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Methine-Brigded Five-Membered Heterocycles as Precursors for Low-Gap Polymers

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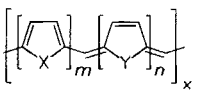
The synthesis of suitable precursors of polyarenemethines (PAM) **1**, which are predicted to be potential low gap polymers, is described. The Knoevenagel condensation of heteroaromatic aldehydes with 2,5-dihydrothiophene 1,1-dioxide (**5**), 2,5-dihydrothiophene 1-oxide (**9**), and its benzo-annulated analogs [**6**] and [**10**] yields the methine-bridged compounds **7**, [**8**], **11**, and [**12**], respectively. Reduction of the methine-bridged sulfoxides **11** and [**12**] leads to the corresponding sulfides **13** and [**14**]. For compound **18** with a high sterical demand another route has been developed. Thus, the reaction of the dicarbinol **17** with HI yields directly the heteroaromatic quinodimethane **18**. The molecular structures of **7a** and **18** are determined by X-ray analysis.

In recent years the discovery of highly conducting (doped) polymers has generated substantial interest among chemists and physicists. The development of new materials, combining processability, light weight, and durability of plastics with electrical conductivities of metals or semiconductors, is the driving force of the increasing activity in this new area. Higher conductivities of these polymers, e.g. polyacetylene (PA)[1], poly-*p*-phenylene (PPP)[2], polypyrrole (PPy)[3], and polythiophene (PT)[4], are reached however only after chemical or electrochemical oxidative (p) or reductive (n) doping. Thereby conductivities up to $\approx 10^5$ S/cm, e.g. with PA, can be reached[1]. However, the thermal and chemical stability of many of the doped systems is not very high. Therefore, the search for polymers which, due to a low band gap, at least show semiconducting properties without doping, is an important task for chemists[5,6].

Among the solid-state properties of such polymers the band gap value is one of the significant parameters that rule the intrinsic electronic properties, including electrical transport, optical properties, and magnetic behavior. Recently, the possibility to obtain low-gap polymers has been predicted in a theoretical work[7]. Based on VEH (Valence Effective Hamiltonian) calculations it has been suggested, that the gap E_g in polymers related to PPy or PT is a function of the quinonoid character of these polymers; E_g decreases with increasing quinonoid character of the subunits.

The first species of this type is the recently synthesized polyisothianaphthene (PITN) with a gap of ≈ 1 eV[8], which means half the gap value of PT. The ring annulation in PITN stabilizes the quinonoid contributions in the ground state in comparison to PT. Another system in which alternating aromatic and quinonoid subunits are combined is the methine-bridged polymer **1**. Based on extended Hückel[9] and VEH calculations[10,11] polymers of the general formula **1** have been predicted to possess a small band gap ($\approx$ 1 eV).

Several attempts to synthesize the polymer **1** based on thiophene subunits (X = Y = S) have been reported in the literature. The condensation of heteroaromatic compounds, e.g. thiophene or bithiophene with *p*-substituted benzaldehydes followed by oxidation with bromine[12,13] and the electrochemical polymerization of diheteroarenemethanes[14], e.g. dipyrrolylmethane, results in doped polymers with a chemical non-uniform structure and a maximum conductivity of 1 S/cm[14].



X = O, S, N–R, CH=CH
Y = O, S, SO, SO_2, N–R, CH=CH

1

Another approach is the condensation of heterocyclic aldehydes like pyrrole-2-carbaldehyde, catalyzed by Lewis acids[15] ($FeCl_3$, $POCl_3$ etc.), which results in the formation of polymers with conductivities of 10^{-4} S/cm. These have been described to have a composition given in formula **1**.

To study the predicted electronic properties, we have decided to follow a different route for the synthesis of a structurally uniform polymer **3**. An important requirement for this is the synthesis of precursors **2** in which the quinonoid structure is already present. For polymerization of **2** several methods can then be applied. Electrochemical polymerization[4] or polymerization using oxidizing agents like e.g. $NOBF_4$[16] will lead to the oxidized form of **3**. For the synthesis of the non-doped polymer **3**, precursors **2** with reactive side groups (Z = Cl, Br, I), which can be converted into organometallic intermediates, are needed. The addition of a transition-metal catalyst starts polymerization[17, 18, 19], yielding the undoped species **3**. As a consequence of the alternation of two aromatic and one quinonoid subunits, the electronic groundstate in the resulting polymer **3** is not

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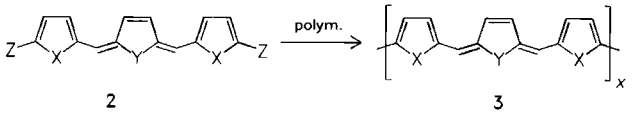
degenerated. Recently, we have reported on some benzenoid and anthracenoid precursors and their polymerization[6].



2 3

X = O, S, N–R, CH=CH
Y = O, S, SO, SO_2, N–R, CH=CH
Z = Cl, Br, I

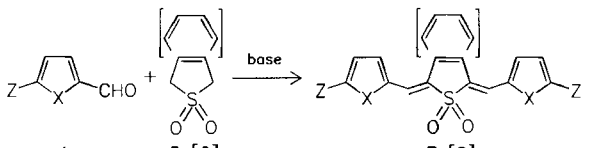
For the preparation of polymers **3**, the synthesis of suitable precursors **2** has to be developed first. Some examples of methine-bridged oligomers with X = N–H, Y = S, R = (*t*Bu)phenyl[20] and X,Y = S,R = phenyl[13] have been reported; however, no detailed information about experimental and/or analytical data are given.

In this paper we present a general synthesis for a variety of heteroaromatic methine-bridged oligomers **2** as suitable precursors of this new class of potential low-gap polymers **3**.

Synthesis

In order to develop a synthesis for the methine-bridged precursors **2**, we have studied the Knoevenagel-type condensation of aldehydes **4** with 2,5-dihydrothiophene 1,1-dioxide (**5**). According to the literature[21] and our own experience, the reaction works well with aromatic aldehydes **4**. However, the yields are low, because of a possible rearrangement of the double bond in **5**, self-condensation of the aldehyde **4**, and other undesired side reactions. In the case of the benzo-annulated species [**6**] the protected double bond allows higher yields. With e.g. di-2-thienyl ketone the reaction does not work because of the high steric demand of the thienyl substituent and the low carbonyl activity of the carbonyl group. Treatment of 3-sulfolene (**5**) with 5-bromothiophene-2-carbaldehyde (**4d**) yields **7d**, a compound with reactive side groups in the 5,5′-position.

| | = Annulation

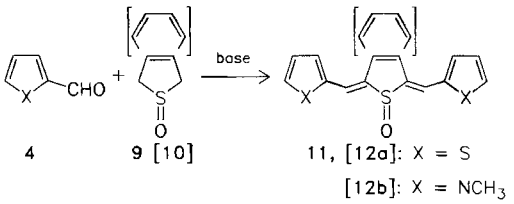


4 5 [6] 7 [8]

4, 7, [8]	a, [a]	b, [b]	c, [c]	d
Z	H	H	H	Br
X	S	NCH_3	NH	S

The obtained products **7a–d** and the benzo-annulated derivatives [**8a–c**] are air-stable and slightly soluble in organic solvents, e.g. acetone. Thermal analysis shows that decomposition occurs a few degrees above the melting point with extrusion of SO_2, as indicated by elemental analysis of the residue.

Because of the lack of reactivity of the sulfonyl group towards chemical reduction to form the sulfide, we have synthesized the corresponding methine-bridged sulfoxides **11** and [**12**] by condensation of heteroaromatic aldehydes **4a** and **4b** with 2,5-dihydrothiophene 1-oxide (**9**) and its fused ring compound [**10**] in a similar synthetic procedure as discussed for sulfones **7** and [**8**]. The obtained products **11** and [**12**] are air-stable compounds similar to **7** and [**8**].

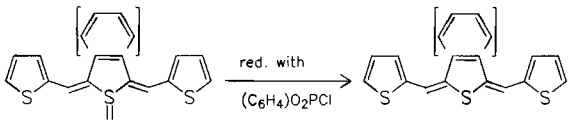


4 9 [10] 11, [12a]: X = S
[12b]: X = NCH_3

Only a few vinylic sulfoxides like **11** and [**12**] have been synthesized by direct Knoevenagel condensation. In general, the reaction of the CH-activated sulfoxides with aldehydes yields the β-hydroxyalkyl derivative; the elimination of water needs acid catalysis. Moreover, in basic medium, these compounds have a tendency to give different side reactions[22], which do not occur to the same extent in the case of the cyclic sulfoxides **9** and [**10**].

Especially in case of **11**, the yield is low. For further yield optimization the Knoevenagel reaction with different bases, e.g. amines, alkoxides and solvents, e.g. alcohols will be studied.

The sulfinyl group can be easily reduced with 2-chloro-1,3,2-benzodioxaphosphole[23] as the reducing agent in the presence of pyridine yielding 2,5-dihydro-2,5-bis(2-thienylmethylene)thiophene (**13**) and its more stable benzo-annulated analog [**14**]. This process requires a short reaction time and low temperatures (ambient). The obtained products **13** and [**14**] are the first examples fulfilling the structural requirements for precursor **2** containing aromatic and quinonoid subunits.



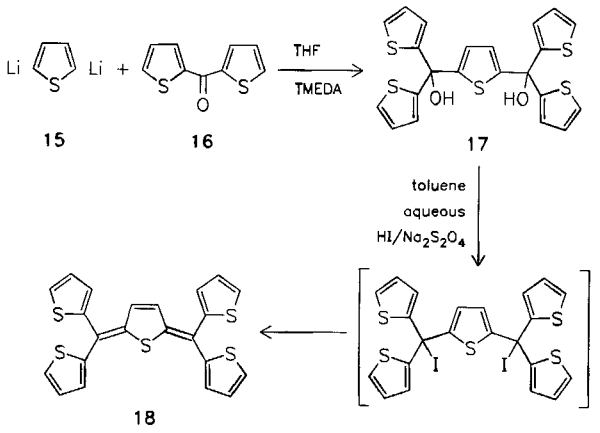
11, [12a] 13, [14]

In order to study the electronic and steric effects of substituents at the methine bridge on the properties of the polymer **3**, we have extended our investigations to substituted precursor molecules, e.g. **18**. The synthetic pathway described above is not applicable to compounds with a high steric demand, i.e. with two thienyl groups at the methine carbon. Therefore, we have developed a new synthetic route for **18**.

Dilithiothiophene (**15**)[20] is prepared by addition of *n*BuLi to thiophene in the presence of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine), which stabilizes the resulting dianion. Addition of the highly nucleophilic **15** to di-2-thienyl ketone (**16**) in THF yields the dicarbinol **17**.

Formation of the conjugated 2,5-bis(di-2-thienylmethylene)-2,5-dihydrothiophene (**18**) occurs in one step by addi-

tion of aqueous HI to a solution of the diol **17** in toluene, probably via an instable diiodide as an intermediate. The resulting product **18** is air-stable and soluble in organic solvents. Because of four reactive peripheric thiophene rings the polymerization of **18** by suitable methods[4, 16] could result in a branched polymer **3**.



Crystal Structure Analysis of 7a and 18

In order to obtain additional information about the geometry of the precursor molecules in the solid state, we have investigated **7a** and **18** by X-ray analysis. The exact geometrical data of these model compounds are a suitable basis for further theoretical calculations of the electronic structure of potential low-gap polymers of the same type.

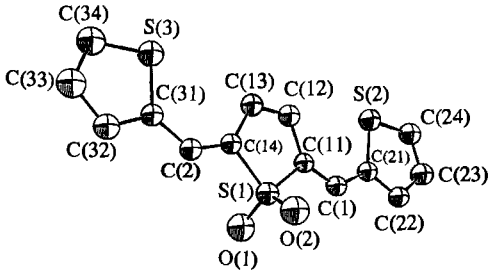


Figure 1. Perspective view of the molecular structure of **7a**

Table 1. Selected bond lengths [Å] and bond angles [°] for **7a**

S(1) -O(1)	1.434(3)	C(2) -C(14)	1.342(5)
S(1) -C(11)	1.761(3)	C(11)-C(12)	1.440(5)
S(1) -C(14)	1.767(4)	C(12)-C(13)	1.340(5)
S(2) -C(21)	1.727(4)	C(13)-C(14)	1.438(6)
S(2) -C(24)	1.684(4)	C(21)-C(22)	1.402(5)
C(1) -C(11)	1.333(5)	C(22)-C(23)	1.400(5)
C(1) -C(21)	1.430(5)	C(23)-C(24)	1.346(6)
O(1) -S(1) -O(2)	116.8(2)	C(12)-C(13)-C(14)	115.8(3)
C(11)-S(1) -C(14)	94.9(2)	S(1) -C(14)-C(2)	118.6(3)
C(21)-S(2) -C(24)	92.3(2)	S(1)- C(14)-C(13)	106.7(2)
C(11)-C(1) -C(21)	131.3(3)	S(2) -C(21)-C(1)	124.8(3)
C(14)-C(2) -C(31)	131.4(4)	S(2) -C(21)-C(22)	109.6(3)
S(1) -C(11)-C(1)	118.9(3)	C(1) -C(21)-C(22)	125.6(3)
S(1) -C(11)-C(12)	106.7(2)	C(21)-C(22)-C(23)	112.3(4)
C(1) -C(11)-C(12)	134.5(3)	C(22)-C(23)-C(24)	113.0(3)
C(11)-C(12)-C(13)	116.0(3)	S(2) -C(24)-C(23)	112.9(4)

Compound **7a** crystallizes in the monoclinic system with the space group $P2_1/c$. The lattice constants are a = 1522.7(6), b = 1225.8(2), c = 730.5(2) pm, α = 90, β = 80.39(2), γ = 90°. All H atoms have been found (R = 0.034) in a difference Fourier map.

The three five-membered rings including the bridging atoms are nearly coplanar with only 3° deviation from the perfect plane (Figure 1). Regarding the exocyclic double bonds, an *E,E* arrangement is found for the peripheric thiophene rings. The bond lengths (Table 1) indicate a high degree of π-conjugation over the whole molecule.

The molecular geometry of **18** in the solid state is shown in Figures 2a, b. Both types of peripheric rings (plane 2–5) are twisted toward the inner quinonoid ring plane (plane 1). In Table 2 the dihedral angles between the different planes are listed.

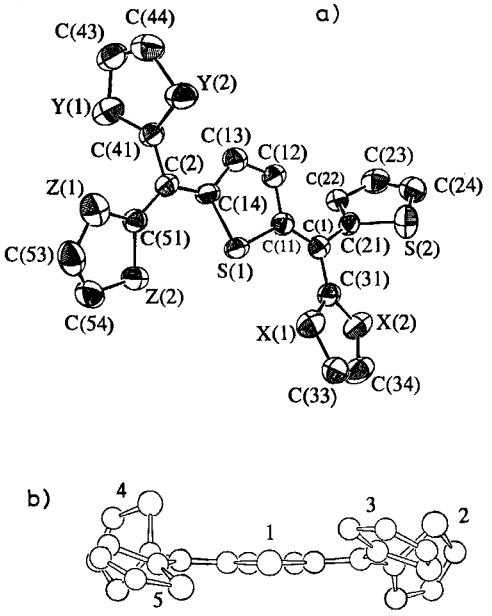


Figure 2. a) Perspective view of the molecular structure of **18**; X, Y, Z are expressions for the statistical disordered S and C atoms; b) Perspective view of **18** along the quinonoid ring (plane 1); plane 2–5: peripheric rings

Table 2. Dihedral angles [°] between the ring planes of **18**

Plane No.	Plane No.	Dihedral angle
1	2	57.4
1	3	27.9
1	4	110.3
1	5	28.0

Compound **18** crystallizes in the monoclinic system with the space group $P2_1/n$ and the lattice constants a = 1234.0(4), b = 1256.8(5), c = 1359.1(6) pm, α = 90, β = 104.93(4), γ = 90°.

The exact solution of the structure is not possible as the molecule crystallizes in a statistically disordered way. This conformational isomerism results from the 180° rotation of the three peripheric thiophene rings with indices 3, 4, and 5

Table 3. Selected bond lengths [Å] and bond angles [°] for **18**, which are not influenced by the statistical disorder

S(1) -C(11)	1.774(5)	C(2) -C(41)	1.480(9)
S(1) -C(14)	1.772(6)	C(2) -C(51)	1.455(7)
S(2) -C(21)	1.725(5)	C(11)-C(12)	1.439(9)
S(2) -C(22)	1.697(7)	C(12)-C(13)	1.360(8)
C(1) -C(11)	1.367(8)	C(13)-C(14)	1.437(8)
C(1) -C(21)	1.474(7)	C(21)-C(22)	1.415(8)
C(1) -C(31)	1.467(8)	C(22)-C(23)	1.448(7)
C(2) -C(14)	1.358(8)	C(23)-C(24)	1.350(9)
C(11)-S(1) -C(14)	92.9(3)	C(12)-C(13)-C(14)	115.2(6)
C(21)-S(2) -C(24)	93.4(4)	S(1) -C(14)-C(2)	126.0(4)
C(11)-C(1) -C(21)	117.8(5)	S(1) -C(14)-C(13)	108.5(4)
C(11)-C(1) -C(31)	124.1(5)	S(2) -C(21)-C(1)	121.5(4)
C(21)-C(1) -C(31)	118.2(6)	S(2) -C(21)-C(22)	110.3(4)
S(1) -C(11)-C(1)	124.8(4)	C(1) -C(21)-C(22)	128.1(5)
S(1) -C(11)-C(12)	108.7(5)	C(21)-C(22)-C(23)	110.3(5)
C(1) -C(11)-C(12)	126.6(5)	C(22)-C(23)-C(24)	114.1(7)
C(11)-C(12)-C(13)	114.6(6)	S(2) -C(24)-C(23)	111.9(5)

(Figure 2) between two nearly equivalent positions [X(1) ⇄ X(2); Y(1) ⇄ Y(2); Z(1) ⇄ Z(2)]. As a consequence, the electron density between the opposite S and C atoms in the thiophene rings is averaged. This leads to mixed bond lengths and bond angles in these thiophene rings, because they have contributions of the C–S and C–C bonds. Refinement with isotropic thermal parameters for all atoms results in $R = 0.164$. Surprisingly, in the case of the thiophene ring with index 2 there is only a minor statistical disorder. The calculated bond lengths and bond angles are nearly correct. The geometrical data of the quinonoid ring system and the attached methine carbons are also reliable (Table 3), due to the rigidity of the inner ring plane. In a further refinement step the electron density of the hydrogen atoms has been found in the correct distances in the case of the aromatic ring 2 and the inner quinonoid system.

The refinement of the structure has been performed in a simple approach with mixed atomic scattering factors of the two kinds of atoms. This contribution of the C and S atoms has been estimated with the help of the ratio of the electron density, which has been calculated by Fourier methods. The estimated statistical distribution is listed in the footnotes of Table 8.

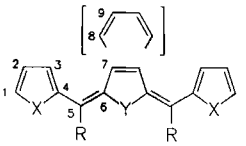
Under these conditions the refinement with isotropic thermal parameters can be optimized reaching $R = 0.118$ and by the use of anisotropic thermal parameters $R = 0.059$. Attempts to force the molecule into a more uniform structural arrangement by metal coordination (M = Ru, Mo) have been unsuccessful.

NMR Spectroscopy

The ^{1}H resonances of the heterocyclic rings in **7**, **8**, **11**, **12**, **13**, **14**, and **18** are assigned by analysis of their coupling pattern and their coupling constants. Compared to the protons in the thiophene rings of **7a**, **7d**, **8a**, **11**, **12a**, **13**, **14**, and **18** an upfield shift is observed in the less aromatic but more electron-rich pyrrole systems **7b**, **7c**, **8b**, **8c**, and **12b**. Thus, the methine proton (5-H) in the pyrrole derivatives **7b**, **7c**, **8b**, **8c**, and **12b** appears at higher field (Table 4). In the case of the benzo-annulated species **[8]**, **[12]**, and **[14]**, the signal of the methine hydrogen (5-H) is influenced by the ring current of the benzene ring and shifted downfield. The sulfonyl and the sulfinyl group in **7**, **[8]**, **11**, and **[12]**, respectively, have a similar – I-effect resulting in a similar downfield shift of the ^{1}H resonances, compared to the spectra of the oxygen-free sulfides **13** and **[14]**, in which chemical shifts are mainly dominated by mesomeric effects.

In all of the described examples, there is no evidence for the existence of a mixture of *E,E*, *Z,E* or *Z,Z* isomers in solution, because the signal of the methine proton 5-H appears as a singlet. According to the crystal structure of **7a** (Figure 1), a planar molecule with an *E,E* arrangement of the peripheric rings can be discussed for the molecular structures of **7**, **11**, and **13** in solution. In the benzo-annulated species **[8]**, **[12]**, and **[14]**, the ring current of the phenyl-ring has a strong effect on the chemical shift of the methine proton (5-H) ($\Delta\delta \approx 0.5$ ppm). Therefore we suggest a *Z,Z* arrangement of the peripheric rings in the case of the benzo-annulated species **[8]**, **[12]**, and **[14]**.

Table 4. ^{1}H-NMR data (δ values) of **7**, **[8]**, **11**, **[12]**, **13**, **[14]**, and **18** in [D$_6$]DMSO with [D$_6$]DMSO as internal standard



	1-H	2-H	3-H	5-H	7-H	8-H	9-H
7a	7.91 d	7.28 dd	7.67 dd	7.49 s	7.46 s	-	-
7b[a]	7.1 dd	6.23 dd	6.83 dd	6.89 s	7.35 s	-	-
7c[b]	7.1 dd	6.31 dd	6.77 dd	6.86 s	7.35 s	-	-
7d	-	7.385 d	7.51 d	7.39 s	7.44 s	-	-
[8a][c]	7.90 d	7.25 dd	7.87 d	8.05 s	-	7.91 dd	7.47 dd
[8b][d]	7.09 dd	6.20 dd	7.34 dd	7.47 s	-	7.86 dd	7.36 dd
[8c][e]	7.19 d	6.32 dd	7.19 d	7.52 s	-	7.62 dd	7.38 dd
11	7.82 d	7.20 dd	7.53 d	7.51 s	7.40 s	-	-
[12a]	7.88 d	7.24 dd	7.67 d	8.18 s	-	7.89 dd	7.43 dd
[12b][f]	7.07 dd	6.23 dd	7.17 dd	7.75 s	-	7.91 dd	7.36 dd
13	7.68 d	7.17 dd	7.26 d	7.24 s	7.00 s	-	-
[14]	7.73 d	7.21 dd	7.38 d	7.91 s	-	8.04 dd	7.45 dd
[14][f]	6.95 d	6.82 dd	7.19 d	-	7.26 s	7.24 dd	6.98 dd
18[f]	6.835 dd 6.87 dd	6.66 dd 6.68 dd	7.28 dd 6.85 dd	-	6.77 s	planar ring nonplanar ring (Index ')	

[a] δ(NCH$_3$) = 3.75. – [b] δ(NH) = 10.67 ([D$_6$]acetone). – [c] δ(NCH$_3$) = 3.82. – [d] δ(NH) = 11.23. – [e] δ(NCH$_3$) = 3.77. – [f] [D$_6$]Benzene.

The characterization of **18** by NMR spectroscopy is difficult, since a number of different protons have similar chemical shifts and give superimposed spectra in most of the NMR solvents, except in [D$_6$]benzene, in which the ^{1}H-NMR resonances are shifted and are better separated (Figure 3a). Different ^{1}H resonances of the protons of two dif-

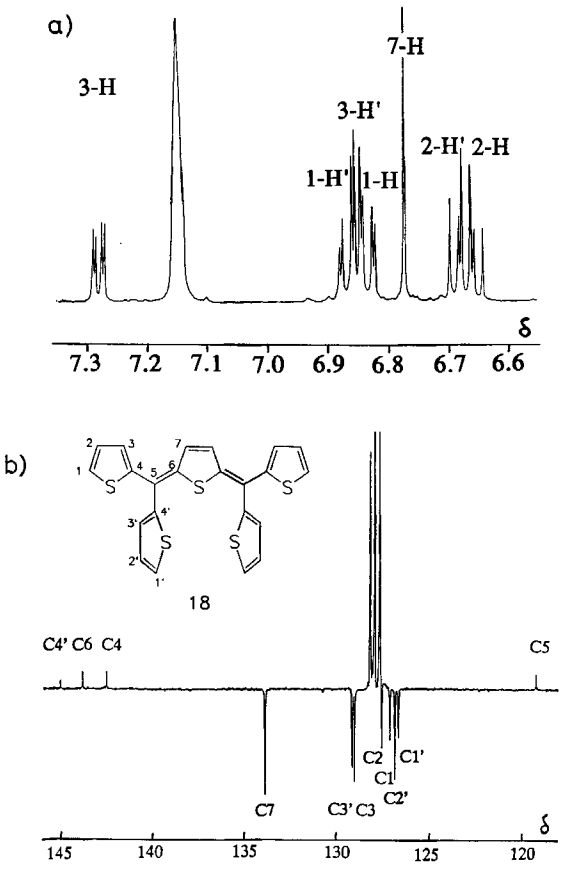


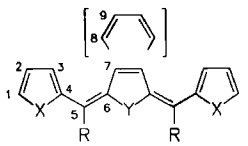
Figure 3. a) ^{1}H NMR and b) ^{13}C NMR (spin echo) of **18** in [D$_6$]benzene

ferent kinds of peripheric thiophene rings have been found, indicating two different spatial arrangements of the two thiophene rings at each methine carbon. We suppose that in solution one ring is coplanar to the inner quinonoid system and the other is twisted. That means, the spatial arrangement of the peripheric thiophene rings in solution is different from the molecular geometry in the solid state (Figure 2) in which all four peripheric rings are twisted. This difference can be explained by packing effects in the crystal, forcing the peripheric rings into the nonplanar arrangement, while in solution the coplanar arrangement of two peripheric rings relative to the inner quinonoid system is energetically more stable.

The protons belonging to the two types of rings can be assigned by analysis of the coupling constants. The planar ring is assigned by a comparison with the NMR spectra of **14** in [D$_6$]benzene (Table 4). In temperature-dependent NMR experiments performed in [D$_6$]DMSO the signals do not coalesce until 120°C, indicating thermal stability of this conformation.

The assignment of signals in the ^{13}C-NMR spectra is listed in Table 5. In the case of **7c** and the benzo-annulated compound **[8c]** the ^{13}C-NMR spectra indicate a mixture of *N*-deuterated and *N*-protonated species, because the H-D exchange is slow with respect to the NMR time scale. Therefore, the assignment of the NMR resonances of the carbon atoms neighboring the N atoms has been carried out on the basis of their deuterium shift (Δ^2 = 0.16 ppm, Δ^3 = 0.035 ppm) according to a reported method[24].

Table 5. ^{13}C-NMR data (δ value) of **7**, **[8]**, **11**, **[12]**, **13**, **[14]**, and **18** in [D$_6$]DMSO with [D$_6$]DMSO as internal standard



	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
7a	132.2	128.6	134.77	136.7	120.7	134.83	124.6	-	-
7b[a]	127.9	109.8	113.8	127.01	114.0	132.5	123.2	-	-
7c[b]	124.15	112.1	115.0	128.1	117.0	133.3	123.6	-	-
7d	117.7	131.85	135.0	138.3	119.8	135.15	124.8	-	-
[8a]	132.6	128.4	134.0	134.9	120.45	129.2	131.6	121.1	130.2
[8b][c]	128.3	109.4	115.4	125.7	117.0	127.9	129.7	120.4	128.4
[8c]	124.4	111.25	116.9	125.3	117.8	126.6	129.5	119.7	129.0
11	130.5	128.2	132.6	137.8	124.5	144.5	129.5	-	-
[12a]	131.7	128.2	132.9	135.2	124.6	140.0	137.2	121.85	129.75
[12b][d]	127.6	109.3	114.9	128.0	120.1	136.5	135.4	121.2	128.6
13	127.3	128.0	134.5	140.4	113.85	140.83	127.9	-	-
[14]	127.5	127.95	128.5	140.2	118.2	133.8	138.2	121.1	128.2
18[e]	127.2	127.6	129.1	142.6	119.2	143.9	144.0	planar ring	
	126.7	126.9	129.2	145.1				nonplanar ring (Index ')	

[a] δ(NCH$_3$) = 33.8. – [b] [D$_6$]Acetone. – [c] δ(NCH$_3$) = 34.0. – [d] δ(NCH$_3$) = 33.9. – [e] [D$_6$]Benzene.

The ^{13}C-NMR spectra of **7** and [**8**] as well as **11** and [**12**] are alike because of the similar inductive effects of the sulfonyl and sulfinyl groups. On the other hand , the spectra of the reduced species **13** and [**14**] are dominated by mesomeric effects, and as a result the ^{13}C resonances in the quinonoid unit are shifted upfield. For all compounds, we observe only one signal for the methine carbon and in the case of **7a**, **7b**, **7c**, [**8c**], and [**12b**] the ^{13}C-^{1}H coupling pattern indicates that there is no evidence for the existence of a mixture of *E,E* and *Z,Z* isomers in solution. The ^{13}C-^{1}H coupling pattern for **7** indicates an *E,E* arrangement of the molecules in solution.

In the ^{13}C-NMR spectrum of **18** different ^{13}C resonances of two kinds of peripheric rings are observed, which can be interpreted as a coplanar and a twisted arrangement with respect to the inner quinonoid ring plane (Figure 3b).

Conclusion

In this paper we present a general synthesis of methine-bridged oligomers in a large structural variety as precursors for conducting polymers. The investigation of the chemical and electrochemical polymerization is in progress. The electronic properties of thin polymer films can be studied in situ by absorption spectroscopy. According to the theory, we expect a polymer with electronic transitions in the near infrared, indicating a low band gap between the valence band (HOMO) and the conduction band (LUMO) as observed in the case of electronic semiconductors.

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Experimental

All boiling points and melting points are uncorrected. – ^{1}H- and ^{13}C-NMR: Bruker WM 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Bruker AC 250 (^{1}H, 250 MHz; ^{13}C, 62.5 MHz). – FTIR: Bruker IFS 48. – TG/DTA/DTG: Netzsch Simultan Thermoanalyser STA 429. – UV/VIS: Shimadzu UV 365. – MS: Varian MAT 711 (70 eV). – Elemental analyses: Carlo Erba Elemental Analyser 1104, 1106.

3-Sulfolene (**5**), the heterocyclic aldehydes, thiophene, and 2-chloro-1,3,2-benzodioxaphosphole are commercially available. 2,5-dihydrothiophene[25], 2,5-dihydrothiophene 1-oxide[25], 1,3-dihydroisothianaphthene (1,3-dihydrobenzo[*b*]thiophene)[26], 1,3-dihydroisothianaphthene 2-oxide[26], 1,3-dihydroisothianaphthene 2,2-dioxide[27], and di-2-thienyl ketone[28] were prepared according to literature methods. – The chromatographic isolation of the pure products was carried out by flash chromatography[29] (silica gel 40–63 μm).

2,5-Dihydro-2,5-bis(2-thienylmethylene)thiophene 1,1-Dioxide (**7a**): To a solution of 1 g of NaOH in 70 ml of ethanol were added 9.4 g (80 mmol) of 3-sulfolene (**5**) and 170 mmol of thiophene-2-carbaldehyde (**4a**). After stirring at room temp. for 3 d, the yellow precipitate was filtered and washed several times with water and ethanol to yield 2.5 g of crude product. The filtrate contained additional amounts of the product, which could be isolated by chromatography (after removal of the solvent) on silica gel with acetone as eluent to give 1 g of crude product. Crystallization of the combined crude product from acetone afforded 2 g (9%) of orange needles, m.p. 220°C. – IR (KBr): $\tilde{\nu}$ = 3113 cm^{-1}, 3097, 3084, 3073, 1603 (C=C), 1429, 1420, 1402, 1285 (SO), 1219, 1160, 1122 (SO), 1050, 851, 825, 759, 715, 680, 652. – UV (methanol): λ_{max} = 392 nm. – ^{1}H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 306 [M^+], 242 [$M^+ - SO_2$], 208, 197, 165, 134, 121 [$M^{2+} - SO_2$] (100), 108, 89, 77, 69, 63, 51, 45.

$C_{14}H_{10}O_2S_3$ (306.4)
Calcd. C 54.87 H 3.29 S 31.40
Found C 54.95 H 3.36 S 30.26

2,5-Dihydro-2,5-bis[(1-methyl-2-pyrrolyl)methylene]thiophene 1,1-Dioxide (**7b**): To a cold saturated solution of $NaOCH_3$ in methanol were added 3.56 g (30 mmol) of 3-sulfolene (**5**) and 8.6 ml (80 mmol) of 1-methylpyrrole-2-carbaldehyde (**4b**). After refluxing for 4 d the precipitate was filtered and washed with water and methanol. Two recrystallizations from acetone gave 4.0 g (44%) of red crystals, m.p. 243–246°C. – IR (KBr): $\tilde{\nu}$ = 3104 cm^{-1}, 3083, 2980, 2949, 1608 (C=C), 1559, 1525, 1484, 1467, 1431, 1417, 1396, 1354, 1312, 1302, 1266 (SO), 1247, 1167, 1149, 1124 (SO), 1067, 818, 795, 713, 657. – UV (methanol): λ_{max} = 430 nm. – ^{1}H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 300 [M^+], 236 [$M^+ - SO_2$], 222, 206, 194, 150, 118 [$M^{2+} - SO_2$] (100), 94, 77, 64, 51, 42.

$C_{16}H_{16}N_2O_2S$ (300.4)
Calcd. C 63.98 H 5.37 N 9.33 S 10.68
Found C 64.52 H 5.59 N 8.84 S 10.30

2,5-Dihydro-2,5-bis(2-pyrrolylmethylene)thiophene 1,1-Dioxide (**7c**): 2.36 g (20 mmol) of 3-sulfolene (**5**) and 4.0 g (42 mmol) of pyrrole-2-carbaldehyde (**4c**) were dissolved in an alkaline solution of 1.5 g of NaOH and 1.9 g of $NaOCH_3$ in 70 ml of methanol. The mixture was stirred at room temp. for 5 d with the exclusion of light. Removal of the solvent gave a brown oil, which was chromatographed successively on silica gel (ether), silica gel (toluene/ether 2:3), and aluminium oxide (ether). Yield: 80 mg (1.5%), m.p. 174°C (dec. without definite melting point). – IR (KBr): $\tilde{\nu}$ = 3394 cm^{-1} (NH), 3114, 1614 (C=C), 1435, 1418, 1381, 1261 (SO), 1147, 1129, 1117 (SO), 1097, 1048, 734, 658. – UV (methanol): λ_{max} = 408 nm. – ^{1}H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 272 [M^+], 208 [$M^+ - SO_2$], 192, 180, 104 [$M^{2+} - SO_2$] (100), 77, 64, 51.

$C_{14}H_{12}N_2O_2S$ (272.3)
Calcd. C 61.74 H 4.44 N 10.29
Found C 61.7 H 4.56 N 9.18

2,5-Bis[(5-bromo-2-thienyl)methylene]-2,5-dihydrothiophene 1,1-Dioxide (**7d**): To a mixture of 0.6 g of NaOH in 25 ml of water and 10 ml of THF were added 1.18 g (10 mmol) of 3-sulfolene (**5**) and 4.2 g (22 mmol) of 5-bromothiophene-2-carbaldehyde (**4d**). The heterogeneous mixture was rapidly stirred at room temp. for 2 d. Removal of the solvent gave a brown residue which was taken up in ethyl acetate and chromatographed first on silica gel (ethyl acetate) and then again on silica gel (toluene). Evaporation of the solvent gave a yellow powder, which was crystallized from acetone to yield 500 mg (11%) of yellow crystals, m.p. 249–250°C. – IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1}, 1607 (C=C), 1432, 1420, 1281 (SO), 1169, 1136 (SO), 964 (CBr), 791, 652. – UV (methanol): λ_{max} = 418 nm. – ^{1}H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 462 [M^+], 400 [$M^+ - SO_2$], 308, 200 [$M^{2+} - SO_2$], 189, 120, 82, 64 (100), 48, 44.

$C_{14}H_8Br_2O_2S_3$ (464.2)
Calcd. C 36.22 H 1.74 Br 34.42 S 20.73
Found C 36.11 H 1.61 Br 36.35 S 21.85

General Procedure for the Synthesis of 1,3-Bis(heteroarylmethylene)-1,3-dihydroisothianaphthene 2,2-Dioxide ([**8**]): In a cold saturated solution of $NaOCH_3$ in methanol were dissolved 1.68 g (10

mmol) of 1,3-dihydroisothianaphthene 2,2-dioxide ([**6**]) und 22 mmol of heteroarene-2-carbaldehyde **4a,b,c**. After refluxing for 2 d, the resulting precipitate was filtered, intensively washed with methanol, and crystallized from acetone.

1,3-Dihydro-1,3-bis(2-thienylmethylene)isothianaphthene 2,2-Dioxide ([**8a**]): Yellow crystals, yield: 600 mg (17%), m.p. 223°C. – IR (KBr): $\tilde{\nu}$ = 3104 cm^{-1}, 1604 (C=C), 1586, 1414, 1365, 1288 (SO), 1255, 1130 (SO), 1053, 858, 752, 730, 708. – UV (methanol): λ_{max} = 368 nm, 335. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 356 [M^+] (100), 292 [$M^+ - SO_2$], 275, 258, 245, 178, 163, 154, 129, 122, 69, 64, 45.

$C_{18}H_{12}O_2S_3$ (356.5)
Calcd. C 60.34 H 3.39 S 26.99
Found C 60.76 H 3.49 S 25.88

1,3-Dihydro-1,3-bis[(1-methyl-2-pyrrolyl)methylene]isothianaphthene 2,2-Dioxide ([**8b**]): Yellow needles, yield: 1.5 g (43%), m.p. 298°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3130 cm^{-1}, 3023, 1611 (C=C), 1583, 1524, 1484, 1447, 1411, 1383, 1329, 1311, 1297, 1276 (SO), 1148, 1121 (SO), 1093, 1070, 881, 756, 747, 728, 656. – UV (methanol): λ_{max} = 396 nm, 355. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 350 [M^+] (100), 286 [$M^+ - SO_2$], 270, 204, 194, 151, 121, 94, 64, 44.

$C_{20}H_{18}N_2O_2S$ (350.4)
Calcd. C 68.56 H 5.18 N 8.0 S 9.15
Found C 67.32 H 4.7 N 7.2 S 9.67

1,3-Dihydro-1,3-bis(2-pyrrolylmethylene)isothianaphthene 2,2-Dioxide ([**8c**]): The experimental procedure was the same as that described for [**8**]. Chromatography of the reaction mixture on silica gel (ethyl acetate) and silica gel (toluene) and crystallization of the crude product from acetone yielded 1.1 g (34%) of yellow crystals, m.p. 233°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3373 cm^{-1} (NH), 3110, 1606 (C=C), 1586, 1536, 1450, 1426, 1406, 1316, 1266 (SO), 1258, 1250, 1132, 1108 (SO), 1093, 1041, 880, 744, 718. – UV (methanol): λ_{max} = 387 nm, 345. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 322 [M^+] (100), 258 [$M^+ - SO_2$], 241, 230, 161 [M^{2+}], 128, 114, 101, 80.

$C_{18}H_{14}N_2O_2S$ (322.4)
Calcd. C 67.06 H 4.38 N 8.69 S 9.95
Found C 67.18 H 4.45 N 8.34 S 9.9

2,5-Dihydro-2,5-bis(2-thienylmethylene)thiophene 1-Oxide (**11**): 3.06 g (30 mmol) of 2,5-dihydrothiophene 1-oxide (**9**) and 7.84 g (70 mmol) of thiophene-2-carbaldehyde (**4a**) were dissolved in a solution of 0.9 g of NaOH in 50 ml of water and 12.5 ml of THF. The solution was stirred at room temp. for 2 d. The reaction mixture was chromatographed on a silica gel column. Starting compounds like thiophene-2-carbaldehyde and some other impurities were eluted with ether. The product was eluted with ethyl acetate. Evaporation of the solvent afforded 500 mg (6%) of a yellow powder, m.p. 136–137°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 1594 (C=C), 1462, 1424, 1312, 1215, 1140, 1050, 1019 (SO), 870, 855, 756, 725, 703. – UV (methanol): λ_{max} = 392 nm. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 290 [M^+], 274 [$M^+ - O$] (100), 261, 240, 229, 208, 179, 171, 134, 121, 108, 97, 89, 77, 69, 63, 51, 45.

$C_{14}H_{10}OS_3$ (290.4)
Calcd. C 57.89 H 3.47
Found C 57.09 H 3.97

1,3-Dihydro-1,3-bis(2-thienylmethylene)isothianaphthene 2-Oxide ([**12a**]): To a solution of 1 g of NaOH in 30 ml of methanol were added 1.82 g (12 mmol) of 1,3-dihydroisothianaphthene 2-oxide (**10**) and 2.84 g (26 mmol) of thiophene-2-carbaldehyde (**4a**). After stirring at 40°C for 3 d, the precipitate was filtered, washed with methanol, and crystallized from acetone to afford 1.8 g (44%) of a pale yellow product, m.p. 195°C. – IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1}, 3060, 1612, 1601 (C=C), 1587, 1419, 1364, 1257, 1240, 1053, 1005 (SO), 885, 855, 757, 749, 732, 716. – UV (methanol): λ_{max} = 361 nm, 330. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 340 [M^+], 324 [$M^+ - O$] (100), 307, 290, 258, 243, 227, 184, 179, 152, 139, 129, 97, 69, 45.

$C_{18}H_{12}OS_3$ (340.5)
Calcd. C 63.49 H 3.55 S 28.26
Found C 63.79 H 3.54 S 27.05

1,3-Dihydro-1,3-bis[(1-methyl-2-pyrrolyl)methylene]isothianaphthene 2-Oxide ([**12b**]): A solution of 1.82 g (12 mmol) of 1,3-dihydroisothianaphthene 2-oxide ([**10**]), 2.8 g (26 mmol) of 1-methylpyrrole-2-carbaldehyde (**4b**) and 1 g of NaOH in 30 ml of methanol was stirred at 40°C for 3 d. After removal of the solvent the reaction mixture was taken up in ether and chromatographed on silica gel using ether as eluent to remove unreacted starting compounds and impurities. Elution with ethyl acetate and evaporation of the solvent gave 500 mg (13%) of purple crystals, m.p. 228–231°C. – IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1}, 3084, 3045, 3017, 3000, 2928, 2855, 1618, 1612, 1600 (C=C), 1587, 1482, 1464, 1414, 1323, 1308, 1291, 1250, 1145, 1095, 1066, 999 (SO), 766, 742, 729, 602. – UV (methanol): λ_{max} = 390 nm, 354. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 334 [M^+], 318 [$M^+ - O$] (100), 302, 286, 270, 239, 151, 143, 130, 109, 94, 80, 61, 43.

$C_{20}H_{18}N_2OS$ (334.4)
Calcd. C 71.82 H 5.43 N 8.38 S 9.59
Found C 72.48 H 5.68 N 7.98 S 9.2

2,5-Dihydro-2,5-bis(2-thienylmethylene)thiophene (**13**): To a solution of 300 mg (1.03 mmol) of **11** and 0.1 g (1.25 mmol) of pyridine in 30 ml of dry toluene 0.19 g (1.1 mmol) of 2-chloro-1,3,2-benzodioxaphosphole was slowly added under nitrogen during 30 min. The mixture was stirred at room temp. for 2–3 h. After evaporation of the solvent the reaction mixture was chromatographed on silica gel with ether/*n*-hexane (1:1) as eluent. Removal of the solvent yielded 220 mg (80%) of an air-sensitive product, m.p. 125–130°C (slow dec. without a sharp melting point). – IR (KBr): $\tilde{\nu}$ = 3097 cm^{-1}, 3090, 3077, 3007, 1531, 1411, 1261, 1118, 1110, 1079, 1045, 857, 852, 848, 816, 806, 704, 696, 680. – UV (methanol): λ_{max} = 433 nm, 415. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 274 [M^+] (100), 240, 229, 208, 179, 149, 135, 123, 111, 97, 91, 69, 57, 45.

$C_{14}H_{10}S_3$ (274.4)
Calcd. C 61.27 H 3.67 S 35.06
Found C 59.1 H 3.08 S 36.04

1,3-Dihydro-1,3-bis(2-thienylmethylene)isothianaphthene ([**14**]): To a mixture of 0.98 g (3.0 mmol) of [**12a**] and 0.32 g (4 mmol) of pyridine in 20 ml of dry toluene was slowly added 0.7 g (4 mmol) of 2-chloro-1,3,2-benzodioxaphosphole. The reaction conditions and isolation procedure used were the same as for **13**; yield: 800 mg (82%) of a relatively air-stable product, m.p. 183°C. – IR (KBr): $\tilde{\nu}$ = 3098 cm^{-1}, 3064, 3022, 1594, 1579, 1575, 1566, 1466, 1456, 1417, 1294, 1049, 915, 856, 838, 823, 755, 694. – UV (methanol): λ_{max} = 423 nm, 400. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 324 [M^+] (100), 290, 264, 258, 245, 227, 208, 162, 145, 132, 91, 69, 45.

$C_{18}H_{12}S_3$ (324.5)
Calcd. C 66.62 H 3.73 S 29.65
Found C 67.04 H 3.97 S 28.26

2,5-Bis(hydroxy-di-2-thienylmethyl)thiophene (**17**): 0.55 g (6.5 mmol) of thiophene and 1.68 g (14.5 mmol) of *N,N,N',N'*-tetramethylethylenediamine were dissolved in *n*-hexane with exclusion of oxygen and moisture and cooled to −40 °C. After slow addition of 9.4 ml of a 1.6 N solution of *n*-butyllithium in *n*-hexane the reaction mixture was allowed to warm up to room temp. and heated at gentle reflux until the generation of butane was finished. The resulting dilithiothiophene suspension (**15**) was transferred to a dropping funnel and slowly added at −40 °C to a solution of 2.91 g (15 mmol) of di-2-thienyl ketone (**16**) in 30 ml of THF. After warming up to room temp. and stirring for 3 h, the reaction mixture was poured into an icecold 1 M aqueous NH_4Cl solution. After extraction of the aqueous phase with $CHCl_3$, the organic layer was dried with Na_2SO_4. After evaporation of the solvent the crude product was chromatographed on silica gel with ethyl acetate/*n*-hexane (1 : 4) as eluent to yield 2.0 g (67%) of a white pure product, m.p. 118 °C. − ^{1}H NMR ([D$_6$]acetone): δ = 6.24 (s, OH), 6.82 (s, 2H, 7-H), 6.99−6.9 (m, 8H, 1-, 3-H), 7.38 (dd, 4H, 2-H). − ^{13}C NMR ([D$_6$]acetone): δ = 76.18 (C-5), 125.5 (C-7), 126.09 (C-3), 126.39 (C-2), 126.94 (C-1), 152.59 (C-4), 152.81 (C-6). − IR (KBr): $\tilde{\nu}$ = 3488 cm^{-1} (OH), 3100, 1430, 1352, 1298, 1234, 1228, 1149, 1107, 1041, 986, 812, 795, 706. − MS (70 eV): *m/z* (%) = 472 (M^+), 455 (M^+ − OH), 438 (M^+ − 2 OH), 361, 343, 276, 194, 178, 111 (100), 83, 69, 43.

$C_{22}H_{16}O_2S_5$ (472.7)
Calcd. C 55.9 H 3.41
Found C 57.1 H 3.52

2,5-Bis(di-2-thienylmethylene)-2,5-dihydrothiophene (**18**): To a solution of 2.8 g (6 mmol) of **17** in 100 ml of toluene was added a solution of 10 g of $Na_2S_2O_4$ and 5 ml of conc. HI in 100 ml of H_2O. The two-phase system was rapidly stirred at room temp. for 12 h. The purple reaction mixture was neutralized with $NaHCO_3$ and extracted several times with ether. The combined ethereal extracts

Table 6. Compilation of crystal data and experimental details for compounds **7a** and **18**

Compound	**7a**	**18**
formula	$C_{14}H_{10}O_2S_3$	$C_{22}H_{14}S_5$
molecular mass	306.4	439.7
space group	$P2_1/c$	$P2_1/n$
a [pm]	1522.7(6)	1234.0(4)
b [pm]	1225.9(2)	1256.8(5)
c [pm]	730.5(2)	1359.1(6)
ß [°]	80.39(2)	104.93(4)
V [pm^3]	1344 x 10^6	2036.6 x 10^6
Z	4	4
ρ_{calcd} [g·cm^3]	1.51	1.43
crystal size [mm]	0.1 x 0.15 x 0.45	0.2 x 0.23 x 0.3
radiation	Cu-K_α	Mo-K_α
number of reflections measured	2827	4088
number of reflections $I \geq 3\sigma$	2494	2120
number of unique reflections	1394	2027
collection range θ [°]	6 - 52	5 - 27
number of parameters	203	244
absorption correction	DIFABS[32]	Psi-scan[33]
structure solution	Direct methods[31]	Direct methods[31]
R	0.034	0.059
R_w [a]	0.037	0.063
largest peak [e/Å^3]	0.21	0.45

[a] $w = 1/\sigma(F)^2$.

Table 7. Atomic coordinates with their estimated standard deviations in parentheses for **7a** and the isotropic equivalent displacement parameters $B_{eq} = 4/3\ [a^2B_{11} + b^2B_{22} + c^2B_{33} + ac(\cos\beta)B_{13}]$

Atom	x	y	z	B_{eq}
S(1)	0.75085(6)	0.07005(8)	0.5755(1)	3.07(2)
S(2)	0.47625(7)	0.28720(8)	0.8497(1)	3.37(2)
S(3)	0.98161(7)	0.37055(9)	0.4066(1)	3.60(2)
O(1)	0.7359(2)	0.0138(2)	0.4115(4)	4.71(7)
O(2)	0.7772(2)	0.0047(2)	0.7203(4)	4.87(7)
C(1)	0.5819(2)	0.1049(3)	0.7341(5)	2.79(8)
C(2)	0.9105(2)	0.1591(3)	0.4519(5)	2.76(8)
C(11)	0.6587(2)	0.1526(3)	0.6627(5)	2.45(8)
C(12)	0.6881(2)	0.2641(3)	0.6373(5)	3.06(8)
C(13)	0.7738(2)	0.2786(3)	0.5629(5)	2.99(8)
C(14)	0.8248(2)	0.1806(3)	0.5183(5)	2.53(8)
C(21)	0.4978(6)	0.1497(3)	0.8154(4)	2.67(8)
C(22)	0.4202(2)	0.0898(3)	0.8777(5)	3.11(9)
C(23)	0.3483(3)	0.1567(4)	0.9499(5)	3.9(1)
C(24)	0.369(3)	0.2635(4)	0.9433(5)	3.65(9)
C(31)	0.9852(2)	0.2298(3)	0.3983(5)	2.79(8)
C(32)	1.0711(2)	0.1959(4)	0.3360(5)	3.47(9)
C(33)	1.1311(3)	0.2816(4)	0.2976(5)	4.2(1)
C(34)	1.0929(3)	0.3796(4)	0.3301(5)	4.1(1)

Table 8. Atomic coordinates with their estimated standard deviations in parentheses for **18** and the isotropic equivalent displacement parameters $B_{eq} = 4/3\ [a^2B_{11} + b^2B_{22} + c^2B_{33} + ac(\cos\beta)B_{13}]$

Atom	x	y	z	Beq
S(1)	0.0137(1)	0.8082(1)	0.0794(1)	4.49(4)
S(2)	0.4553(2)	0.7824(2)	0.2891(2)	5.99(5)
C(1)	0.2464(5)	0.7910(5)	0.1475(4)	3.5(1)
C(2)	-0.1598(5)	0.9398(5)	0.1040(4)	3.6(1)
C(11)	0.1513(5)	0.8481(5)	0.1445(4)	3.8(1)
C(12)	0.1452(5)	0.9490(5)	0.1928(5)	4.2(1
C(13)	0.0395(5)	0.9871(5)	0.1805(5)	4.3(1)
C(14)	-0.0482(5)	0.9208(5)	0.1215(4)	3.7(1)
C(21)	0.3552(4)	0.8424(5)	0.1928(4)	3.7(1)
C(22)	0.3924(4)	0.9441(5)	0.1709(4)	3.3(1)
C(23)	0.5018(5)	0.9668(6)	0.2376(5)	5.2(2)
C(24)	0.5438(5)	0.8879(6)	0.3034(6)	5.3(2)
C(31)	0.2468(5)	0.6824(5)	0.1080(4)	4.0(1)
X(1) [a]	0.1442(3)	0.5983(2)	0.0896(3)	6.03(8)
C(33)	0.2004(7)	0.5020(6)	0.0503(6)	7.2(2)
C(34)	0.3048(8)	0.5212(6)	0.0395(5)	7.4(2)
X(2) [a]	0.3521(3)	0.6346(2)	0.0696(2)	5.73(7)
C(41)	-0.1959(5)	1.0291(5)	0.1592(4)	3.9(1)
Y(1) [b]	-0.2516(3)	1.1354(3)	0.1080(3)	6.88(9)
C(43)	-0.2661(6)	1.1947(6)	0.2065(6)	5.7(2)
C(44)	-0.2315(6)	1.1410(6)	0.2938(5)	5.7(2)
Y(2) [b]	-0.1789(2)	1.0240(2)	0.2837(2)	5.67(7)
C(51)	-0.2495(5)	0.8786(5)	0.0375(4)	3.6(1)
Z(1) [c]	-0.3733(3)	0.8787(3)	0.0455(3)	5.92(9)
C(53)	-0.4302(6)	0.8066(6)	-0.0388(6)	5.9(2)
C(54)	-0.3650(7)	0.7639(6)	-0.0958(6)	6.1(2)
Z(2) [c]	-0.2340(2)	0.7992(2)	-0.0584(2)	4.96(5)

[a] X(1), X(2): 50% S, 50% C. − [b] Y(1): 44% S, 56% C; Y(2): 56% S, 44% C. − [c] Z(1): 34% S, 66% C; Z(2): 66% S, 34% C.

were dricd with $MgSO_4$. After evaporation of the solvent the purple residue was chromatographed first on silica gel with *n*-hexane and then on silica gel with ethyl acetate/*n*-hexane (1:20) as eluent to give a red crystalline product, which was recrystallized from acetone, yield: 600 mg (23%), m.p. 157°C. – IR (KBr): $\tilde{\nu}$ = 3098 cm^{-1}, 3068, 1430, 1411, 1265, 1226, 1217, 1144, 1134, 857, 835, 819, 795, 789, 718, 712, 699. – UV (methanol): λ_{max} = 472 nm. – ^1H and ^{13}C NMR: see Tables 4 and 5. – MS (70 eV): *m/z* (%) = 438 [M^+] (100), 372, 359, 327, 219, 203, 177, 158, 127, 69, 57.

$C_{22}H_{14}S_5$ (438.7)

Calcd. C 60.23 H 3.22 S 36.55

Found C 59.3 H 3.08 S 35.54

Crystal Structure Analysis of **7a** *and* **18**[30]: The intensity data for **7a** were mcasured using Cu-K_α radiation (λ = 1.54178 Å) with a CAD 4 Enraf Nonius diffractometer. The data for **18** were measured with Mo-K_α radiation (λ = 0.71069 Å). A compilation of the crystal data and experimental details are given in Table 6. The two structures were each solved by means of the direct methods (SHELXS[31]) yielding the coordinates for all non-hydrogen atoms (Tables 7, 8). The usual sequence of refinement with isotropic and anisotropic displacement parameters was followed.

In the case of **7a** all H atoms were found and refined with fixed isotropic thermal parameters by using the values of the corresponding carbon atoms attached to the H atoms. Full matrix refinement; $\Sigma w(\Delta F)^2$ was minimized for 203 parameters. The highest peak in the final difference Fourier map was 0.21 $e^-/Å^3$.

In the case of **18** the thiophene rings were statistically disordered in the crystal. That was the reason why the H atoms were not taken into account. The estimation of the statistical distribution of C and S atoms in the rings with indices 3, 4, and 5 (Figure 2) was made with the help of the ratio of the peak heights in a Fourier map. Further refinement was performed with mixed scattering factors taken from the International Tables[34]. Full matrix refinement; $\Sigma w(\Delta F)^2$ was minimized for 244 parameters. The highest peak in the final difference Fourier map was 0.45 $e^-/Å^3$.

CAS Registry Numbers

4a: 98-03-3 / **4b**: 1192-58-1 / **4c**: 1003-29-8 / **4d**: 4701-17-1 / **5**: 77-79-2 / **7a**: 133626-43-4 / **7b**: 133626-44-5 / **7c**: 133626-45-6 / **7d**: 133626-46-7 / **8a**: 133626-47-8 / **8b**: 133626-48-9 / **8c**: 133626-49-0 / **9**: 14852-22-3 / **10**: 3533-72-0 / **11**: 133626-50-3 / **12a**: 133626-51-4 / **12b**: 133626-52-5 / **13**: 133626-53-6 / **14**: 133626-54-7 / **16**: 704-38-1 / **17**: 133626-55-8 / **18**: 133626-56-9 / thiophene: 110-02-1

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