.p. 265 °C/9 mm) colourless oil (n_{D}^{20} = 1.5475); yield: 18.10 g (68%).

C_{18}H_{36}S_{2} (278.5)
Calcd C 69.01 H 7.96%
Found C 69.03 H 7.96%

MS (m/z): 278 (41) (M+); 123 (4) (C_{7}H_{7}S); 111 (24) (C_{6}H_{7}S); 97 (100) (C_{5}H_{5}S).

1.9-Di(2-thienyl)nonane (2g)

After distillation (b.p. 230 °C/9 mm) colourless oil (n_{D}^{20} = 1.5415); yield: 15.70 g (56%).

C_{19}H_{40}S_{2} (292.5)
Calcd C 69.81 H 8.27%
Found C 69.83 H 8.29%

MS (m/z): 292 (20) (M+); 123 (3) (C_{7}H_{7}S); 111 (27) (C_{6}H_{7}S); 97 (100) (C_{5}H_{5}S).

1.10-Di(2-thienyl)decan (2h)

After distillation (b.p. 169 °C/0.7 mm) colourless oil (n_{D}^{20} = 1.5355); yield: 16.50 g (56.2%).

C_{18}H_{36}S_{2} (306.5)
Calcd C 70.53 H 8.55%
Found C 70.51 H 8.53%

MS (m/z): 306 (25) (M+); 123 (4) (C_{7}H_{7}S); 111 (20) (C_{6}H_{7}S); 97 (100) (C_{5}H_{5}S).

General synthesis of the α,ω-di(2-thienyl)alkanes (21–2l) by Wolf-Kishner-reduction

In a 2 l three-necked flask with reflux-condenser connected with a gas-outlet-tube, electric stirrer and distillation piece 0.164 mol α,ω-di(2-thienyl)-alkane-α,ω-dione [16] (1a–1l) and 60.00 g (1.2 mol) 100%-hydrazine hydrate were dissolved in 600 ml ethyleneglycol and heated for 2 h at 120 °C and then 3 h at 150 °C. While this heating procedure the water was distilled off. The reaction mixture was allowed to cool to room temperature while the hydrazone derivatives settled down as yellow crystals. For introducing the reduction a solution of 61.00 g (1.08 mol) KOH in 100 ml ethyleneglycol was added to the reaction mixture and the resulting solution was heated to 150 °C for 18 h. The end of the reaction can be seen with the end of the N_{2} development. The reaction solution was mixed with 11 l water and extracted three times with toluene. The toluene phase was dried with Na_{2}SO_{4} and distilled under vacuum. More purification of the product was done by chromatography (neutral Al_{2}O_{3}-Merck, column 30 cm, α = 3 cm, hexane).

1.11-Di(2-thienyl)undecane (2i)

From 14.00 g (0.04 mol) 1,11-di(2-thienyl)-undecane-1,11-dione, 15.00 g (0.3 mol) 100% hydrazine hydrate, 15.00 g KOH (0.27 mol) and 175 ml ethyleneglycol; colourless oil, yield: 7.50 g (59%).

C_{19}H_{42}S_{2} (320.6)
Calcd C 71.19 H 8.80%
Found C 71.17 H 8.81%

{^1}H NMR (CDCl_{3}) δ (ppm) = 7.07 (d, d, 2H, J_{5_4} = 6 Hz, J_{3_5} = 1 Hz, Th-H_{5}); 6.89 (d, 2H, J_{4_3} = 6 Hz, J_{4_5} = 4 Hz, Th-H_{4}); 6.75 (d, 2H, J_{3_4} = 4 Hz, J_{3_5} = 1 Hz, Th-H_{3}); 2.8 (t, 4H, J = 8 Hz, Th-(CH_{2})_{2}); 1.67 (m, 4H, Th-(CH_{2})_{2}-CH_{2}); 1.28 (m, 14H, Th-(CH_{2})_{2}-(CH_{2})_{4}).

This spectrum is similar to these of 2k and 2l.

MS (m/z): 320 (15) (M+); 97 (100) (C_{5}H_{5}S); 111 (29) (C_{6}H_{7}S); 153 (3) (C_{7}H_{7}S).

1.12-Di(2-thienyl)dodecane (2k)

From 60.00 g (0.164 mol) 1,12-di(2-thienyl)-dodecane-1,12-dione, 60.00 g (1.2 mol) 100% hydrazine hydrate, 61.00 g (1.08 mol) KOH and
700 ml ethyleneglycol; colourless crystals, m. p. 35 °C, yield: 30.00 g (58%).

C_{30}H_{30}S_2 (334.6)
Calcd C 71.80 H 9.04% ,
Found C 71.78 H 9.02%.

MS (m/z): 334 (14) (M⁺); 97 (100) (C₅H₅S)⁺; 111 (30) (C₆H₇S)⁺; 153 (3) (C₉H₁₃)⁺.

1,16-Di(2-thienyl)hexadecane (21)
From 1.30 g (4 mmol) 1,16-di(2-thienyl)hexadecane-1,16-dione, 1.45 g (29 mmol) 100% hydrazine hydrate, 1.50 g KOH (27 mmol) and 15 ml ethyleneglycol; colourless crystals, m. p. 45-47 °C, yield: 550 mg (46%).

C_{24}H_{38}S_2 (390.7)
Calcd C 73.78 H 9.80% ,
Found C 73.74 H 9.83%.

MS (m/z): 390 (16) (M⁺); 97 (100) (C₅H₅S)⁺; 111 (28) (C₆H₇S)⁺; 153 (4) (C₉H₁₃)⁺.

1.3-Di(5-formyl-2-thienyl)propane (3c)
From 20.00 g (0.096 mol) 2a, 145 ml 15% butyllithium solution in hexane (1.43 mol/l) and 35 ml DMF, light green crystals from ethanol/water; m. p.: 49 °C; yield: 12.1 g (48%).

C_{13}H_{12}O_7 S_2 (264.4)
Calcd C 59.06 H 4.58% ,
Found C 59.00 H 4.52%.

IR (KBr), v(cm) = 3100 (w) v(C-H Ar); 2930, 2830, 2860 (w-s) v(C-H); 1660 (vs) v(C=O); 1625 (sh) v(Ar-C=C); 1530 (w), 1460 (vs) v(aromat); 1225 (s) v(Ar-C=C); 820 (m) δ(Ar-C-H)oop.

These absorptions are also typical for these of 3e-3l.

1.4-Bis(5-formyl-2-thienyl)butane (3d)
From 20.00 g 2b (0.09 mol), 135 ml 15% butyllithium solution in hexane (1.43 mol/l) and 33 ml DMF, light green crystals from ethanol/water; m. p.: 96 °C; yield: 19.2 g (77%).

C_{14}H_{14}O_7 S_2 (278.4)
Calcd C 60.4 H 5.07% ,
Found C 60.1 H 5.02%.

1H NMR (CDCl₃) δ(ppm) = 9.84 (s, 2H, -CH=O); 7.64 (d, 2H, J = 3 Hz, Th-H₄); 6.94 (d, 2H, J = 3 Hz, Th-H₃); 2.85 (t, 4H, J = 7.5 Hz, Th-CH₂); 2.14 (quint. 2H, J = 7.5 Hz, Th-CH₂-CH₂). - MS (m/z): 278 (31) (M⁺); 152 (15) (C₃H₅OS)⁺; 139 (40) (C₂H₇OS)⁺; 126 (84) (C₆H₉OS)⁺; 111 (13) (C₇H₉OS)⁺. - UV (CHCl₃) λ(nm)/log ε: 265 (3.85), 297 (4.14).

This spectrum is similar to these of 3c-3l.

1.5-Bis(5-formyl-2-thienyl)pentane (3e)
From 20.00 g 2c (0.085 mol) 127 ml 15% butyllithium solution in hexane (1.43 mol/l) and 31 ml ethyleneglycol; colourless crystals, m. p. 35 °C, yield: 30.00 g (58%).

C_{30}H_{30}S_2 (334.6)
Calcd C 71.80 H 9.04% ,
Found C 71.78 H 9.02%.

MS (m/z): 334 (14) (M⁺); 97 (100) (C₅H₅S)⁺; 111 (30) (C₆H₇S)⁺; 153 (3) (C₉H₁₃)⁺.
DMF, light yellow crystals from ethanol/water m.p.: 33 °C; yield: 10.00 g (40%).

C₁₅H₁₆O₂S₂ (292.4)
  Calcd C 61.61 H 5.51% ,
  Found C 61.39 H 5.49% .

¹H NMR (CDCl₃) δ (ppm) = 9.82 (s, 2H, CH=O); 7.62 (d, 2H, J = 3 Hz Th–H₂); 6.9 (d, 2H, J = 3 Hz Th–H₂); 2.88 (t, 4H, J = 7.5 Hz Th–CH₂); 1.78 (m, 4H, Th–CH₂–CH₂); 1.45 (m, 2H, Th–(CH₂)₂–CH₂).

This spectrum is also typical for these of 3f–3i.

MS (m/z): 292 (13) (M⁺); 264 (19) (M–CO)⁺; 166 (3) (C₉H₁₀O⁺); 152 (3) (C₈H₈O⁺); 139 (40) (C₇H₇O⁺); 126 (32) (C₆H₆O⁺); 111 (12) (C₅H₃O⁺).

1.6-Bis(5-formyl-2-thienyl)hexane (3f)
From 20.00 g 2d (0.08 mol), 120 ml 15% butyl-lithium solution in hexane (1.43 mol/1) and 29 ml DMF, colourless crystals from ethanol/water, m.p.: 85 °C; yield: 19.30 g (79%).

C₁₆H₁₈O₂S₂ (306.4)
  Calcd C 62.71 H 5.92% ,
  Found C 62.49 H 5.90% .

MS (m/z): 306 (34) (M⁺); 278 (21) (M–CO)⁺; 166 (5) (C₉H₁₀O⁺); 152 (3) (C₈H₈O⁺); 139 (40) (C₇H₇O⁺); 126 (21) (C₆H₆O⁺); 111 (12) (C₅H₃O⁺).

1.7-Bis(5-formyl-2-thienyl)heptane (3g)
From 20.00 g 2e (0.076 mol), 113 ml 15% butyl-lithium solution in hexane (1.43 mol/1) and 28 ml DMF, colourless crystals from ethanol/water, m.p.: 37 °C; yield: 15.60 g (64%).

C₁₇H₂₀O₂S₂ (320.5)
  Calcd C 63.71 H 6.29% ,
  Found C 63.63 H 6.31% .

MS (m/z): 320 (51) (M⁺); 292 (16) (M–CO)⁺; 166 (6) (C₉H₁₀O⁺); 152 (4) (C₈H₈O⁺); 139 (4) (C₇H₇O⁺); 126 (48) (C₆H₆O⁺); 111 (20) (C₅H₃O⁺).

1.8-Bis(5-formyl-2-thienyl)octane (3h)
From 20.00 g 2f (0.072 mol), 108 ml 15% butyl-lithium solution in hexane (1.43 mol/1) and 26 ml DMF, colourless crystals from ethanol/water; m.p.: 99 °C; yield: 21.00 g (88%).

C₁₈H₂₂O₂S₂ (334.5)
  Calcd C 64.63 H 6.63% ,
  Found C 64.49 H 6.57% .

MS (m/z): 334 (24) (M⁺); 306 (4) (M–CO)⁺; 196 (4) (C₉H₁₀O⁺); 167 (7) (C₈H₈O⁺); 153 (4) (C₇H₇O⁺); 139 (39) (C₆H₆O⁺); 126 (27) (C₅H₃O⁺); 111 (18) (C₄H₃O⁺).

1.9-Bis(5-formyl-2-thienyl)nonane (3i)
From 21.00 g 2g (0.072 mol), 108 ml 15% butyl-lithium solution in hexane (1.43 mol/1) and 26 ml DMF, colourless crystals from ethanol/water; m.p.: 55 °C; yield: 19.30 g (77%).

C₁₉H₂₄O₂S₂ (348.5)
  Calcd C 65.48 H 6.94% ,
  Found C 65.39 H 6.97% .

MS (m/z): 348 (18) (M⁺); 320 (5) (M–CO)⁺; 210 (4) (C₉H₁₂O⁺); 187 (11) (C₈H₈O⁺); 153 (4) (C₇H₇O⁺); 139 (50) (C₆H₆O⁺); 126 (25) (C₅H₃O⁺); 111 (21) (C₄H₃O⁺).

1.10-Bis(5-formyl-2-thienyl)decane (3k)
From 15.00 g 2h (0.049 mol), 74 ml 15% butyl-lithium solution in hexane (1.43 mol/1) and 18 ml DMF, colourless crystals from ethanol/water m.p.: 104 °C; yield: 15.5 g (87%).

C₂₀H₂₆O₂S₂ (362.6)
  Calcd C 66.26 H 7.23% ,
  Found C 66.14 H 7.26% .

¹H NMR (CDCl₃) δ (ppm) = 9.82 (s, 2H, CH=O); 7.63 (d, 2H, J = 3 Hz Th–H₂); 6.93 (d, 2H, J = 3 Hz Th–H₂); 2.88 (t, 4H, J = 7.5 Hz Th–CH₂); 1.72 (m, 4H, Th–CH₂–CH₂); 1.4 and 1.36 (m, 12H, Th–(CH₂)₂–CH₂–CH₂–CH₂).

This spectrum is also typical for these of 3l–3n.

MS (m/z): 362 (16) (M⁺); 334 (5) (M–CO)⁺; 224 (4) (C₁₃H₁₀O⁺); 197 (9) (C₉H₈O⁺); 153 (5) (C₇H₇O⁺); 139 (41) (C₆H₆O⁺); 126 (21) (C₅H₃O⁺); 111 (25) (C₄H₃O⁺).

1.11-Bis(5-formyl-2-thienyl)dodecane (3l)
From 7.00 g 2i (0.022 mol), 33 ml 15% butyl-lithium solution in hexane (1.43 mol/1) and 8 ml DMF, colourless crystals from ethanol/water; m.p.: 55 °C; yield: 7.60 g (92%).

C₂₁H₂₈O₂S₂ (376.6)
  Calcd C 66.98 H 7.49% ,
  Found C 66.76 H 7.50% .

MS (m/z): 376 (26) (M⁺); 348 (4) (M–CO)⁺; 238 (4) (C₁₃H₁₂O⁺); 197 (9) (C₉H₈O⁺); 153 (4) (C₇H₇O⁺); 139 (60) (C₆H₆O⁺); 126 (31) (C₅H₃O⁺); 111 (22) (C₄H₃O⁺).
1.12-Bis(5-formyl-2-thienyl)dodecane (3m)

From 25.00 g 2k (0.075 mol), 112 ml 15% butyllithium solution in hexane (1.43 mol/l) and 27 ml DMF, colourless crystal from ethanol/water, m.p.: 106 °C; yield: 24.30 g (83%).

\[ \text{C}_{22}\text{H}_{30}\text{O}_{2}\text{S}_{2} \] (390.6)
Calcd C 67.65 H 7.74% ,
Found C 67.44 H 7.69% .

MS (m/z): 390(52) (M +); 362(6) (M - CO)+; 252 (3) (C_{15}F_{10}O_{5}S)+; 167(8) (C_{9}H_{6}O_{5}S)+; 153(4) (C_{8}H_{7}OS)+; 139 (67) (C_{7}H_{7}OS)+; 126(30) (C_{6}H_{6}O_{5}S)+; 111 (22) (C_{5}H_{3}O_{5}S)+.

1.16-Bis(5-formyl-2-thienyl)hexadecane (3n)

From 10.00 g 21 (0.0275 mol) 41.2 ml 15% butyllithium solution in hexane (1.43 mol/l) and 10 ml DMF, colourless crystals from ethanol/water, m.p.: 86 °C; yield 8.10 g (70%).

\[ \text{C}_{26}\text{H}_{38}\text{O}_{2}\text{S}_{2} \] (446.7)
Calcd C 69.90 H 8.57% ,
Found C 69.78 H 8.53% .

MS (m/z): 446(100) (M +); 418 (15) (M - CO)+; 252 (3) (C_{15}F_{10}O_{5}S)+; 167(8) (C_{9}H_{6}O_{5}S)+; 153(4) (C_{8}H_{7}OS)+; 139 (65) (C_{7}H_{7}OS); 126 (32) (C_{6}H_{6}OS); 111 (33) (C_{5}H_{3}O_{5}S).

General synthesis of the \( \alpha,\alpha'-\text{bis}[5-(\text{N-phenylimino})\text{methylidene}-2\text{-thienyl}]\)-alkanes (4a-4d), \( \alpha,\alpha'-\text{bis}[5-(\text{N}-4\text{-butylphenylimino})\text{methylidene}-2\text{-thienyl}]\)-alkanes (5a, 5b), \( \alpha,\alpha'-\text{bis}[5-(\text{N}-4\text{-butoxyphenyl-4-yl})\text{imino}]\text{methylidene-2-thienyl}]\)-alkanes (6a-6c), \( \alpha,\alpha'-\text{bis}[5-(\text{N}-2\text{-fluorenyl})\text{imino}]\text{methylidene-2-thienyl}]\)-alkanes (7a-7l)

For preparing the Schiff bases, the amino compounds and the dialdehydes were refluxed for 8 h in absol. xylene or absol. ethanol with drypearl (3 A) in an argon atmosphere. The reaction mixture was allowed to cool down to room temperature and the precipitate was filtered off by means of vacuum and recrystallized from absol. ethanol and then absol. tetrahydrofuran. The products were dried over \( \text{P}_{2}\text{O}_{5} \) in vacuum.

1.3-Bis(5-(N-phenylimino)methylidene-2-thienyl)-propane (4a)

From 2.38 g 3c (9 mmol) and 2.0 g (20 mmol) aniline in 50 ml absol. ethanol, colourless crystals from ethanol; m.p.: 88 °C; yield: 3.30 g (88%).

\[ \text{C}_{25}\text{H}_{32}\text{N}_{2}\text{S}_{2} \] (414.6)
Calcd C 72.43 H 5.35 N 6.76% ,
Found C 72.31 H 5.35 N 6.51% .

IR (KBr), \( \nu(\text{cm}^{-1}) = 3060, 3018 (\text{w}) \nu(\text{C-H Ar}); 2920 (s), 2840 (w), 1605 (vs) \nu(\text{C=N}); 1575 (vs), 1360 (w), 1270 (w) \nu(\text{Ar-C=H}). \)

**These absorptions are also typical for these of 4b-4d.**

1.5-Bis(5-(N-phenylimino)methylidene-2-thienyl)-pentane (4b)

From 2.63 g 3e (9 mmol) and 2.00 g (20 mmol) aniline in 50 ml absol. ethanol, colourless crystals from ethanol; m.p.: 75 °C; yield: 3.60 g (92%).

\[ \text{C}_{27}\text{H}_{32}\text{N}_{2}\text{S}_{2} \] (442.6)
Calcd C 73.26 H 5.92 N 6.33% ,
Found C 73.13 H 5.95 N 6.22% .

**This spectrum is also typical for this of 4c.**

MS (m/z): 442 (49) (M +); 221 (4) (M^{2+}); 365 (100) (M-C_{8}H_{5})^{+}; 214 (6) (C_{13}H_{12}NS)^{+}.

1.7-Bis(5-(N-phenylimino)methylidene-2-thienyl)-heptane (4c)

From 3.00 g 3g (9 mmol) and 2.00 g (20 mmol) aniline in 50 ml absol. ethanol; colourless crystals from ethanol; m.p.: 84 °C; yield: 3.6 g (81%).

\[ \text{C}_{29}\text{H}_{36}\text{N}_{2}\text{S}_{2} \] (470.7)
Calcd C 73.73 H 6.36 N 5.39% ,
Found C 73.65 H 6.31 N 5.24% .

**These absorptions are also typical for these of 4b-4d.**

1.1-Bis(5-formyl-2-thienyl)hexadecane (3n)

From 10.00 g 21 (0.0275 mol) 41.2 ml 15% butyllithium solution in hexane (1.43 mol/l) and 10 ml DMF, colourless crystals from ethanol/water, m.p.: 86 °C; yield 8.10 g (70%).

\[ \text{C}_{26}\text{H}_{38}\text{O}_{2}\text{S}_{2} \] (446.7)
Calcd C 69.90 H 8.57% ,
Found C 69.78 H 8.53% .

MS (m/z): 446 (100) (M^{+}); 418 (15) (M-CO)^{+}; 167 (11) (C_{9}H_{11}OS)^{+}; 153 (5) (C_{8}H_{2}OS)^{+}; 139 (65) (C_{7}H_{2}OS)^{+}; 126 (32) (C_{6}H_{2}OS); 111 (33) (C_{5}H_{2}OS).

1.5-Bis[5-(N-phenylimino)methylidene-2-thienyl]-pentane (4b)

From 2.63 g 3e (9 mmol) and 2.00 g (20 mmol) aniline in 50 ml absol. ethanol, colourless crystals from ethanol; m.p.: 75 °C; yield: 3.60 g (92%).

\[ \text{C}_{27}\text{H}_{32}\text{N}_{2}\text{S}_{2} \] (442.6)
Calcd C 73.26 H 5.92 N 6.33% ,
Found C 73.13 H 5.95 N 6.22% .

**This spectrum is also typical for this of 4c.**

MS (m/z): 442 (49) (M^{+}); 221 (4) (M^{2+}); 365 (100) (M-C_{8}H_{5})^{+}; 214 (6) (C_{13}H_{12}NS)^{+}.

1.7-Bis[5-(N-phenylimino)methylidene-2-thienyl]-heptane (4c)

From 3.00 g 3g (9 mmol) and 2.00 g (20 mmol) aniline in 50 ml absol. ethanol; colourless crystals from ethanol; m.p.: 84 °C; yield: 3.6 g (81%).

\[ \text{C}_{29}\text{H}_{36}\text{N}_{2}\text{S}_{2} \] (470.7)
Calcd C 73.73 H 6.36 N 5.39% ,
Found C 73.65 H 6.31 N 5.24% .

**These absorptions are also typical for these of 4b-4d.**
1.12-Bis[5-N-(phenylimino)methylidene-2-thienyl]-dodecane (4d)

From 3.50 g 3m (9 mmol) and 2.00 g (20 mmol) aniline in 50 ml absol. ethanol; colourless crystals from ethanol; m.p.: 105 °C; yield: 4.5 g (92%).

C₃₄H₄₀N₂S₂ (540.8)
Calcd C 75.51 H 7.45 N 5.18%,
Found C 75.51 H 7.46 N 5.17%.

¹H NMR (CDCl₃) δ (ppm) = 8.48 (s, 2H, -CH=N); 7.36 (dd, 4H, J₂₋₃ = J₃₋₄ = 8 Hz, BzH₂H₄); 7.3 (d, 2H, J₄₋₃ = 4 Hz, ThH₄); 7.24 (d, 2H, J₁₋₂ = 8 Hz, BzH₂H₄); 7.19 (d, 4H, J₂₋₃ = 8 Hz, BzH₂H₄); 6.84 (d, 2H, J₁₋₂ = 4 Hz, ThH₄); 2.86 (t, 4H, J = 5.3 Hz, CH₂-Th); 1.7 (m, 4H, CH₃-CH₂-Th); 1.4 and 1.36 (m, 16H, (CH₂)₄-(CH₂)₂-Th). - MS (m/z): 540 (100) (M⁺); 270 (23) (M²⁺); 463 (39) (M⁻-C₆H₅)⁺; 214 (47) (C₂₁H₁₂NS⁺).

1.6-Bis[5-(N-4-butylphenylimino)methylidene-2-thienyl]hexane (5a)

From 275.00 mg 3f (0.9 mmol) and 300.00 mg (2 mmol) 4-butylaniline in 50 ml absol. ethanol; colourless crystals from ethanol; m.p.: 101 °C; yield: 450 mg (89%).

C₃₆H₄₄N₂S₂ (568.9)
Calcd C 76.01 H 7.80 N 4.92%,
Found C 75.91 H 7.75 N 5.01%.

IR (KBr) cm⁻¹ = 3020 (w) ν (C-H Ar); 2950 (m), 2910 (vs), 2840 (s) ν (C-H); 1610 (s) ν (C=N); 1545 (w), 1500 (m) ν (Ar-C= C); 795 (s) < S (Ar-C-H)oop.

These absorptions are also typical for this of 5b.

¹H NMR (CDCl₃) δ (ppm) = 8.48 (s, 2H, -CH=N); 7.27 (d, 2H, J₂₋₃ = 3 Hz, Th-H₄); 7.17 (d, 4H, J₁₋₂ = 8 Hz, Bz-H₂H₄); 7.11 (d, 4H, J₂₋₃ = 8 Hz, Bz-H₂H₄); 6.78 (d, 2H, J₁₋₂ = 3 Hz, Th-H₄); 2.83 (t, 4H, J = 5.3 Hz, Th=CH₂); 2.58 (t, 4H, J = 6 Hz, Bz=CH₂); 1.7 (m, 4H, Th=CH₂=CH₂); 1.6 (m, 4H, Bz=CH₂=CH₂); 1.2 (m, 8H, Bz=CH₂=CH₂=CH₂); 0.93 (t, 6H, J = 5 Hz, CH₃).

This spectrum is also typical for this of 5b.

MS (m/z): 568 (100) (M⁺); 284 (11) (M²⁺); 539 (57) (M⁻-C₆H₅)⁺; 435 (88) (C₂₁H₁₂NS⁺); 257 (7) (C₁₆H₁₉NS⁺); 270 (12) (C₁₇H₂₁NS⁺). - UV (CHCl₃) λ (nm)/log ε: 268 (3.89), 312 (4.22), 339 (4.36).

1.4-Bis[5-(N-(2-fluorenyl)imino)methylidene-2-thienyl]butane (6a)

From 300.00 mg (1.08 mmol) 3d and 405.00 mg (2.24 mmol) 2-aminofluorene in 100 ml absol. xylene; green crystals from absol. THF; m.p. (decomp.): 244 °C; yield: 339.00 mg (52%).

C₄₀H₄₄N₂S₂ (604.8)
Calcd C 79.43 H 5.33 N 4.63%,
Found C 79.31 H 5.28 N 4.45%.

IR (KBr) cm⁻¹ = 3060 (w) ν (C=H Ar); 2920 (vs), 2850 (vs) ν (C-H); 1615 (m) ν (C=N); 1595 (s), 1400 (w), 1255 (vw) ν (Th-C= C); 805 (m) < S (Ar-C-H)oop.

This spectrum is similar to these for 6b and 6c.

MS (m/z): 604 (23) (M⁺); 440 (57) (M⁻-C₆H₅)⁺; 287 (8) (C₁₉H₁₃NS⁺). - UV (KBr) λ (nm)/log ε: 280 (4.77), 308 (4.73), 360 (4.86).

1.10-Bis[5-(N-(2-fluorenyl)imino)methylidene-2-thienyl]decane (6b)

From 300.00 mg (0.83 mmol) 3k and 311.00 mg (1.72 mmol) 2-aminofluorene in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 196 °C; yield: 223.00 mg (39%).

C₄₈H₅₂N₂S₂ (689.0)
Calcd C 80.19 H 6.44 N 4.07%,
Found C 80.00 H 6.51 N 3.89%.

¹H NMR (CDCl₃) δ (ppm) = 8.56 (s, 2H, -CH=N); 7.76 (d, 4H, J₄₋₃ = 7.5 Hz, Fl-H₄H₄); 7.53 (d, 2H, J₆₋₅ = 7.5 Hz, Fl-H₂H₂); 7.38 (s, 2H, Fl-H₂H₂); 7.34 (d, 2H, J₃₋₂ = 7.5 Hz, Fl-H₂); 7.28 (d, 2H, J₄₋₃ = 3 Hz, Th-H₄); 7.24 (dd, 4H, J₆₋₅ = 7.5 Hz, J₃₋₂ = 2.5 Hz, Fl-H₁H₁); 6.88 (d, 2H, J₄₋₃ = 3 Hz, Th-H₄); 3.9 (s, 4H, Fl-H₂H₂); 2.83 (t, 4H, Th-CH₂); 1.74 (m, 4H, Th=CH₂=CH₂); 1.32 (m, 6H, Th=CH₂=CH₂=CH₂); 0.93 (t, 6H, J=5 Hz, CH₃).

This spectrum is also typical for this of 5b.

MS (m/z): 688 (47) (M⁺); 344 (30) (M²⁺); 523 (32)
From 300.00 mg (1.14 mmol) 3e and 570.00 mg (2.37 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 224 °C; c.p.: 236 °C; yield: 146 mg (18%).

C48H54N12O4S2 (711.0)
Calcd C 76.02 H 6.52 N 3.94%
Found C 75.85 H 6.48 N 4.01%

IR (KBr), v (cm⁻¹): 3030 (w), 3080 (w)

1.5-Bis-[5-{N-(4'-butoxybiphenyl-4-yl)imino/methylidene-2-thiényl}pentane (7c)
From 300.00 mg (1.03 mmol) 3e and 515.00 mg (2.14 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 194 °C; c.p.: 241 °C; yield: 161.00 mg (21%).

C44H58N2O2S2 (739.0)
Calcd C 76.38 H 6.82 N 3.79%
Found C 76.20 H 6.87 N 3.92%

1H NMR (CDCl3) δ (ppm) = 8.5 (s, 2H, CH=CH); 7.5 (m, 8H, BiP-H2H2H2H2); 7.26 (d, 2H, J4-4 = 3 Hz, Th-H2); 7.0 (m, 4H, BiP-H2H2); 6.64 (d, 4H, J6-6 = 7.5 Hz, BiP-H2H2); 6.37 (d, 2H, J4-4 = 3 Hz, Th-H2); 3.96 (t, 4H, J = 5.3 Hz, CH2-OBiP); 2.8 (t, 4H, J = 5.3 Hz, Th-CH2); 1.78 (m, 4H, CH2-CH2-OBiP); 1.78 (m, 4H, ThCH2-CH2); 1.5 (m, 4H, CH2-(CH2)3OBiP); 1.45 (m, 2H, Th-(CH2)3-CH2); 0.94 (t, 6H, J = 6.3 Hz, -CH3). - MS (m/z): 738 (23) (M⁺); 695 (3) (M-C6H4); 512 (70) (M-C16H19NO); 498 (1) (M-C16H19NO)+; 361 (22) (C28H22N3OS)+; 241 (13) (C16H16NO)⁺; 185 (100) (C16H19NO)⁺. - UV (CHCl3) λ (nm)/log ε: 270 (43.3); 315 (43.2); 354 (46.4).

This spectrum is also typical for these of 7d, 7e, 7g, 7i, 7k and 7l.

1.6-Bis-[5-{N-(4'-butoxybiphenyl-4-yl)imino/methylidene-2-thiényl}hexane (7d)
From 300.00 mg (0.98 mmol) 3f and 489.00 mg (2.03 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 214 °C; c.p.: 259 °C; yield: 276.00 mg (37%).

C48H56N2O2S2 (753.1)
Calcd C 76.56 H 6.96 N 3.72%
Found C 76.63 H 6.96 N 3.60%

MS (m/z): 752 (42) (M⁺); 709 (7) (M-C3H7); 527 (17) (M-C16H19); 512 (17) (M-C16H19NO); 362 (16) (C28H22N3OS); 241 (11) (C16H19NO); 185 (16) (C12H11NO).
1H NMR (CDCl₃) δ (ppm) = 8.5 (s, 2H, CH=N); 7.5 (m, 8H, BiP–H₂₃H₂H₂); 7.26 (d, 2H, J₄₋₃ = 3 Hz, TH–H₂); 7.2 (m, 4H, BiP–H₂); 6.94 (d, 4H, J₅₋₄ = 7.5 Hz, BiP–H₁₂H₂); 6.78 (d, 2H, J₆₋₅ = 3 Hz, TH–H); 3.96 (t, 4H, J = 5.3 Hz, CH₂–OBiP); 2.84 (t, 4H, J = 5.3 Hz, TH–CH₃); 1.78 (m, 4H, CH₂–CH₂OBiP); 1.78 (m, 4H, ThCH₂–CH₂); 1.5 (m, 4H, CH₂–(CH₂)₂OBiP); 1.34 (m, 2H, Th–(CH₂)₂–CH₂); 0.94 (t, 6H, J = 6.3 Hz, –CH₃). This spectrum is also typical for these of 7g, 7i, 7k and 7l.

MS (m/z): 766 (100) (M⁺); 723 (1) (M–C₆H₅)⁺; 541 (76) (M–C₁₆H₁₇O)⁺; 526 (10) (M–C₁₆H₁₈NO)⁺; 362 (26) (C₂₃H₂₃NOS)⁺; 241 (8) (C₁₆H₁₉NOS)⁺; 185 (12) (C₁₂H₁₁NO)⁺.

1.11-Bis[5-[N-(4'-butoxybiphenyl-4-yl)imino]-methylidene-2-thienyl]undecane (7j)

From 300.00 mg (0.80 mmol) 3l and 395.00 mg (1.64 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 167 °C; c.p.: 222 °C; yield: 730.00 mg (94%).

C₆₅H₄₂N₂O₂S₂ (823.2)
Calcd C 76.59 H 7.50 N 3.28%.
Found C 76.34 H 7.46 N 3.31%.

1.12-Bis[5-[N-(4'-butoxybiphenyl-4-yl)imino]-methylidene-2-thienyl]dodecane (7k)

From 300.00 mg (0.77 mmol) 3m and 385.00 mg (1.60 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 193 °C; c.p.: 221 °C; yield: 483.00 mg (75%).

C₅₈H₄₄N₂O₂S₂ (837.2)
Calcd C 77.47 H 7.11 N 3.34%.
Found C 77.45 H 7.16 N 3.35%.

1.16-Bis[5-[N-(4'-butoxybiphenyl-4-yl)imino]-methylidene-2-thienyl]hexadecane (7l)

From 300.00 mg (0.67 mmol) 3n and 335.00 mg (1.39 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 178 °C; c.p.: 195 °C; yield: 377.00 mg (63%).

C₅₈H₇₂N₂O₂S₂ (893.3)
Calcd C 78.12 H 8.12 N 3.14%.
Found C 77.73 H 7.88 N 3.33%.
MS (m/z): 892 (100) (M⁺); 667 (4) (M–C₁₆H₁₆O⁺); 652 (4) (M–C₁₆H₁₆O⁺); 362 (10) (C₂₃H₂₄NO⁺); 241 (61) (C₁₆H₁₉NO⁺); 185 (100) (C₁₃H₁₁NO⁺).

**General synthesis of the**

**E,E-α,ω-bis[5-(2-fluorenylvinyl)-2-thienyl]alkanes (8a–8l)**

In a 11 three-necked flask with gas-inlet-tube, dropping funnel and reflux-condenser, a solution of the appropriate α,ω-bis(5-formyl-2-thienyl)-alkanes (3a–3l) and 2-fluorenylmethyltriphenyl-phosphonium bromide (10) (1:2) in absol. ethanol, methanol, DMF or in their mixtures was cooled to 10 °C while a constant stream of argon is blowing through the solution. At this temperature the reaction was started by addition of CH₂OLi (1 M in methanol), which is to get by dissolving 70 mg lithium in 10 ml absol. methanol in an ice bath. The reaction mixture was refluxed for 3 h, while a yellow-orange product was precipitated. From the cooled solution the crude substance was filtered off by means of vacuum. The E/Z-isomer mixture was rearranged to the pure E-isomer by refluxing through the solution. A t this temperature the reaction was started by addition of CH₂OLi (1 M solution in CH₃OH), orange crystals were dried over P₂O₅.

**E,E-1.4-Bis[5-(2-fluorenylvinyl)-2-thienyl]butane (8b)**

From 500.00 mg 3d (1.8 mmol) 2.00 g Wittig-salt 10 [18] (3.8 mmol) in 30 ml absol. CH₂OH and 4 ml CH₂OLi (1 M solution in CH₂OH), yellow crystals from toluene; m.p.: 249 °C; c.p.: 276 °C; yield: 750.00 mg (70%).

C₄₂H₃₄S₂ (602.9)

Calcd C 83.68 H 5.68%.

Found C 83.62 H 6.04%.

**E,E-1.5-Bis[5-(2-fluorenylvinyl)-2-thienyl]-pentane (8c)**

From 400.00 mg 3e (1.37 mmol) 1.60 g Wittig-salt 10 [18] (3.07 mmol) in 60 ml absol. ethanol and 4.1 ml CH₂OLi (1 M solution in CH₂OH), light brown crystals from CHCl₃/ethanol; m.p.: 240 °C; yield: 680.00 mg (81%).

C₄₃H₳₆S₂ (616.9)

Calcd C 83.72 H 5.88%.

Found C 83.68 H 5.84%.

**E,E-1.6-Bis[5-(2-fluorenylvinyl)-2-thienyl]hexane (8d)**

From 400.00 mg 3f (1.31 mmol) 1.50 g Wittig-salt 10 [18] (2.87 mmol) in 30 ml absol. CH₂OH
and 3 ml CH₃OLi (1 M solution in CH₃OH), light brown crystals from CH₃Cl/ethanol; m.p.: 227 °C; c.p.: 234 °C; yield: 718.0 mg (87%).

**C₄₄H₃₈S₂ (630.9)**

- Calcd C 83.77 H 6.07%.
- Found C 83.71 H 6.04%.

H NMR (CDCl₃) δ(ppm) = 7.72 (d, 2H, J₅₋₆ = 7 Hz, FlH₆); 7.73 (d, 2H, J₄₋₅ = 7.5 Hz, FlH₄); 7.65 (s, 2H, FlH₂); 7.54 (d, 2H, J₅₋₆ = 7.5 Hz, FlH₅); 7.46 (d, 2H, J₁₋₄ = 7.5 Hz, FlH₁); 7.41 (m, 4H, FlH₃, H); 7.21 (d, 4H, J = 7.5 Hz, Th-CH₃); 6.89 (d, 2H, J = 16.3 Hz, Fl-CH=CH-Th); 6.88 (d, 2H, J₄₋₃ = 3.8 Hz, ThH₄); 6.68 (d, 2H, J₃₋₄ = 3.8 Hz, ThH₃); 3.9 (s, 4H, FlH₉); 2.79 (t, 4H, J = 7.5 Hz, Th-CH₂); 1.71 (quint., 4H, J = 7.5 Hz, Th-CH₂-CH₂); 1.4 (m, 6H, Th-CH₂-CH₂-CH₂).

This spectrum is similar to these of 8f-8h.

MS (m/z): 630 (100) (M⁺); 315 (7) (M₂⁺); 316 (11) (C₂₂H₁₇S⁺); 300 (3) (C₁₉H₁₇S⁺); 287 (63) (C₂₀H₁₅S⁺); 253 (24) (C₂₀H₁₃⁺); 179 (7) (C₁₄H₁₁⁺).

**E,E-1,7-Bis[5-(2-fluorenylvinyl)-2-thienyl]heptane (8e)**

From 600.00 mg 3g (1.88 mmol) 2.10 g Wittig-salt 10 [18] (4.02 mmol) in 100 ml absol. ethanol and 6.2 ml CH₃OLi (1 M solution in CH₃OH), yellow-gold crystals from ethanol and then toluene; m.p.: 223 °C; yield: 821 mg (68%).

**C₄₅H₄₀S₂ (644.9)**

- Calcd C 83.81 H 6.25%.
- Found C 83.88 H 6.24%.

H NMR (CDCl₃) δ(ppm) = 7.72 (d, 2H, J₅₋₆ = 7 Hz, FlH₆); 7.73 (d, 2H, J₄₋₅ = 7.5 Hz, FlH₄); 7.65 (s, 2H, FlH₂); 7.54 (d, 2H, J₅₋₆ = 7.5 Hz, FlH₅); 7.46 (d, 2H, J₁₋₄ = 7.5 Hz, FlH₁); 7.21 (t, 4H, J = 7.5 Hz, Th-CH₃); 6.89 (d, 2H, J = 16.3 Hz, Fl-CH=CH-Th); 6.88 (d, 2H, J₄₋₃ = 3.8 Hz, ThH₄); 6.68 (d, 2H, J₃₋₄ = 3.8 Hz, ThH₃); 3.9 (s, 4H, FlH₉); 2.79 (t, 4H, J = 7.5 Hz, Th-CH₂); 1.69 (quint., 4H, J = 7.5 Hz, Th-CH₂-CH₂); 1.3 (m, 6H, Th-CH₂-CH₂-CH₂).

This spectrum is similar to these of 8f-8h.

MS (m/z): 644 (100) (M⁺); 322 (10) (M₂⁺); 287 (15) (C₂₀H₁₅S⁺); 253 (5) (C₂₀H₁₃⁺).

**E,E-1,8-Bis[5-(2-fluorenylvinyl)-2-thienyl]octane (8f)**

From 290.00 mg 3h (0.87 mmol) 1.00 g Wittig-salt 10 [18] (1.92 mmol) in 70 ml absol. ethanol/DMF (5:2) and 3 ml CH₃OLi (1 M solution in CH₃OH), yellow-gold crystals from ethanol/CHCl₃ and then toluene; m.p.: 222 °C; yield: 453.00 mg (81%).

**C₄₆H₄₂S₂ (659.0)**

- Calcd C 83.84 H 6.42%.
- Found C 83.78 H 6.40%.

MS (m/z): 658 (100) (M⁺); 329 (17) (M₂⁺); 287 (93) (C₂₀H₁₅S⁺); 253 (40) (C₂₀H₁₃⁺); 179 (64) (C₁₄H₁₁⁺).

**E,E-1,9-Bis[5-(2-fluorenylvinyl)-2-thienyl]nonane (8g)**

From 500.00 mg 3i (1.44 mmol) 1.70 g Wittig-salt 10 [18] (3.26 mmol) in 50 ml absol. ethanol and 430.00 mg (3.8 mmol) K-tert-butanolate, yellow crystals from ethanol/CHCl₃ and then toluene; m.p.: 212 °C; yield: 751 mg (78%).

**C₄₇H₄₄S₂ (673.0)**

- Calcd C 83.88 H 6.59%.
- Found C 83.75 H 6.52%.

MS (m/z): 672 (100) (M⁺); 336 (17) (M₂⁺); 287 (70) (C₂₀H₁₅S⁺); 253 (24) (C₂₀H₁₃⁺); 179 (21) (C₁₄H₁₁⁺).

**E,E-1,10-Bis[5-(2-fluorenylvinyl)-2-thienyl]decane (8h)**

From 290.00 mg 3k (1.65 mmol) 2.00 g Wittig-salt 10 [18] (3.8 mmol) in 60 ml absol. ethanol and 4 ml CH₃OLi (1 M solution in CH₃OH), yellow crystals from ethanol/CHCl₃ and then toluene; m.p.: 213 °C; yield: 930.00 mg (82%).

**C₄₈H₄₆S₂ (687.0)**

- Calcd C 83.92 H 6.75%.
- Found C 83.87 H 6.78%.

MS (m/z): 686 (100) (M⁺); 343 (12) (M₂⁺); 287 (44) (C₂₀H₁₅S⁺); 253 (18) (C₂₀H₁₃⁺); 179 (12) (C₁₄H₁₁⁺).

**E,E-1,11-Bis[5-(2-fluorenylvinyl)-2-thienyl]undecane (8i)**

From 200.00 mg 3l (1.33 mmol) 1.50 g Wittig-salt 10 [18] (2.87 mmol) in 100 ml absol. ethanol and 4 ml CH₃OLi (1 M solution in CH₃OH), yellow crystals from ethanol/CHCl₃ and then toluene; m.p.: 206 °C; yield: 875.00 mg (94%).

**C₄₉H₄₈S₂ (701.0)**

- Calcd C 83.95 H 6.90%.
- Found C 83.88 H 6.95%.

MS (m/z): 700 (100) (M⁺); 350 (13) (M₂⁺); 287 (34) (C₂₀H₁₅S⁺); 253 (13) (C₂₀H₁₃⁺); 179 (9) (C₁₄H₁₁⁺).
E,E-1,12-Bis[5-(2-fluorenylvinyl)-2-thienyl]-dodecane (8k)

From 500.00 mg 3m (1.33 mmol) 1.50 g Wittig-salt 10 [18] (2.87 mmol) in 50 ml abs. CH₃OH and 3 ml CH₃OH (1M solution in CH₃OH), light yellow crystals from ethanol/CHCl₃ and then toluene; m.p.: 201 °C; yield: 769.00 mg (84%).

$$C_{54}H_{52}S_2$$ (715.1)
Calcd C 83.98 H 7.05%
Found C 83.91 H 7.03%

MS (m/z): 714 (100) (M⁺); 357 (18) (M²⁺); 287 (70) (C₂₀H₁₅S⁺); 253 (27) (C₂₀H₁₃⁺); 179 (44) (C₁₄H₁₁⁺).

E,E-1,16-Bis[5-(2-fluorenylvinyl)-2-thienyl]-hexadecane (8l)

From 400.00 mg 3n (0.9 mmol) 1.10 g Wittig-salt 10 [18] (2.87 mmol) in 35 ml abs. DMF/ethanol (1.5:1) and 3 ml CH₃OLi (1M solution in CH₃OH), light yellow crystals from ethanol/CHCl₃ and then toluene; m.p.: 196 °C; yield: 492 mg (71%).

$$C_{54}H_{58}S_2$$ (771.2)
Calcd C 84.10 H 7.58%
Found C 83.98 H 7.49%

MS (m/z): 770 (100) (M⁺); 385 (16) (M²⁺); 287 (47) (C₂₀H₁₅S⁺); 253 (16) (C₂₀H₁₃⁺); 179 (30) (C₁₄H₁₁⁺).

3.6-Di(2-thienyl)pyridazine (9)

1.00 g (0.004 mol) 1.4-bis(2-thienyl)butane-1.4-dione and 1.4 g (0.0287 mol) 100% hydrazine hydrate in 50.0 ml ethylene glycol was heated 2 h to 120 °C. To the reaction mixture with the reaction temperature 100 °C 1.68 g KOH (0.03 mol) was added. For completing the formation of the product the reaction mixture was heated 3 h to 180 °C. While this procedure the reaction water was distilled off and the product was precipitated. The crude product was filtered by means of vacuum. The green yellow plates were recrystallized from hexane; m.p.: 171 °C; yield: 527 mg (54%).

$$C_{12}H_8N_2S_2$$ (244.3)
Calcd C 58.99 H 3.30 N 11.47%
Found C 58.87 H 3.21 N 11.29%

'H NMR (CDCl₃) δ (ppm) = 8.28 (s, 2H, Pyri-H₄H₅); 7.95 (d, 2H, J₃₄ = 3.8, Th-H₅); 7.77 (d, 2H, J₁₃ = 5.5, Th-H₃); 7.26 (dd, 2H, J₄₅ = 5.5, J₄₅ = 3.8, Th-H₄). - MS (m/z): 244 (63) (M⁺); 216 (4) (M⁺-N₂); 108 (100) (C₅H₂N⁺). - UV (CHCl₃) λ (nm)/log ε: 334 (3.41).