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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Compounds which have two mesogenic groups with and without terminal alkyl chains containing thiophene systems, were prepared from α,ω -bis(5-formyl-2-thienyl)alkanes (**3a–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 α,ω -bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]formyl-2-thienyl}alkanes (**7a–7l**) showed enantiotropic smectic and nematic mesophases. The series of E,E- α,ω -bis[5-(2-fluorenylvinyl)-2-thienyl]alkanes (**8a–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–8l**, E-1-(5-butyl-2-thienyl)-2-(2-fluorenyl)ethylene 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]

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

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 hetero-aromatic systems of this structural type.

Synthesis

The synthesis of the α,ω -bis(2-thienyl)alkanes (**2a–2l**) is well known by the reduction of the corresponding α,ω -bis(2-thienyl)alkane- α,ω -diones [16] (**1a–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–2h** are also available by a direct step reacting freshly distilled thiophene with butyllithium and α,ω -dibromoalkanes (with 3 to 10 methylene groups) in absolute tetrahydrofuran (see Scheme 2).

⁺ Part 5, G. Koßmehl, C. Pithart, Z. Naturforsch. **47b**, 567 (1992).

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Scheme 2. Synthesis of the α,ω -bis(2-thienyl)alkanes (**2a–2l**), the α,ω -bis(5-formyl-2-thienyl)alkanes (**3a–3l**) and 3,6-(2-thienyl)pyridazine (**9**).

In contrast to the Wolf-Kishner-reduction, this last mentioned synthesis leads easily to the α,ω -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 α,ω -dibromoalkanes 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 α,ω -bis(2-thienyl)alkanes was carried out either by liquid chromatography (neutral Al_2O_3 /hexane) or vacuum distillation.

The α,ω -bis(5-formyl-2-thienyl)alkanes (**3a–3n**) were synthesized from α,ω -di(2-thienyl)alkanes (**2a–2l**) by dilithiation in their α -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 recrystallation

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'-butoxy-biphenyl was synthesized by the method of Young *et al.* [17].

The homologous series of the divinylenes **8a–8l** were synthesized from the dialdehydes **3c–3n** and 2-fluorenylmethyltriphenylphosphonium 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 α,ω -bis{5-[N-(phenyl)imino]formyl-2-thienyl}alkanes (**4a-4d**), the α,ω -bis{5-[N-(4-butylphenyl)imino]formyl-2-thienyl}alkanes (**5a, 5b**), the α,ω -bis{5-[N-(2-fluorenyl)imino]formyl-2-thienyl}alkanes (**6a-6c**), the α,ω -bis{5-[N-(4'-butoxybiphenyl-4-yl)imino]formyl-2-thienyl}alkanes (**7a-7l**) and the α,ω -bis[5-(2-fluorenylvinyl)-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(azomethine)s **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 α,ω -bis(5-formyl-2-thienyl)-alkanes (**3a-3n**) with different chain lengths n , ∇ = transition temperature crystal $\rightarrow$ 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/°C·mol]
3a [8]	1	C 95 I			
3b [9]	2	C 137 I			
3c	3	C 49 I		18.4	57.0
3d	4	C 96 I	I 91 C	30.5	82.7
3e	5	C 33 I	I 23 C	22.6	73.9
3f	6	C 85 I	I 76 C	36.3	101.3
3g	7	C 37 I	I 15 C	28.7	92.7
3h	8	C 99 I	I 86 C	44.6	119.9
3i	9	C 55 I	I 33 C	33.0	100.5
3k	10	C 104 I	I 89 C	55.7	147.7
3l	11	C 55 I	I 35 C	31.1	94.9
3m	12	C 106 I	I 95 C	52.9	139.4
3n	16	C 86 I	I 73 C	55.5	154.6

t.t._h = transition temperature while heating, t.t._c = transition temperature while cooling, ΔH_h = transition enthalpy while heating, ΔS_h = transition entropy while heating, C = crystal, I = isotropic.

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 divinylenes **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)imino]formyl-2-thienyl}alkanes (**4a–4d**), the α,ω -bis{5-[N-(4-butylphenyl)imino]formyl-2-thienyl}alkanes (**5a** and **5b**) and the α,ω -bis{5-[N-(2-fluorenyl)imino]formyl-2-thienyl}alkanes (**6a–6c**) with different chain lengths n and the model compounds 4-(5-alkyl-2-thienyl)methylideneamino)butylbenzenes and 2-(5-pentyl-2-thienyl-methylideneamino)fluorenes.

Comp.	n	t.t. _h [°C]	t.t. _c [°C]	ΔH_h [kJ/mol]	ΔS_h [J/°C·mol]	t.t. _h of the model compounds
4a	3	C ₁ 70 C ₂ C ₂ 88 I	I 88 C	0.5 27.8	1.6 76.8	
4b	5	C 75 I	I 75 C	22.8	65.2	
4c	7	C 84 I	I 84 C	36.0	100.6	
4d	12	C ₁ 99 C ₂ C ₂ 105 I	I 76 C	15.2 48.4	40.8 127.7	
5a	6	C 101 I	I 96 C	37.8	100.7	(C 8 I) H ₇ C ₃ –Th–CH=N–Ph–C ₄ H ₉ [20]
5b	12	C ₁ 82 C ₂ C ₂ 94 I	I 89 C	8.3 54.8	23.3 149.1	(C 13 I) H ₁₃ C ₆ –Th–CH=N–Ph–C ₄ H ₉ [20]
6a	4	C 244 I (dec.)	(66.8)	(129.0)		
6b	10	C 196 I	I 161 N* N 132 C*	63.9	136.2	(C 120 I) Fl–N=CH–Th–C ₃ H ₁₁ [19]
6c	12	C ₁ 140 C ₂ C ₂ 192 I	I 150 C' ₂ C' ₂ 136 C' ₁	4.7 75.6	11.3 162.1	

t.t._h = transition temperature while heating, t.t._c = transition temperature while cooling, ΔH_h = transition enthalpy while heating, ΔS_h = transition entropy while heating, * = verified by microscopy (cooling rate 20 K/min), N = nematic, C = crystal, I = isotropic, dec. = decomposition.

Fig. 2. Phase diagram of the α,ω -bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]formyl-2-thienyl}alkanes (**7a-7l**) with different chain lengths n , ∇ = transition temperature crystal $\rightarrow$ nematic, $\bullet$ = transition temperature nematic $\rightarrow$ isotropic.

Fig. 3. Phase diagram of the E,E- α,ω -bis[5-(2-fluorenylvinyl)-2-thienyl]alkanes (**8a-8l**) with different chain lengths n , ∇ = transition temperature (t.t.) crystal $\rightarrow$ isotropic, $\blacktriangledown$ = t.t. crystal $\rightarrow$ nematic, $\times$ = t.t. nematic $\rightarrow$ isotropic, $\bullet$ = t.t. isotropic $\rightarrow$ nematic, $\blacklozenge$ = t.t. nematic $\rightarrow$ crystal.

Table III. Thermal transitions of the α,ω -bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]formyl-2-thienyl}alkanes (**7a-7b**) with different chain lengths n and the model compounds 5-[N-(4'-alkyloxybiphenyl-4-yl)imino]formyl-2-methylthiophenes.

Comp.	n	t.t. _h [°C]	t.t. _c [°C]	ΔH_h [kJ/mol]	ΔS_h [J/°C·mol]	t.t. _h of the model compounds
7a	3	C 224 N N 236 I (dec.)		60.3** (29.1)	121.3** (57.2)**	
7b	4	C 230 N N 279 I (dec.)		58.2 (5.6)	115.7 (10.1)	
7c	5	C 194 N N 241 I	I 240 N N 193 C	51.9 5.8	111.1 11.3	(C 160 N 211 I) H ₃ C-Th-CH=N-Ph-Ph-OCH ₃
7d	6	C 214 N N 259 I	I 258 N N 197 C	64.2 5.5	131.8 10.3	
7e	7	C 178 N N 237 I	I 237 N N 173 S ₁ * S ₁ 158 C	50.0 5.3	110.9 10.4	
7f	8	C 202 N N 242 I	I 240 N N 188 C	69.2 5.6	145.7 10.9	(C 150 N 181 I) H ₃ C-Th-CH=N-Ph-Ph-OC ₈ H ₁₇)
7g	9	C 164 N N 220 I	I 218 N N 161 S ₁ * S ₁ 157 S ₂ * S ₂ 148 C*	56.0 5.3	128.1 10.8	
7h	10	C 198 N N 232 I	I 232 N N 176 C	78.1 5.6	165.8 11.1	
7j	11	C 167 N N 222 I	I 220 N N 163 S ₁ * S ₁ 162 S ₂ * S ₂ 157 C*	56.6 5.1	104.8 10.3	
7k	12	C 193 N N 221 I	I 220 N N 175 C	78.4 5.2	168.2 10.5	
7l	16	C 178 N N 195 I	I 194 N N 165 C	83.4 5.8	184.9 12.4	

t.t._h = transition temperature while heating, t.t._c = transition temperature while cooling, ΔH_h = transition enthalpy while heating, ΔS_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- α,ω -bis[5-(2-fluorenylvinyl)-2-thienyl]alkanes (**8a–8l**) with different chain lengths n and the model compound E-1-(5-butyl-2-thienyl)-2-(2-fluorenyl)ethylene.

Comp.	n	t.t. _h [°C]	t.t. _c [°C]	ΔH_h [kJ/mol]	ΔS_h [J/°C·mol]	t.t. _h of the model compounds
8a	3	C 276 I (dec.)		(50.5)	(92.0)	
8b	4	C 249 N N 276 I	N 226 C	45.0 3.0	86.2 5.5	
8c	5	C 240 I	I 232 C	51.1	99.6	
8d	6	C 227 N N 234 I	I 232 N N 207 C	48.2 1.5	96.4 3.0	
8e	7	C 223 I	I 218 N N 208 C	54.2 2.5*	109.3 5.1*	
8f	8	C 222 I	I 230 N N 198 C	51.7 3.2*	104.4 6.4*	(C 118 S 143 I) H ₉ C ₄ -Th-CH=CH-FI [19]
8g	9	C 212 I	I 209 N N 195 C	59.5 2.9*	122.7 6.0*	
8h	10	C 213 I	I 214 N N 195 C	61.4 4.4*	126.3 9.0*	
8j	11	C 206 I	I 203 N N 193 C	61.1 2.5*	127.6 5.3*	
8k	12	C 201 I	I 195 N N 189 C	48.1 3.1*	101.5 6.6*	
8l	16	C 196 I	I 189 C	66.8	142.4	

t.t._h = transition temperature while heating, t.t._c = transition temperature while cooling, ΔH_h = transition enthalpy while heating (* = while cooling), ΔS_h = transition entropy while heating (* = while cooling), C = crystal, I = isotropic, N = nematic, S = smectic, dec. = decomposition.

Scheme 4. Stereochemical formulas of the E,E- α,ω -bis[5-(2-fluorenylvinyl)-2-thienyl]alkanes (**8a**, **8b**, containing three and four methylene groups).

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 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 careout 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

Fig. 4. Transition enthalpies (t.e.) of the α,ω -bis-[5-[N-(4'-butoxybiphenyl-4-yl)imino]formyl-2-thienyl]-alkanes (**7a–7l**) and the E,E- α,ω -bis[5-(2-fluorenylvinyl)-2-thienyl]alkanes (**8a–8l**) with different chain lengths *n*, ◆ = t.e. of series **7** (crystal $\rightarrow$ nematic), ● = t.e. of series **7** (nematic $\rightarrow$ isotropic), ◇ = t.e. of series **8** (crystal $\rightarrow$ isotropic), ○ = t.e. of series **8** (isotropic $\rightarrow$ nematic).

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 ^1H 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-Recorder 56. The phase transitions were determined by a Heraeus-TA-500 instrument with a scanning speed of $10\text{ }^\circ\text{C/min}$ (sometimes $20\text{ }^\circ\text{C/min}$) for heating and cooling runs. 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.

General synthesis of the α,ω -di(2-thienyl)alkanes (**2a–2l**) by nucleophilic substitution

20.00 g (0.24 mol) thiophene were dissolved in 100 ml absol. tetrahydrofuran 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 $-56\text{ }^\circ\text{C}$ 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–2l** precipitated, also LiBr is separated. For completing the reaction the mixture was stirred for additional 2 h at $-56\text{ }^\circ\text{C}$, then 0.5 h at room temperature and at least 1 h at $50\text{ }^\circ\text{C}$. The reaction solution was poured onto ice (500 ml), neutralized with diluted HCl and extracted three times with diethylether. The combined organic lay-

ers were washed with water and dried over Na_2SO_4 . After evaporating the solvent the residue was distilled under vacuum.

1,3-Di(2-thienyl)propane (**2a**)

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

$\text{C}_{11}\text{H}_{12}\text{S}_2$ (208.3)

Calcd	C 63.41	H 5.80%,
Found	C 63.39	H 5.80%.

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

These absorptions are also typical for **2b–2l**.

^1H NMR (CDCl_3) $\delta(\text{ppm}) = 7.07\text{ (d, d, 2H, } J_{5-4} = 6\text{ Hz, } J_{5-3} = 1\text{ Hz, Th-H}_5); 6.89\text{ (d, d, 2H, } J_{4-5} = 6\text{ Hz, } J_{4-3} = 4\text{ Hz, Th-H}_4); 6.75\text{ (d, d, 2H, } J_{3-4} = 4\text{ Hz, } J_{3-5} = 1\text{ Hz, Th-H}_3); 2.86\text{ (t, 4H, } J = 8\text{ Hz, Th-CH}_2); 2.03\text{ (quintett, 2H, } J = 8\text{ Hz, Th-CH}_2\text{-CH}_2)$. – MS (m/z): 208 (34) (M^+); 124 (7) ($\text{C}_7\text{H}_8\text{S}^+$); 111 (17) ($\text{C}_6\text{H}_7\text{S}^+$); 98 (100) ($\text{C}_5\text{H}_6\text{S}^+$).

1,4-Di(2-thienyl)butane (**2b**)

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

$\text{C}_{12}\text{H}_{14}\text{S}_2$ (222.4)

Calcd	C 64.82	H 6.35%,
Found	C 64.84	H 6.38%.

^1H NMR (CDCl_3) $\delta(\text{ppm}) = 7.07\text{ (d, d, 2H, } J_{5-4} = 6\text{ Hz, } J_{5-3} = 1\text{ Hz, Th-H}_5); 6.89\text{ (d, d, 2H, } J_{4-5} = 6\text{ Hz, } J_{4-3} = 4\text{ Hz, Th-H}_4); 6.75\text{ (d, d, 2H, } J_{3-4} = 4\text{ Hz, } J_{3-5} = 1\text{ Hz, Th-H}_3); 2.86\text{ (t, 4H, } J = 8\text{ Hz, Th-CH}_2); 1.98\text{ (m, 4H, Th-CH}_2\text{-CH}_2)$. – MS (m/z): 222 (50) (M^+); 124 (26) ($\text{C}_7\text{H}_8\text{S}^+$); 111 (21) ($\text{C}_6\text{H}_7\text{S}^+$); 97 (100) ($\text{C}_5\text{H}_5\text{S}^+$).

1,5-Di(2-thienyl)pentane (**2c**)

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

$\text{C}_{13}\text{H}_{16}\text{S}_2$ (236.4)

Calcd	C 66.05	H 6.82%,
Found	C 66.04	H 6.79%.

^1H NMR (CDCl_3) $\delta(\text{ppm}) = 7.07\text{ (d, d, 2H, } J_{5-4} = 6\text{ Hz, } J_{5-3} = 1\text{ Hz, Th-H}_5); 6.89\text{ (d, d, 2H, } J_{4-5} = 6\text{ Hz, } J_{4-3} = 4\text{ Hz, Th-H}_4); 6.75\text{ (d, d, 2H, } J_{3-4} = 4\text{ Hz, } J_{3-5} = 1\text{ Hz, Th-H}_3); 2.86\text{ (t, 4H, } J = 8\text{ Hz, Th-CH}_2); 1.7\text{ (m, 4H, Th-CH}_2\text{-CH}_2); 1.34\text{ (m, 6H, Th-(CH}_2)_2\text{-CH}_2)$. This spectrum is simi-

lar to these of **2d–2h** (contains six to ten methylene groups). – MS (m/z): 236 (17) (M^+); 123 (5) ($C_7H_7S^+$); 111 (17) ($C_6H_7S^+$); 97 (100) ($C_5H_5S^+$).

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%).

$C_{14}H_{18}S_2$ (250.4)

Calcd C 67.15 H 7.24%,

Found C 67.16 H 7.26%.

MS (m/z): 250 (17) (M^+); 123 (3) ($C_7H_7S^+$); 111 (15) ($C_6H_7S^+$); 97 (100) ($C_5H_5S^+$).

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%).

$C_{15}H_{20}S_2$ (264.4)

Calcd C 68.13 H 7.62%,

Found C 68.14 H 7.59%.

MS (m/z): 264 (41) (M^+); 123 (3) ($C_7H_7S^+$); 111 (15) ($C_6H_7S^+$); 97 (100) ($C_5H_5S^+$).

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%).

$C_{16}H_{22}S_2$ (278.5)

Calcd C 69.01 H 7.96%,

Found C 69.03 H 7.96%.

MS (m/z): 278 (41) (M^+); 123 (4) ($C_7H_7S^+$); 111 (24) ($C_6H_7S^+$); 97 (100) ($C_5H_5S^+$).

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%).

$C_{17}H_{24}S_2$ (292.5)

Calcd C 69.81 H 8.27%,

Found C 69.83 H 8.29%.

MS (m/z): 292 (20) (M^+); 123 (3) ($C_7H_7S^+$); 111 (27) ($C_6H_7S^+$); 97 (100) ($C_5H_5S^+$).

1.10-Di(2-thienyl)decane (**2h**)

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

$C_{18}H_{26}S_2$ (306.5)

Calcd C 70.53 H 8.55%,

Found C 70.51 H 8.53%.

MS (m/z): 306 (25) (M^+); 123 (4) ($C_7H_7S^+$); 111 (20) ($C_6H_7S^+$); 97 (100) ($C_5H_5S^+$).

General synthesis of the α,ω -di(2-thienyl)alkanes (**2i–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 1 l water and extracted three times with toluene. The toluene phase was dried with Na_2SO_4 and distilled under vacuum. More purification of the product was done by chromatography (neutral Al_2O_3 -Merck, column 30 cm, $\varnothing = 3$ 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%).

$C_{19}H_{28}S_2$ (320.6)

Calcd C 71.19 H 8.80%,

Found C 71.17 H 8.81%.

1H NMR ($CDCl_3$) δ (ppm) = 7.07 (d, d, 2H, $J_{5-4} = 6$ Hz, $J_{5-3} = 1$ Hz, Th- H_5); 6.89 (d, d, 2H, $J_{4-5} = 6$ Hz, $J_{4-3} = 4$ Hz, Th- H_4); 6.75 (d, d, 2H, $J_{3-4} = 4$ Hz, $J_{3-5} = 1$ Hz, Th- H_3); 2.8 (t, 4H, $J = 8$ Hz, Th- $\underline{CH_2}$), 1.67 (m, 4H, Th- $\underline{CH_2-CH_2}$); 1.28 (m, 14H, Th-($\underline{CH_2})_2$ -($\underline{CH_2})_4$).

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

MS (m/z): 320 (15) (M^+); 97 (100) ($C_5H_5S^+$); 111 (29) ($C_6H_7S^+$); 153 (3) ($C_9H_{13}^+$).

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%).

$C_{20}H_{30}S_2$ (334.6)

Calcd C 71.80 H 9.04%,
Found C 71.78 H 9.02%.

MS (*m/z*): 334 (14) (M^+); 97 (100) ($C_5H_5S^+$); 111 (30) ($C_6H_7S^+$); 153 (3) ($C_9H_{13}^+$).

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) ($C_5H_5S^+$); 111 (28) ($C_6H_7S^+$); 153 (4) ($C_9H_{13}^+$).

General synthesis of the α,ω -bis(5-formyl-2-thienyl)-alkanes (**3c–3l**)

In a 1 l three-necked flask with a gas-inlet-tube, reflux-condenser and dropping funnel a solution of 150 ml 15% butyllithium in hexane (1.43 mol/l) (Merck) was cooled to –10 °C under a nitrogen atmosphere. To this mixture a solution of 0.1 mol α,ω -di(2-thienyl)alkanes **2a–2l** in 70 ml absolute diethylether were added while the reaction temperature was held to be not higher than –5 °C. The resulting mixture was heated to reflux and stirred for 1 h, while the dilithium-salt of α,ω -di(2-thienyl)alkanes settled down as colourless precipitates. This suspension was cooled to 0 °C and 35 ml absol. DMF and 100 ml absol. diethylether were added. For completing the reaction the mixture has to be stirred for 12 h. The resulting complex is hydrolyzed by diluted HCl in an ice bath, washed with water and recrystallized first from cyclohexane and than twice from ethanol/water (8:2). For further purification the product was dissolved in acetone or ethanol/water (8:2) and heated with charcoal. The dialdehydes with 3, 5 or 7 methylene groups in the connecting chain were purified by hydrolysis of 1,3- or 1,5- or 1,7-bis[5-(N-phenylimino)formyl-2-thienyl]propane, -pentane or -heptane by stirring in diluted HCl at room temperature and recrystallization from ethanol/water (8:2). The dialdehyde with a chain length of three methylene groups could be distilled (205 °C/

0.2 mm). The products were dried over P_2O_5 in vacuum.

1.3-Bis(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%).

$C_{13}H_{12}S_2O_2$ (264.4)

Calcd C 59.06 H 4.58%,
Found C 59.00 H 4.52%.

IR (KBr), $\nu(\text{cm})$ = 3100 (w) $\nu(\text{C-H}_{\text{Ar}})$; 2930, 2830, 2860 (w-vs) $\nu(\text{C-H})$; 1660 (vs) $\nu(\text{C=O})$; 1625 (sh) $\nu(\text{Ar-C=C})$; 1530 (w), 1460 (vs) $\nu(\text{aromat})$; 1225 (s) $\nu(\text{Ar-C=C})$; 820 (m) $\delta(\text{Ar-C-H})_{\text{oop}}$.

These absorptions are also typical for these of **3c–3l**.

^1H NMR (CDCl_3) $\delta(\text{ppm})$ = 9.84 (s, 2H, $-\text{CH=O}$); 7.64 (d, 2H, J = 3 Hz, Th- H_4); 6.94 (d, 2H, J = 3 Hz, Th- H_3); 2.85 (t, 4H, J = 7.5 Hz, Th- CH_2); 2.14 (quint. 2H, J = 7.5 Hz, Th- CH_2-CH_3). – MS (*m/z*): 264 (31) (M^+); 152 (15) ($\text{C}_8\text{H}_8\text{OS}^+$); 139 (40) ($\text{C}_7\text{H}_7\text{OS}^+$); 126 (84) ($\text{C}_6\text{H}_6\text{OS}^+$); 111 (13) ($\text{C}_5\text{H}_3\text{OS}^+$). – UV (CHCl_3) $\lambda(\text{nm})/\log \epsilon$: 265 (3.85), 297 (4.14).

This spectrum is similar to these of **3c–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%).

$C_{14}H_{14}O_2S_2$ (278.4)

Calcd C 60.4 H 5.07%,
Found C 60.1 H 5.02%.

^1H NMR (CDCl_3) $\delta(\text{ppm})$ = 9.84 (s, 2H, $-\text{CH=O}$); 7.6 (d, 2H, J = 3 Hz Th- H_4); 6.92 (d, 2H, J = 3 Hz, Th- H_3); 2.9 (t, 4H, J = 7.5 Hz, Th- CH_2); 1.8 (m, 4H, Th- CH_2-CH_2). – MS (*m/z*): 278 (48) (M^+); 250 (13) ($M-\text{CO}$) $^+$; 166 (8) ($\text{C}_9\text{H}_{10}\text{OS}^+$); 152 (15) ($\text{C}_8\text{H}_8\text{OS}^+$); 139 (44) ($\text{C}_7\text{H}_7\text{OS}^+$); 126 (23) ($\text{C}_6\text{H}_6\text{OS}^+$); 111 (13) ($\text{C}_5\text{H}_3\text{OS}^+$).

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

DMF, light yellow crystals from ethanol/water
m. p.: 33 °C; yield: 10.00 g (40%).

$C_{15}H_{16}O_2S_2$ (292.4)

Calcd C 61.61 H 5.51%,

Found C 61.39 H 5.49%.

1H NMR ($CDCl_3$) δ (ppm) = 9.82 (s, 2H, $-CH=O$); 7.62 (d, 2H, $J = 3$ Hz Th- H_4); 6.9 (d, 2H, $J = 3$ Hz Th- H_3); 2.88 (t, 4H, $J = 7.5$ Hz Th- $\underline{CH_2}$); 1.78 (m, 4H, Th- $\underline{CH_2}-CH_2$); 1.45 (m, 2H, Th- $(CH_2)_2-CH_2$).

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

MS (m/z): 292 (13) (M^+); 264 (19) ($M-CO$) $^+$; 166 (3) ($C_9H_{10}OS$) $^+$; 152 (3) (C_8H_8OS) $^+$; 139 (40) (C_7H_7OS) $^+$; 126 (32) (C_6H_6OS) $^+$; 111 (12) (C_5H_3OS) $^+$.

1.6-Bis(5-formyl-2-thienyl)hexane (**3f**)

From 20.00 g **2d** (0.08 mol), 120 ml 15% butyllithium solution in hexane (1.43 mol/l) and 29 ml DMF, colourless crystals from ethanol/water, m. p.: 85 °C; yield: 19.30 g (79%).

$C_{16}H_{18}O_2S_2$ (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) ($C_9H_{10}OS$) $^+$; 152 (8) (C_8H_8OS) $^+$; 139 (35) (C_7H_7OS) $^+$; 126 (21) (C_6H_6OS) $^+$; 111 (12) (C_5H_3OS) $^+$.

1.7-Bis(5-formyl-2-thienyl)heptane (**3g**)

From 20.00 g **2e** (0.076 mol), 113 ml 15% butyllithium solution in hexane (1.43 mol/l) and 28 ml DMF, colourless crystals from ethanol/water, m. p.: 37 °C; yield: 15.60 g (64%).

$C_{17}H_{20}O_2S_2$ (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) ($C_9H_{10}OS$) $^+$; 152 (4) (C_8H_8OS) $^+$; 139 (4) (C_7H_7OS) $^+$; 126 (48) (C_6H_6OS) $^+$; 111 (20) (C_5H_3OS) $^+$.

1.8-Bis(5-formyl-2-thienyl)octane (**3h**)

From 20.00 g **2f** (0.072 mol), 108 ml 15% butyllithium solution in hexane (1.43 mol/l) and 26 ml DMF, colourless crystals from ethanol/water; m. p.: 99 °C; yield: 21.00 g (88%).

$C_{18}H_{22}O_2S_2$ (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) ($C_{11}H_{16}OS$) $^+$; 167 (7) ($C_9H_{11}OS$) $^+$; 153 (4) (C_8H_9OS) $^+$; 139 (39) (C_7H_7OS) $^+$; 126 (27) (C_6H_6OS) $^+$; 111 (18) (C_5H_3OS) $^+$.

1.9-Bis(5-formyl-2-thienyl)nonane (**3i**)

From 21.00 g **2g** (0.072 mol), 108 ml 15% butyllithium solution in hexane (1.43 mol/l) and 26 ml DMF, colourless crystals from ethanol/water; m. p.: 55 °C; yield: 19.30 g (77%).

$C_{19}H_{24}O_2S_2$ (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) ($C_{12}H_{18}OS$) $^+$; 167 (11) ($C_9H_{11}OS$) $^+$; 153 (4) (C_8H_9OS); 139 (50) (C_7H_7OS); 126 (25) (C_6H_6OS); 111 (21) (C_5H_3OS) $^+$.

1.10-Bis(5-formyl-2-thienyl)decane (**3k**)

From 15.00 g **2h** (0.049 mol), 74 ml 15% butyllithium solution in hexane (1.43 mol/l) and 18 ml DMF, colourless crystals from ethanol/water m. p.: 104 °C; yield: 15.5 g (87%).

$C_{20}H_{26}O_2S_2$ (362.6)

Calcd C 66.26 H 7.23%,

Found C 66.14 H 7.26%.

1H NMR ($CDCl_3$) δ (ppm) = 9.82 (s, 2H, $-CH=O$); 7.63 (d, 2H, Th- H_4); 6.9 (d, 2H, Th- H_3); 2.88 (t, 4H, Th- $\underline{CH_2}$); 1.72 (m, 4H, Th- $\underline{CH_2}-CH_2$); 1.4 and 1.36 (m, 12H, Th- $(CH_2)_2-CH_2-CH_2-CH_2$).

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

MS (m/z): 362 (16) (M^+); 334 (5) ($M-CO$) $^+$; 224 (4) ($C_{13}H_{20}OS$) $^+$; 167 (9) ($C_9H_{11}OS$) $^+$; 153 (5) (C_8H_9OS) $^+$; 139 (41) (C_7H_7OS) $^+$; 126 (21) (C_6H_6OS) $^+$; 111 (25) (C_5H_3OS) $^+$.

1.11-Bis(5-formyl-2-thienyl)undecane (**3l**)

From 7.00 g **2i** (0.022 mol), 33 ml 15% butyllithium solution in hexane (1.43 mol/l) and 8 ml DMF, colourless crystals from ethanol/water; m. p.: 55 °C; yield: 7.60 g (92%).

$C_{21}H_{28}O_2S_2$ (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) ($C_{14}H_{22}OS$) $^+$; 167 (9) ($C_9H_{11}OS$) $^+$; 153 (4) (C_8H_9OS); 139 (60) (C_7H_7OS); 126 (31) (C_6H_6OS); 111 (22) (C_5H_3OS).

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%).

$C_{22}H_{30}O_2S_2$ (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) ($C_{15}H_{22}OS^+$); 167 (8) ($C_9H_{11}OS^+$); 153 (4) ($C_8H_9OS^+$); 139 (67) ($C_7H_7OS^+$); 126 (30) ($C_6H_6OS^+$); 111 (22) ($C_5H_3OS^+$).

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%).

$C_{26}H_{38}O_2S_2$ (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) ($C_9H_{11}OS^+$); 153 (5) ($C_8H_9OS^+$); 139 (65) ($C_7H_7OS^+$); 126 (32) ($C_6H_6OS^+$); 111 (33) ($C_5H_3OS^+$).

General synthesis of the

α,ω-bis[5-(N-phenylimino)methylidene-2-thienyl]alkanes (4a–4d), *α,ω-bis[5-(N-4-butylphenyliminomethylidene-2-thienyl)alkanes (5a, 5b)*, *α,ω-bis[5-[N-(4'-butyloxybiphenyl-4-yl)imino]methylidene-2-thienyl]alkanes (6a–6c)*, *α,ω-bis[5-[N-(2-fluorenyl)imino]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 Å) 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. tetrahydrofurane. The products were dried over P_2O_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%).

$C_{25}H_{22}N_2S_2$ (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 (w) $\nu(\text{C-H}_{\text{Ar}})$; 2920 (s), 2900 (s), 2840 (w) $\nu(\text{C-H})$; 1605 (vs) $\nu(\text{C=N})$; 1575 (vs), 1360 (w), 1270 (w) $\nu(\text{Ar-C=C})$; 800 (m) $\delta(\text{Ar-C-H})_{\text{oop}}$.

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

^1H NMR (CDCl_3) $\delta(\text{ppm})$ = 8.48 (s, 2H, $-\text{CH=N}$); 7.36 (dd, 4H, $J_{3-2} = J_{3-4} = 8$ Hz, BzH_3H_5); 7.3 (d, 2H, $J_{3-4} = 4$ Hz, ThH_4); 7.24 (d, 2H, $J_{4-3} = 8$ Hz, BzH_4); 7.19 (d, 4H, $J_{2-3} = 8$ Hz, BzH_2H_6); 6.84 (d, 2H, $J_{3-4} = 4$ Hz, ThH_3); 2.92 (t, 4H, $J = 5.3$ Hz, $\text{CH}_2\text{-Th}$); 2.21 (quint., 2H, $J = 5.3$ Hz, $\text{H}_2\text{C-H}_2\text{C-Th}$). – MS (*m/z*): 414 (41) (M^+); 207 (9) (M^{2+}); 337 (100) ($M-C_6H_6^+$); 214 (9) ($C_{13}H_{12}NS^+$). – UV (CHCl_3) $\lambda(\text{nm})/\log\epsilon$: 268 (3.96), 313 (sh), 331 (4.61).

This spectrum is similar to these of the compounds **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%).

$C_{27}H_{26}N_2S_2$ (442.6)

Calcd C 73.26 H 5.92 N 6.33%,

Found C 73.13 H 5.95 N 6.22%.

^1H NMR (CDCl_3) $\delta(\text{ppm})$ = 8.48 (s, 2H, $-\text{CH=N}$); 7.36 (dd, 4H, $J_{3-2} = J_{3-4} = 8$ Hz, BzH_3H_5); 7.3 (d, 2H, $J_{4-3} = 4$ Hz, ThH_4); 7.24 (d, 2H, $J_{4-3} = 8$ Hz, BzH_4); 7.19 (d, 4H, $J_{2-3} = 8$ Hz, BzH_2H_6); 6.84 (d, 2H, $J_{3-4} = 4$ Hz, ThH_3); 2.86 (t, 4H, $J = 5.3$ Hz, $\text{CH}_2\text{-Th}$); 1.7 (m, 4H, $\text{CH}_2\text{-CH}_2\text{-Th}$); 1.4 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-Th}$).

This spectrum is also typical for this of **4c**. – MS (*m/z*): 442 (49) (M^+); 221 (4) (M^{2+}); 365 (100) ($M-C_6H_5^+$); 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%).

$C_{29}H_{30}N_2S_2$ (470.7)

Calcd C 73.73 H 6.36 N 5.39%,

Found C 73.65 H 6.31 N 5.24%.

MS (*m/z*): 470 (56) (M^+); 235 (7) (M^{2+}); 393 (100) ($M-C_6H_5^+$); 214 (22) ($C_{13}H_{12}NS^+$).

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, J₃₋₂ = J₃₋₄ = 8 Hz, BzH₃H₅); 7.3 (d, 2H, J₄₋₃ = 4 Hz, ThH₄); 7.24 (d, 2H, J₄₋₃ = 8 Hz, BzH₄); 7.19 (d, 4H, J₂₋₃ = 8 Hz, BzH₂H₆); 6.84 (d, 2H, J₃₋₄ = 4 Hz, ThH₃); 2.86 (t, 4H, J = 5.3 Hz, CH₂-Th); 1.7 (m, 4H, CH₂-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) (C₁₃H₁₂NS⁺).

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) *p*-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), ν(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) δ(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, J₄₋₃ = 3 Hz, Th-H₄); 7.17 (d, 4H, J₃₋₂ = 8 Hz, Bz-H₃H₅); 7.11 (d, 4H, J₂₋₃ = 8 Hz, Bz-H₂H₆); 6.78 (d, 2H, J₃₋₄ = 3 Hz, Th-H₃); 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, Th-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-C₂H₅)⁺; 435 (88) (C₂₆H₃₁N₂S₂)⁺; 257 (7) (C₁₆H₁₉SN)⁺; 270 (12) (C₁₇H₂₁SN)⁺. - UV (CHCl₃) λ(nm)/logε: 268 (3.89), 312 (4.22), 339 (4.36).

This spectrum is also typical for this of **5b**.

1.12-Bis[5-(N-4-butylphenylimino)methylidene-2-thienyl]dodecane (5b)

From 351.00 mg **3m** (0.9 mmol) and 300.00 mg (2 mmol) *p*-butylaniline in 50 ml absol. ethanol; colourless crystals from ethanol; m.p.: 94 °C; yield: 534 mg (91%).

C₄₂H₅₆N₂S₂ (653.0)

Calcd C 77.25 H 8.64 N 4.29%,
Found C 77.31 H 8.67 N 4.40%.

MS (m/z): 652 (100) (M⁺); 326 (12) (M²⁺); 623 (11) (M-C₂H₅)⁺; 519 (16) (C₃₂H₄₃N₂S₂)⁺; 257 (7) (C₁₆H₁₉NS)⁺; 270 (23) (C₁₇H₂₁NS)⁺; 283 (54) (C₁₈H₂₃NS)⁺.

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%).

C₄₀H₃₂N₂S₂ (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)_L; 1615 (m) ν(C=N); 1595 (s), 1400 (w), 1255 (vw) ν(Th-C=C); 805 (m) δ(Ar-C-H)_{oop}.

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

MS (m/z): 604 (2) (M⁺); 440 (57) (M-C₁₃H₉)⁺; 287 (8) (C₁₉H₁₃NS)⁺. - UV (KBr) λ(nm)/logε: 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%).

C₄₆H₄₄N₂S₂ (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-H₄H₅); 7.53 (d, 2H, J₈₋₇ = 7.5 Hz, Fl-H₈); 7.38 (s, 2H, Fl-H₁); 7.34 (d, 2H, J₃₋₄ = 7.5 Hz, Fl-H₃); 7.28 (d, 2H, J₄₋₃ = 3 Hz, Th-H₄); 7.24 (dd, 4H, J₆₋₅ = 7.5 Hz, J₆₋₈ = 2.5 Hz, Fl-H₆H₇); 6.82 (d, 2H, J₃₋₄ = 3 Hz, Th-H₃); 3.9 (s, 4H, Fl-H₉); 2.87 (t, 4H, Th-CH₂); 1.74 (m, 4H, Th-CH₂-CH₂); 1.32 (m, 6H, Th-CH₂-CH₂-(CH₂)₃). - MS (m/z): 688 (47) (M⁺); 344 (30) (M²⁺); 523 (32)

(M-C₁₃H₉)⁺; 508 (100) (M-C₁₃H₉NH)⁺; 289 (37) (C₁₉H₁₅NS)⁺. – UV (CHCl₃) λ (nm)/log ϵ : 275 (4.56), 310 (4.6), 361 (4.8).

These absorptions are also typical for this of **6c**.

1,12-Bis{5-[N-(2-fluorenyl)imino]methylidene-2-thienyl}dodecane (6c)

From 300.00 mg (0.77 mmol) **3m** and 290.00 mg (1.60 mmol) 2-aminofluorene in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 192 °C; yield: 218.00 mg (40%).

C₄₈H₄₈N₂S₂ (717.1)

Calcd C 80.40 H 6.75 N 3.91%,

Found C 80.27 H 6.79 N 3.99%.

MS (*m/z*): 716 (61) (M⁺); 358 (34) (M²⁺); 551 (23) (M-C₁₃H₉)⁺; 536 (100) (M-C₁₃H₉NH)⁺; 289 (24) (C₁₉H₁₅NS)⁺.

1,3-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]methylidene-2-thienyl}propane (7a)

From 300.00 mg (1.14 mmol) **3c** and 570.00 mg (2.37 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene light green crystals from THF; m.p.: 224 °C; c.p.: 236 °C; yield: 146 mg (18%).

C₄₁H₄₆N₂O₂S₂ (711.0)

Calcd C 76.02 H 6.52 N 3.94%,

Found C 75.85 H 6.48 N 4.01%.

IR (KBr), ν (cm⁻¹) = 3030 (w), 3080 (w) ν (C-H_{Ar}); 2950 (s), 2920 (vs), 2870 (s), 2850 (vs) ν (C-H); 1605 (vs) ν (C=N); 1585 (s), 1395 (m), 1250 (vs) ν (Ar-C=C); 805 (s) δ (Ar-C-H)_{oop}.

This spectrum is also typical for these of **7b–7l**.

MS (*m/z*): 710 (57) (M⁺); 667 (15) (M-C₃H₇)⁺; 485 (100) (M-C₁₆H₁₇O)⁺; 470 (1) (M-C₁₆H₁₈NO)⁺; 361 (22) (C₂₃H₂₃NOS)⁺; 241 (26) (C₁₆H₁₉NO)⁺; 185 (51) (C₁₂H₁₁NO)⁺.

1,4-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]methylidene-2-thienyl}butane (7b)

From 300.00 mg (1.08 mmol) **3d** and 539.00 mg (2.24 mmol) 4-amino-4'-butoxybiphenyl [17] in 50 ml absol. xylene, light green crystals from absol. THF; m.p.: 230 °C; c.p.: 279 °C; yield: 164.00 mg (21%).

C₄₂H₄₈N₂O₂S₂ (725.0)

Calcd C 76.21 H 6.67 N 3.86%,

Found C 76.09 H 6.70 N 3.95%.

MS (*m/z*): 724 (3) (M⁺); 681 (11) (M-C₃H₇); 499 (100) (M-C₁₆H₁₇O); 484 (4) (M-C₁₆H₁₈NO)⁺; 362 (7) (C₂₃H₂₄NOS)⁺; 241 (8) (C₁₆H₁₉NO)⁺; 185 (16) (C₁₂H₁₁NO)⁺.

1,5-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]methylidene-2-thienyl}pentane (7c)

From 300.00 mg (1.03 mmol) **3e** and 515.00 mg (2.14 mmol) 4-amino-4'-butyloxybiphenyl [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%).

C₄₄H₅₀N₂O₂S₂ (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=N); 7.5 (m, 8H, BiP-H₂H₂H₆H₆); 7.26 (d, 2H, *J*₄₋₃ = 3 Hz, Th-H₄); 7.2 (m, 4H, BiP-H₃H₅); 6.94 (d, 4H, *J*_{3'-2'} = 7.5 Hz, BiP-H₃H₅); 6.78 (d, 2H, *J*₃₋₄ = 3 Hz, Th-H₃); 3.96 (t, 4H, *J* = 5.3 Hz, CH₂-OBiP); 2.84 (t, 4H, *J* = 5.3 Hz, Th-CH₂); 1.78 (m, 4H, CH₂-CH₂OBiP); 1.78 (m, 4H, ThCH₂-CH₂); 1.5 (m, 4H, CH₂-(CH₂)₂OBiP); 1.45 (m, 2H, Th-(CH₂)₂-CH₂); 0.94 (t, 6H, *J* = 6.3 Hz, -CH₃). – MS (*m/z*): 738 (23) (M⁺); 695 (3) (M-C₃H₇)⁺; 512 (70) (M-C₁₆H₁₇O)⁺; 498 (1) (M-C₁₆H₁₈NO)⁺; 361 (22) (C₂₃H₂₃NOS)⁺; 241 (13) (C₁₆H₁₉NO)⁺; 185 (100) (C₁₂H₁₁NO)⁺. – UV (CHCl₃) λ (nm)/log ϵ : 270 (4.33); 315 (4.32); 354 (4.64).

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

1,6-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]methylidene-2-thienyl}hexane (7d)

From 300.00 mg (0.98 mmol) **3f** and 489.00 mg (2.03 mmol) 4-amino-4'-butyloxybiphenyl [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%).

C₄₈H₅₂N₂O₂S₂ (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-C₁₆H₁₇O)⁺; 512 (17) (M-C₁₆H₁₈NO)⁺; 362 (16) (C₂₃H₂₄NOS); 241 (11) (C₁₆H₁₉NO)⁺; 185 (16) (C₁₂H₁₁NO)⁺.

1,7-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]methylidene-2-thienyl}heptane (7e)

From 300.00 mg (0.94 mmol) **3g** and 470.00 mg (1.95 mmol) 4-amino-4'-butyloxybiphenyl [17] in 50 ml absol. xylene; light green crystals from absol. THF; m.p.: 178 °C; c.p.: 237 °C; yield: 560.00 mg (78%).

C₄₉H₅₄N₂O₂S₂ (767.1)

Calcd C 76.72 H 7.10 N 3.65%,

Found C 76.63 H 7.02 N 3.77%.

^1H NMR (CDCl_3) $\delta(\text{ppm}) = 8.5$ (s, 2H, $\text{CH}=\text{N}$); 7.5 (m, 8H, $\text{BiP}-\text{H}_2\text{H}_2\text{H}_6\text{H}_6$); 7.26 (d, 2H, $J_{4-3} = 3$ Hz, $\text{Th}-\text{H}_4$); 7.2 (m, 4H, $\text{BiP}-\text{H}_3\text{H}_5$); 6.94 (d, 4H, $J_{3'-2'} = 7.5$ Hz, $\text{BiP}-\text{H}_3\text{H}_5$); 6.78 (d, 2H, $J_{3-4} = 3$ Hz, $\text{Th}-\text{H}_3$); 3.96 (t, 4H, $J = 5.3$ Hz, CH_2-OBiP); 2.84 (t, 4H, $J = 5.3$ Hz, $\text{Th}-\text{CH}_2$); 1.78 (m, 4H, $\text{CH}_2-\text{CH}_2\text{OBiP}$); 1.78 (m, 4H, $\text{ThCH}_2-\text{CH}_2$); 1.5 (m, 4H, $\text{CH}_2-(\text{CH}_2)_2\text{OBiP}$); 1.34 (m, 2H, $\text{Th}-(\text{CH}_2)_2-\text{CH}_2$); 0.94 (t, 6H, $J = 6.3$ Hz, $-\text{CH}_3$).

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

MS (m/z): 766 (100) (M^+); 723 (1) ($\text{M}-\text{C}_3\text{H}_7$) $^+$; 541 (76) ($\text{M}-\text{C}_{16}\text{H}_{17}\text{O}$) $^+$; 526 (10) ($\text{M}-\text{C}_{16}\text{H}_{18}\text{NO}$) $^+$; 362 (26) ($\text{C}_{23}\text{H}_{24}\text{NOS}$) $^+$; 241 (8) ($\text{C}_{16}\text{H}_{19}\text{NO}$) $^+$; 185 (12) ($\text{C}_{12}\text{H}_{11}\text{NO}$) $^+$.

1.8-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]-methylidene-2-thienyl}octane (7f)

From 300.00 mg (0.90 mmol) **3h** and 451.00 mg (1.87 mmol) 4-amino-4'-butyloxybiphenyl [17] in 50 ml absol. xylene; light green crystals from absol. THF; m.p.: 202 °C; c.p.: 242 °C; yield: 235.00 mg (34%).

$\text{C}_{50}\text{H}_{56}\text{N}_2\text{O}_2\text{S}_2$ (781.1)
Calcd C 76.88 H 7.23 N 3.59%,
Found C 76.69 H 7.18 N 3.41%.

MS (m/z): 780 (100) (M^+); 737 (1) ($\text{M}-\text{C}_3\text{H}_7$) $^+$; 555 (50) ($\text{M}-\text{C}_{16}\text{H}_{17}\text{O}$) $^+$; 540 (42) ($\text{M}-\text{C}_{16}\text{H}_{18}\text{NO}$) $^+$; 362 (67) ($\text{C}_{23}\text{H}_{24}\text{NOS}$) $^+$; 241 (36) ($\text{C}_{16}\text{H}_{19}\text{NO}$) $^+$; 185 (53) ($\text{C}_{12}\text{H}_{11}\text{NO}$) $^+$.

1.9-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]-methylidene-2-thienyl}nonane (7g)

From 300.00 mg (0.86 mmol) **3i** and 431.00 mg (1.79 mmol) 4-amino-4'-butyloxybiphenyl [17] in 50 ml absol. xylene; light green crystals from absol. THF; m.p.: 164 °C; c.p.: 220 °C; yield: 605.00 mg (80%).

$\text{C}_{51}\text{H}_{58}\text{N}_2\text{O}_2\text{S}_2$ (795.2)
Calcd C 77.04 H 7.35 N 3.52%,
Found C 76.89 H 7.41 N 3.39%.

MS (m/z): 794 (100) (M^+); 751 (1) ($\text{M}-\text{C}_3\text{H}_7$) $^+$; 569 (33) ($\text{M}-\text{C}_{16}\text{H}_{17}\text{O}$) $^+$; 554 (42) ($\text{M}-\text{C}_{16}\text{H}_{18}\text{NO}$) $^+$; 362 (40) ($\text{C}_{23}\text{H}_{24}\text{NOS}$) $^+$; 241 (31) ($\text{C}_{16}\text{H}_{19}\text{NO}$) $^+$; 185 (48) ($\text{C}_{12}\text{H}_{11}\text{NO}$) $^+$.

1.10-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]-methylidene-2-thienyl}decane (7h)

From 300.00 mg (0.83 mmol) **3k** and 415.00 mg (1.72 mmol) 4-amino-4'-butyloxybiphenyl in 50 ml

absol. xylene; light green crystals from absol. THF; m.p.: 198 °C; c.p.: 232 °C; yield: 511.00 mg (75%).

$\text{C}_{52}\text{H}_{60}\text{N}_2\text{O}_2\text{S}_2$ (809.2)
Calcd C 77.18 H 7.47 N 3.46%,
Found C 77.00 H 7.46 N 3.49%.

MS (m/z): 808 (100) (M^+); 765 (1) ($\text{M}-\text{C}_3\text{H}_7$) $^+$; 583 (52) ($\text{M}-\text{C}_{16}\text{H}_{17}\text{O}$) $^+$; 568 (76) ($\text{M}-\text{C}_{16}\text{H}_{18}\text{NO}$) $^+$; 362 (70) ($\text{C}_{23}\text{H}_{24}\text{NOS}$) $^+$; 241 (49) ($\text{C}_{16}\text{H}_{19}\text{NO}$) $^+$; 185 (86) ($\text{C}_{12}\text{H}_{11}\text{NO}$) $^+$.

1.11-Bis{5-[N-(4'-butyloxybiphenyl-4-yl)imino]-methylidene-2-thienyl}undecane (7i)

From 300.00 mg (0.80 mmol) **3l** and 395.00 mg (1.64 mmol) 4-amino-4'-butyloxybiphenyl [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%).

$\text{C}_{53}\text{H}_{62}\text{N}_2\text{O}_2\text{S}_2$ (823.2)
Calcd C 77.33 H 7.59 N 3.40%,
Found C 77.40 H 7.50 N 3.28%.

MS (m/z): 822 (94) (M^+); 779 (1) ($\text{M}-\text{C}_3\text{H}_7$) $^+$; 597 (33) ($\text{M}-\text{C}_{16}\text{H}_{17}\text{O}$) $^+$; 582 (89) ($\text{M}-\text{C}_{16}\text{H}_{18}\text{NO}$) $^+$; 362 (78) ($\text{C}_{23}\text{H}_{24}\text{NOS}$) $^+$; 241 (66) ($\text{C}_{16}\text{H}_{19}\text{NO}$) $^+$; 185 (100) ($\text{C}_{12}\text{H}_{11}\text{NO}$) $^+$.

1.12-Bis{5-[N-(4'-butyloxybiphenyl-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'-butyloxybiphenyl [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%).

$\text{C}_{54}\text{H}_{64}\text{N}_2\text{O}_2\text{S}_2$ (837.2)
Calcd C 77.47 H 7.71 N 3.34%,
Found C 77.45 H 7.68 N 3.42%.

MS (m/z): 836 (100) (M^+); 793 (3) ($\text{M}-\text{C}_3\text{H}_7$) $^+$; 611 (34) ($\text{M}-\text{C}_{16}\text{H}_{17}\text{O}$) $^+$; 596 (83) ($\text{M}-\text{C}_{16}\text{H}_{18}\text{NO}$) $^+$; 362 (88) ($\text{C}_{23}\text{H}_{24}\text{NOS}$) $^+$; 241 (63) ($\text{C}_{16}\text{H}_{19}\text{NO}$) $^+$; 185 (79) ($\text{C}_{12}\text{H}_{11}\text{NO}$) $^+$.

1.16-Bis{5-[N-(4'-butyloxybiphenyl-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'-butyloxybiphenyl [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%).

$\text{C}_{58}\text{H}_{72}\text{N}_2\text{O}_2\text{S}_2$ (893.3)
Calcd C 77.98 H 8.12 N 3.14%,
Found C 77.73 H 8.08 N 3.33%.

MS (m/z): 892 (100) (M^+); 667 (4) ($M-C_{16}H_{17}O$) $^+$; 652 (4) ($M-C_{16}H_{18}O$) $^+$; 362 (10) ($C_{23}H_{24}NOS$) $^+$; 241 (61) ($C_{16}H_{19}NO$) $^+$; 185 (100) ($C_{12}H_{11}NO$) $^+$.

General synthesis of the

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

In a 1 l 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-fluorenylmethyltriphenylphosphonium 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 CH_3OLi (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 about 1 mmol in 30 ml absol. toluene with 2 ml of a $7 \cdot 10^{-5}$ M solution of iodine in toluene. While the toluene-mixture was cooled, the product settled down. More purification was done by recrystallization from ethanol/ $CHCl_3$ or/and toluene. The crystals were dried over P_2O_5 .

E,E-1.3-Bis[5-(2-fluorenylvinyl)-2-thienyl]-propane (**8a**)

From 300.00 mg **3c** (1.14 mmol) 1.20 g Wittig-salt **10** [18] (2.3 mmol) in 60 ml absol. ethanol and 3.5 ml CH_3OLi (1 M solution in CH_3OH), orange coloured crystals from DMF; m.p.: 276 °C; yield: 123.00 mg (18%).

$C_{41}H_{32}S_2$ (588.8)

Calcd C 83.63 H 5.48%,
Found C 83.59 H 5.45%.

IR (KBr) $\nu(\text{cm}^{-1})$ = 3060 (m) $\nu(C-H_{Ar})$; 3020 (m) $\nu(CH=CH)$; 2930 (vs), 2860 (s) $\nu(C-H)$; 1630 (w) $\nu(Ar-C=C)$; 1605 (fl-Aromat); 1540 (w), 1465 (s) $\nu(Aromat)$; 955 (vs) $\delta(CH=CH)_{oop}$; 800,820 (s) $\delta(Th-C-H)_{oop}$.

This spectrum is also typical for these of **8b–8l**.
MS (m/z): 588 (58) (M^+); 294 (9) (M^{2+}); 314 (10) ($C_{22}H_{18}S^+$); 300 (100) ($C_{21}H_{16}S^+$); 287 (61) ($C_{20}H_{15}S^+$); 253 (42) ($C_{20}H_{13}^+$); 179 (19) ($C_{14}H_{11}^+$).
– UV ($CHCl_3$) $\lambda(\text{nm})/\log \epsilon$: 268 (3.84), 278 (sh), 345 (sh), 361 (4.51), 378 (4.25).

These absorptions are also typical for these of **8b–8l**.

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. CH_3OH and 4 ml CH_3OLi (1 M solution in CH_3OH), yellow crystals from toluene; m.p.: 249 °C; c.p.: 276 °C; yield: 750.00 mg (70%).

$C_{42}H_{34}S_2$ (602.9)

Calcd C 83.68 H 5.68%,
Found C 83.62 H 6.04%.

1H NMR ($CDCl_3$) $\delta(\text{ppm})$ = 7.77 (d, 2H, J_{5-6} = 7 Hz, FlH_5); 7.73 (d, 2H, J_{4-3} = 7.5 Hz, FlH_4), 7.65 (s, 2H, FlH_1); 7.54 (d, 2H, J_{8-7} = 7.5 Hz, FlH_8); 7.46 (d, 2H, J_{3-4} = 7.5 Hz, FlH_3); 7.41 (m, 4H, FlH_6H_7); 7.21 (d, 2H, J = 16.3 Hz, $Fl-CH=CH-Th$); 6.89 (d, 2H, J = 16.3 Hz); 6.88 (d, 2H, J_{4-3} = 3.8 Hz, ThH_4); 6.68 (d, 2H, J_{3-4} = 3.8 Hz, ThH_3); 3.9 (s, 4H, FlH_9), 2.85 (m, 4H, $Th-CH_2$); 1.79 (m, 4H, $Th-CH_2-CH_2$). – MS (m/z): 602 (29) (M^+); 301 (9) (M^{2+}); 313 (7) ($C_{22}H_{17}S^+$); 300 (8) ($C_{21}H_{16}S^+$); 287 (43) ($C_{20}H_{15}S^+$); 253 (39) ($C_{20}H_{13}^+$); 179 (10) ($C_{14}H_{11}^+$).

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 CH_3OLi (1 M solution in CH_3OH), light brown crystals from $CHCl_3$ /ethanol; m.p.: 240 °C; yield: 680.00 mg (81%).

$C_{43}H_{36}S_2$ (616.9)

Calcd C 83.72 H 5.88%,
Found C 83.68 H 5.84%.

1H NMR ($CDCl_3$) $\delta(\text{ppm})$ = 7.77 (d, 2H, J_{5-6} = 7 Hz, FlH_5); 7.73 (d, 2H, J_{4-3} = 7.5 Hz, FlH_4), 7.65 (s, 2H, FlH_1); 7.54 (d, 2H, J_{8-7} = 7.5 Hz, FlH_8); 7.46 (d, 2H, J_{3-4} = 7.5 Hz, FlH_3); 7.41 (m, 4H, FlH_6H_7); 7.21 (d, 2H, J = 16.3 Hz, $Fl-CH=CH-Th$); 6.89 (d, 2H, J = 16.3 Hz, $Fl-CH=CH-Th$); 6.88 (d, 2H, J_{4-3} = 3.8 Hz, ThH_4); 6.68 (d, 2H, J_{3-4} = 3.8 Hz, ThH_3); 3.9 (s, 4H, FlH_9), 2.79 (t, 4H, J = 7.5 Hz, $Th-CH_2$); 2.63 (quint., 4H, J = 7.5 Hz, $Th-CH_2-CH_2$), 1.79 (hex., 4H, J = 7.5 Hz, $Th-(CH_2)_2-CH_2$). – MS (m/z): 616 (100) (M^+); 308 (14) (M^{2+}); 316 (2) ($C_{22}H_{17}S^+$); 300 (2) ($C_{21}H_{16}S^+$); 287 (53) ($C_{20}H_{15}S^+$); 253 (21) ($C_{20}H_{13}^+$); 179 (5) ($C_{14}H_{11}^+$).

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. CH_3OH

and 3 ml CH_3OLi (1 M solution in CH_3OH), light brown crystals from CH_2Cl_2 /ethanol; m.p.: 227 °C; c.p.: 234 °C; yield: 718.00 mg (87%).

$\text{C}_{44}\text{H}_{38}\text{S}_2$ (630.9)

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

^1H NMR (CDCl_3) δ (ppm) = 7.77 (d, 2H, J_{5-6} = 7 Hz, FlH_5); 7.73 (d, 2H, J_{4-3} = 7.5 Hz, FlH_4), 7.65 (s, 2H, FlH_1); 7.54 (d, 2H, J_{8-7} = 7.5 Hz, FlH_8); 7.46 (d, 2H, J_{3-4} = 7.5 Hz, FlH_3); 7.41 (m, 4H, FlH_6H_7); 7.21 (d, 2H, J = 16.3 Hz, $\text{Fl}-\text{CH}=\text{CH}-\text{Th}$); 6.89 (d, 2H, J = 16.3 Hz, $\text{Fl}-\text{CH}=\text{CH}-\text{Th}$); 6.88 (d, 2H, J_{4-3} = 3.8 Hz, ThH_4); 6.68 (d, 2H, J_{3-4} = 3.8 Hz, ThH_3); 3.9 (s, 4H, FlH_9), 2.79 (t, 4H, J = 7.5 Hz, $\text{Th}-\text{CH}_2$); 1.71 (quint., 4H, J = 7.5 Hz, $\text{Th}-\text{CH}_2-\text{CH}_2$); 1.4 (hex., 4H, J = 7.5 Hz, $\text{Th}-(\text{CH}_2)_2-\text{CH}_2$). – MS (m/z): 630 (100) (M^+); 315 (7) (M^{2+}); 316 (11) ($\text{C}_{22}\text{H}_{17}\text{S}^+$); 300 (3) ($\text{C}_{21}\text{H}_{16}\text{S}^+$); 287 (63) ($\text{C}_{20}\text{H}_{15}\text{S}^+$); 253 (24) ($\text{C}_{20}\text{H}_{13}^+$); 179 (7) ($\text{C}_{14}\text{H}_{11}^+$).

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 CH_3OLi (1 M solution in CH_3OH), yellow-gold crystals from ethanol and then toluene; m.p.: 223 °C; yield: 821 mg (68%).

$\text{C}_{45}\text{H}_{40}\text{S}_2$ (644.9)

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

^1H NMR (CDCl_3) δ (ppm) = 7.77 (d, 2H, J_{5-6} = 7 Hz, FlH_5); 7.73 (d, 2H, J_{4-3} = 7.5 Hz, FlH_4), 7.65 (s, 2H, FlH_1); 7.54 (d, 2H, J_{8-7} = 7.5 Hz, FlH_8); 7.46 (d, 2H, J_{3-4} = 7.5 Hz, FlH_3); 7.41 (m, 4H, FlH_6H_7); 7.21 (d, 2H, J = 16.3 Hz, $\text{Fl}-\text{CH}=\text{CH}-\text{Th}$); 6.89 (d, 2H, J = 16.3 Hz, $\text{Fl}-\text{CH}=\text{CH}-\text{Th}$); 6.88 (d, 2H, J_{4-3} = 3.8 Hz, ThH_4); 6.68 (d, 2H, J_{3-4} = 3.8 Hz, ThH_3); 3.9 (s, 4H, FlH_9), 2.79 (t, 4H, J = 7.5 Hz, $\text{Th}-\text{CH}_2$); 1.69 (quint., 4H, J = 7.5 Hz, $\text{Th}-\text{CH}_2-\text{CH}_2$), 1.3 (m, 6H, $\text{Th}-(\text{CH}_2)_2-\text{CH}_2-\text{CH}_2$).

This spectrum is similar to these of **8f**–**8h**.

MS (m/z): 644 (100) (M^+); 322 (10) (M^{2+}); 287 (15) ($\text{C}_{20}\text{H}_{15}\text{S}^+$); 253 (5) ($\text{C}_{20}\text{H}_{13}^+$).

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 CH_3OLi (1 M solution in CH_3OH), yellow-gold crystals from ethanol/

CHCl_3 and then toluene; m.p.: 222 °C; yield: 453.00 mg (81%).

$\text{C}_{46}\text{H}_{42}\text{S}_2$ (659.0)

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

MS (m/z): 658 (100) (M^+); 329 (17) (M^{2+}); 287 (93) ($\text{C}_{20}\text{H}_{15}\text{S}^+$); 253 (40) ($\text{C}_{20}\text{H}_{13}^+$); 179 (64) ($\text{C}_{14}\text{H}_{11}^+$).

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/ CHCl_3 and then toluene; m.p.: 212 °C; yield: 751 mg (78%).

$\text{C}_{47}\text{H}_{44}\text{S}_2$ (673.0)

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

MS (m/z): 672 (100) (M^+); 336 (17) (M^{2+}); 287 (70) ($\text{C}_{20}\text{H}_{15}\text{S}^+$); 253 (24) ($\text{C}_{20}\text{H}_{13}^+$); 179 (21) ($\text{C}_{14}\text{H}_{11}^+$).

E,E-1.10-Bis[5-(2-fluorenylvinyl)-2-thienyl]decane (**8h**)

From 600.00 mg **3k** (1.65 mmol) 2.00 g Wittig-salt **10** [18] (3.8 mmol) in 60 ml absol. ethanol and 4 ml CH_3OLi (1 M solution in CH_3OH), yellow crystals from ethanol/ CHCl_3 and then toluene; m.p.: 213 °C; yield: 930.00 mg (82%).

$\text{C}_{48}\text{H}_{46}\text{S}_2$ (687.0)

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

MS (m/z): 686 (100) (M^+); 343 (12) (M^{2+}); 287 (44) ($\text{C}_{20}\text{H}_{15}\text{S}^+$); 253 (18) ($\text{C}_{20}\text{H}_{13}^+$); 179 (12) ($\text{C}_{14}\text{H}_{11}^+$).

E,E-1.11-Bis[5-(2-fluorenylvinyl)-2-thienyl]undecane (**8i**)

From 500.00 mg **3l** (1.33 mmol) 1.50 g Wittig-salt **10** [18] (2.87 mmol) in 100 ml absol. ethanol and 4 ml CH_3OLi (1 M solution in CH_3OH), light yellow crystals from toluene; m.p.: 206 °C; yield: 875.00 mg (94%).

$\text{C}_{49}\text{H}_{48}\text{S}_2$ (701.0)

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

MS (m/z): 700 (100) (M^+); 350 (13) (M^{2+}); 287 (34) ($\text{C}_{20}\text{H}_{15}\text{S}^+$); 253 (13) ($\text{C}_{20}\text{H}_{13}^+$); 179 (9) ($\text{C}_{14}\text{H}_{11}^+$).

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 absol. CH₃OH and 3 ml CH₃OH (1 M solution in CH₃OH), light yellow crystals from ethanol/CHCl₃ and then toluene; m.p.: 201 °C; yield: 769.00 mg (84%).

C₅₀H₅₀S₂ (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] (2.1 mmol) in 35 ml absol. DMF/ethanol (1.5:1) and 3 ml CH₃OLi (1 M solution in CH₃OH), light yellow crystals from ethanol/CHCl₃ and then toluene; m.p.: 196 °C; yield: 492 mg (71%).

C₅₄H₅₈S₂ (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%).

C₁₂H₈N₂S₂ (244.3)

Calcd C 58.99 H 3.30 N 11.47%,

Found C 58.87 H 3.21 N 11.29%.

¹H NMR (CDCl₃) δ(ppm) = 8.28 (s, 2H, Pyri-H₄H₅); 7.95 (d, 2H, J₅₋₄ = 3.8, Th-H₅); 7.77 (d, 2H, J₃₋₄ = 5.5, Th-H₃); 7.26 (dd, 2H, J₄₋₃ = 5.5, J₄₋₅ = 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).

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