Synthesis of Precursor Molecules for Low Band Gap Polymers

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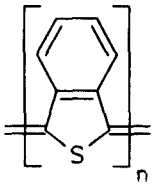
The synthesis and characterization of precursors for polyarene- and hetarenemethylenes (PAM) of structure **3**, which are predicted to be low band gap polymers are described. The precursor molecules **4** are synthesized from the corresponding 2-thiophene- and 2-pyrrole- carbaldehydes **6a** and **6b** by Knoevenagel condensation with 2,5-dihydrothiophene 1-oxide (**9**) and / or the analogous benzo- and naphtho-annulated sulfoxides **9**. The sulfoxide groups in **9** are easily reduced with formation of the sulfides **11**. The synthesis of the precursor molecules **20-22** containing two directly linked quinoid structures is also described. To increase the solubility of the 1,3-bis(2-thienylmethylene)-1,3-dihydroisothianaphthene systems **4** e. g. alkoxy substituents are introduced into the annulated benzene ring of **4**.

Introduction

The discovery of conducting (doped) polymers has generated great interest among chemists and physicists in the last years. The driving force in this area is the development of new materials with e. g. light weight and durability of plastics with semiconducting or even conducting properties. A high conductivity e. g. for polyacetylene (PA),[1] poly-*p*-phenylene (PPP),[2] polypyrrole (PPy),[3] or polythiophene (PT)[4] is reached only after chemical or electrochemical oxidative (p) or reductive (n) doping; e.g. with doped PA, a conductivity of about 10^5 S/cm has been achieved.[1] However, quite often the thermal and chemical stability of doped polymers is not very high. Therefore, polymers possessing at least intrinsic semiconductive properties due to a low band gap are interesting targets for synthesis.

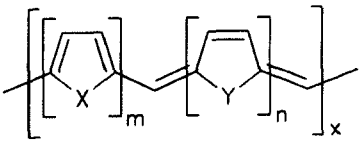
The band gap energy is a significant parameter for solid-state properties controlling intrinsic electronic properties, optical properties, including nonlinear optics, and magnetic behavior. The possibility to synthesize low band gap polymers was predicted based on theoretical work.[5] VEH (Valence Effective Hamiltonian) calculations showed, that in polymers related to PPy and PT, the bandgap E_g is a function of the quinoid character of these polymers.[6] As a result of decreasing bond-length alternation along the C-C-backbone, the bandgap becomes smaller. Thus, with increasing quinoid character of the subunits the bandgap Eg decreases.

Polyisothianaphthene (PITN) (**1**) has been one of the first low bandgap polymers with a band gap energy of about 1 eV;[7] this is half the band gap value of PT. The ring annulation in PITN stabilizes the quinoid contributions in the ground state in comparison to PT.



1

The methine-bridged polymers **2** are combining alternating aromatic and quinoid subunits, they are kown as polyarenemethylenes (PAM). These polymers are predicted to possess intrinsic semiconducting properties. VEH[8] and extended Hückel[9] calculations determined the band gap to be ≈ 1 eV.

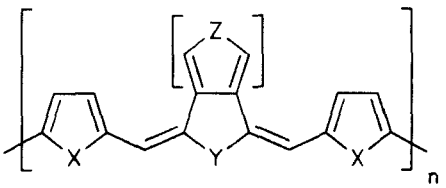


2

X = O, S, N–R, CH=CH

Y = O, S, SO, SO_2, N–R, CH=CH

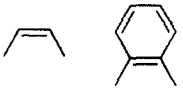
Several attempts for the synthesis of a polymer **2** with thiophene subunits (X = Y = S) were reported: condensation of thiophene or bithiophene with *p*-substituted benzaldehydes and a subsequent oxidation with bromine,[10,11] or electrochemical polymerization[12] of diheteroarenemethanes; however only doped polymers with a undefined structure were formed. Another method is to polymerize heterocyclic aldehydes like 2-pyrrolecarbaldehyde using Lewis-acids as catalysts. The formed polymers exhibit a conductivity of ≈ 10^{-4} S/cm, and have been described with a structure given in Formula **2**.[13] Structure **3** shows a more general formula of polyarenemethylenes, containing the substructures in an alternating arrangement:



3

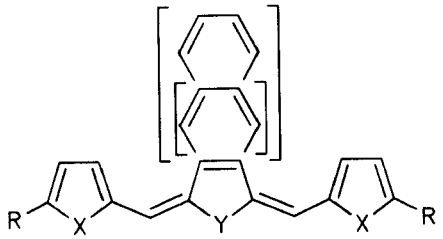
X = O, S, N–R, CH=CH

Y = O, S, SO, SO_2, N–R, CH=CH

Z = S, 

As can be seen from **3**, an additional variation of the structure is possible by annulating one or two benzene rings or even a thiophene ring to the 2,5-dihydrothiophene unit. This should lead to a further lowering of the band gap of the corresponding polymers. As shown by calculations[6] a further decrease of the band gap could be achieved by changing n in **2** from 1 to 2 using a structural subunit in which two dihydrothiophenes are linked together (vide infra).

To study the electronic properties of the polymers given in **3** we have decided to follow a synthetic route which should lead directly to a structurally uniform polymer **3**. The requirement for this is the synthesis of precursors **4** in which the quinoid structure is already present. From the "monomers" **4** it should be possible to obtain either oligomers or polymers of the structure shown in **3**.



4

X = O, S, N–R, CH=CH

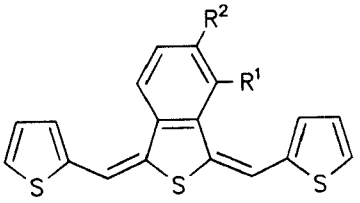
Y = O, S, SO, SO_2, N–R, CH=CH

R = Cl, Br, I, H

In principle, for the polymerization of **4** several methods can be applied: a chemical polymerization leading to the non-doped polymer **3** requires precursor molecules **4** with reactive side groups (e. g. R = Cl, Br), which can be converted into organometallic intermediates. The addition of transition metal catalysts starts polymerization, which leads to the non-doped species **3**.

Attempted electrochemical polymerization of different precursor molecules **4** was studied by us in detail using cyclic voltammetry (CV) and UV-Vis-NIR spectroelectrochemistry (SEC). So far only oxidized electroactive oligomers could be found at the surface of the anode.[14]

In this feature article we will concentrate on the methods we have developed for the preparation of the precursors **4** in many structural variations containing carbocyclic and heterocyclic subunits with one, or two quinoid structures. Many of the methine bridged precursors **4**, especially the ring annulated systems are only slightly soluble in organic solvents. The solubility however, can be increased by using precursors of structure **5**, containing substituents in the annulated benzene ring.



5

R^1 = H, O–C_6H_{13}

R^2 = H, t–Bu

Synthesis

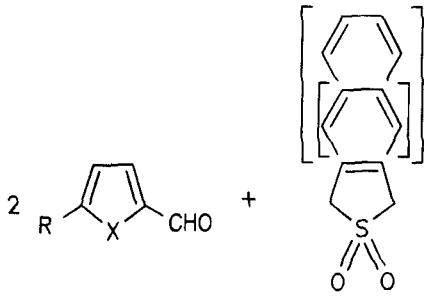
In our earlier attempts for the synthesis of the precursor molecules **4** 2,5-dihydrothiophene 1,1-dioxide (**7**) was condensed with 2-thiophenecarbaldehyde (**6a**, R = H),[15b] to afford the sulfone **8** (R = H) (Scheme 1). However the yields were low because of rearrangement of the double bond in 2,5-dihydrothiophene 1,1-dioxide (**7**), selfcondensation of the aldehyde **6a** (R = H) and other side reactions. X-ray analysis of a pure sample of 2,5-bis(2-thienylmethylene)-2,5-dihydrothiophene 1,1-dioxide (**8**, R = H) shows, that the three five-membered rings are nearly coplanar and the exocyclic bonds are in an *E,E* arrangement.[15b] The condensation was also carried out with the benzoannulated system 1,3-

Biographical Details

Michael Hanack studied chemistry at the universities of Bonn, Freiburg and Tübingen. After completion of his dissertation with Walter Hückel at the University of Tübingen, he did his habilitation on organofluorine compounds and became Privat-Dozent in 1962, subsequently he was made außerordentlicher Professor at the University of Tübingen. In 1971 he was called to the Chair of Organic Chemistry at the University of Saarbrücken (as the successor of B. Eistert) where he worked until 1975, mainly in the field of physical organic chemistry e.g. vinyl cations. He returned to Tübingen in 1975 where he took over the Chair of Organic Chemistry II succeeding Eugen Müller. For more than 10 years he has been actively engaged in the chemistry of material science, e.g. organic conductors and non-linear optics based on phthalocyanine complexes and polyhetarenes. He is one of the editors of Houben-Weyl and the regional editor of "Synthetic Metals". He is a Fellow of the New York Academy of Sciences and he received an Honorary Doctorate from the University Complutense, Madrid.

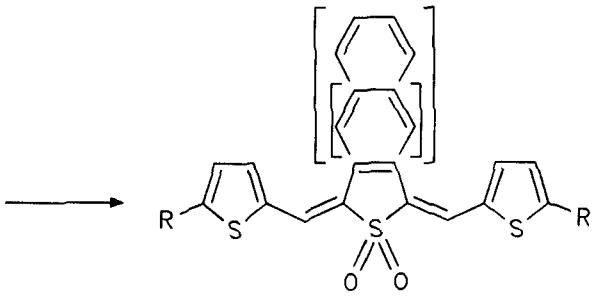
Frank Teichert, Stefan Echinger, Jürgen Hieber, and **Ulrich Schmid** (from left to right) are Ph. D. students working in the group of Michael Hanack.

dihydroisothianaphthene 2,2-dioxide (**7**)[15] to give the corresponding 1,3-bis(2-thienylmethylene)-1,3-dihydroisothianaphthene 2,2-dioxide (**8**) in better yields due to the stabilizing effect of the benzene ring.



6 **7**

6a: X = S, R = H, Br
6b: X = NH, R = H



8

Scheme 1

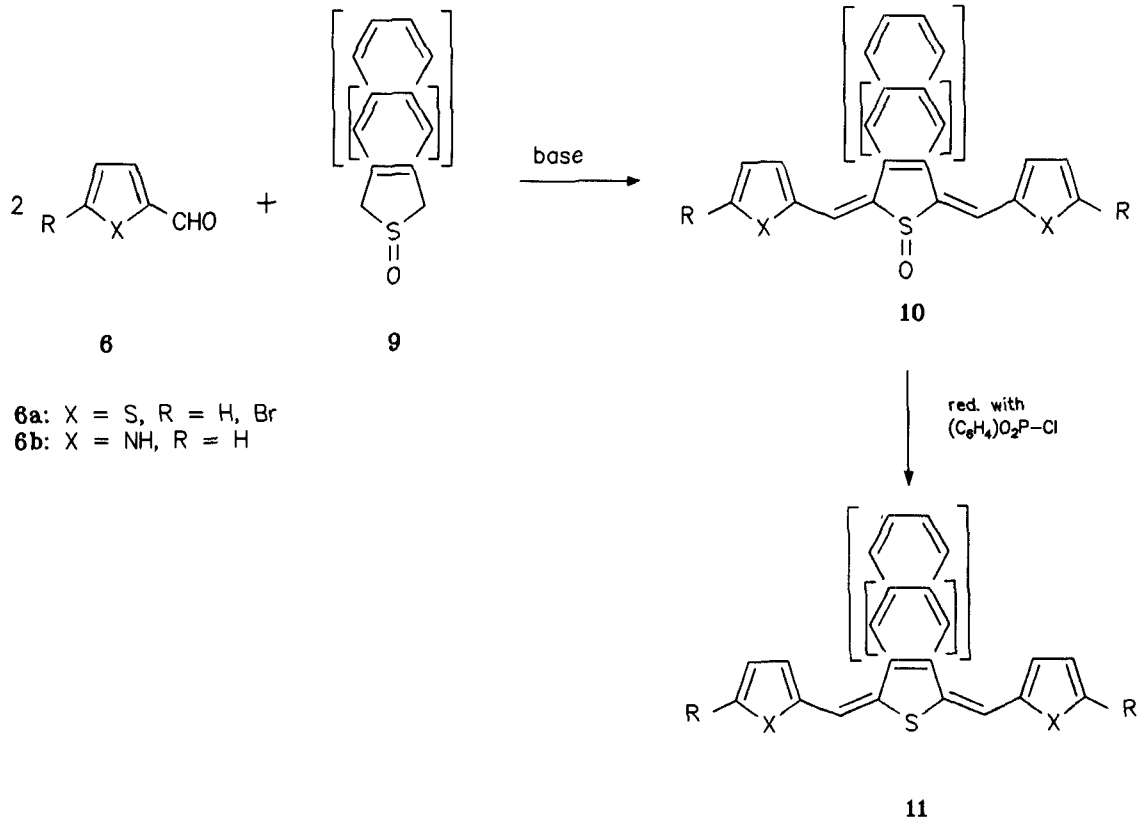
The sulfone group in **8** however could not be reduced chemically to the target molecules, the corresponding sulfides **11**. Therefore the corresponding sulfoxides were used.

A general route for the synthesis of a precursor **4** or **11** is given in Scheme 2: Knoevenagel-type condensation of 2-thiophene- **6a** or 2-pyrrolecarbaldehydes **6b** with 2,5-dihydrothiophene 1-oxide (**9**) and / or analogeous benzo- and naphtho-annulated systems **9** is the key step in the synthesis of the methine-bridged precursor molecules.

Normally vinyl sulfoxides can not be synthesized by direct Knoevenagel-type condensation. In general, the reaction of CH-activated sulfoxides with aldehydes yields the ß-hydroxyalkyl derivatives; the elimination of water needs acid as a catalyst. Moreover, in basic medium, these compounds have a tendency to undergo different side reactions,[16] which do not occur to the same extent in the case of the cyclic sulfoxides **10**.

The sulfoxide group in **10** can be easily reduced with 2-chloro-1,3,2-benzodioxaphosphole [$(C_6H_4)O_2P$-Cl] in the presence of pyridine. The benzo- and naphtho-annulated systems **11** are generally air stable in comparison to the nonannulated dihydrothiophene compounds **11**.

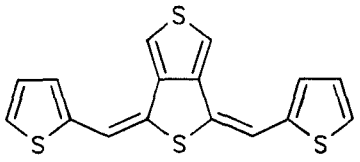
Another methine-bridged precursor molecule **4** is the 1,3-bis(2-thienylmethylene)thieno[3,4-*c*]thiophene (**12**),[14b] which is also stable and has similar physical properties as the benzo- and naphtho-annulated systems **11**.



6 **9** **10** **11**

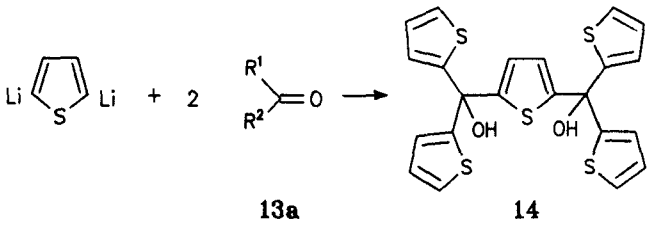
6a: X = S, R = H, Br
6b: X = NH, R = H

Scheme 2



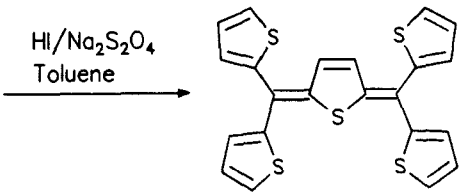
12

A different route for the synthesis of a thienylmethylenedihydrothiophene system is given in Scheme 3:[15b]



13a 14

13a: R^1, R^2 = thienyl



15

Scheme 3

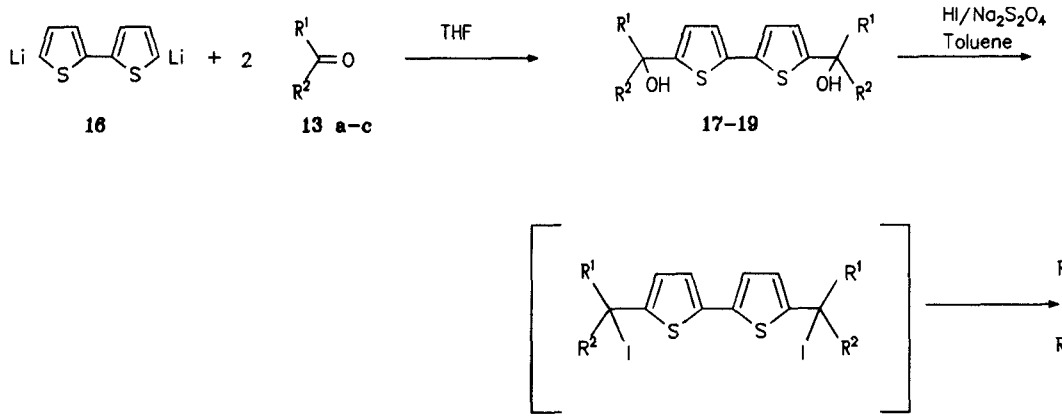
A further structural variation of polymer **2** (n=1) leading to an increased quinoid character, would be a chemical or electrochemical polymerization of subunits **20-22**. Here two quinoid structures are directly linked together, thus leading to polyarenemethylenes **2** with n = 2. Calculations on these type of polymers show a further lowering of the band gap.[6b]

The synthesis of **20**, **21**, and **22** is carried out by the general route given in Scheme 4. 5,5'-Dilithiobithiophene (**16**) is reacted with the corresponding ketones **13a-c** in tetrahydrofuran to afford the diols **17-19**. Treatment of the diols with aqueous hydrogen iodide and sodium dithionite yields the bithiophenes **20-22**, which are purified by column chromatography.

The spectroscopic data of the diols **17-19** and the precursors **20-22** show characteristic differences. The terminal substituents of the diols **17-19** are equivalent. After reduction of the diols, the substituents in the precursors **20-22** are not equivalent anymore according to their NMR-spectra. Both of the substituents in **20-22** are twisted out of the plane of the quinoid subunits.

As pointed out before for a chemical polymerization, precursor molecules **4** with reactive side groups are essential. Because the dibromoderivative **11'** is practically insoluble in organic solvents a chemical polymerization of **11'** was not possible.[17]

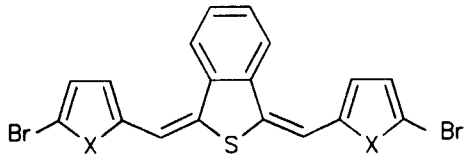
To increase the solubility of the benzo-annulated arenemethylenes **4** we have synthesized the alkoxy substituted derivative **29** according



16 13 a-c 17-19 20-22

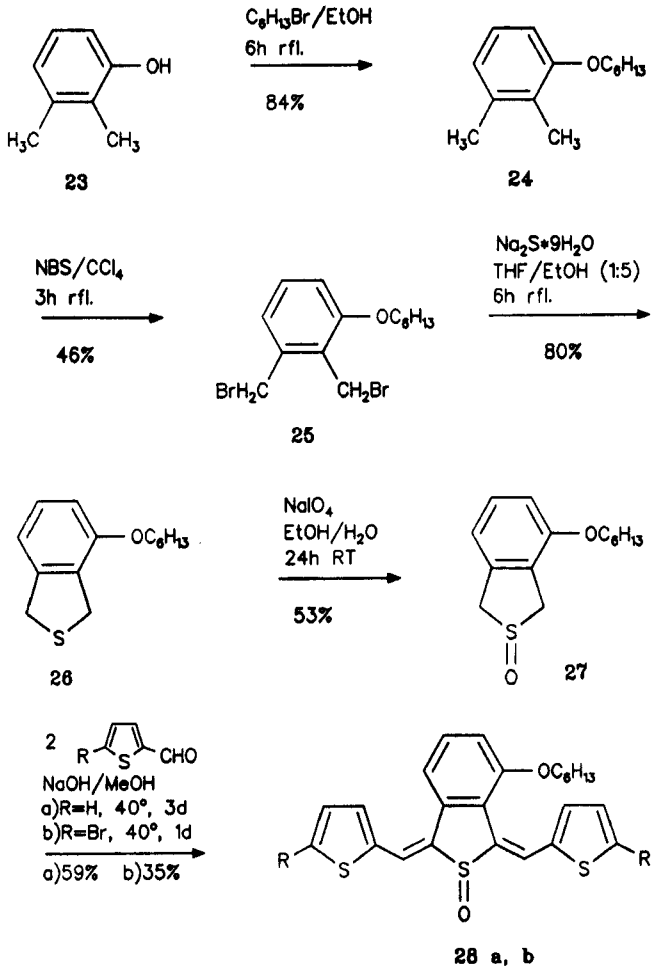
Scheme 4

compound	R^1	R^2	yield (%)
17	thienyl	thienyl	30
18	phenyl	phenyl	86
19	p-tolyl	phenyl	93
20	thienyl	thienyl	24
21	phenyl	phenyl	35
22	p-tolyl	phenyl	38



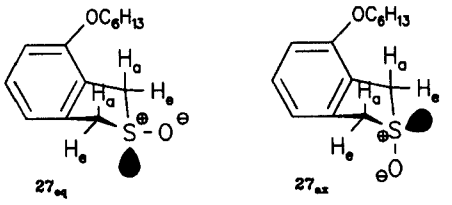
11'

to Scheme 5, which shows the synthetic pathway to obtain the soluble compounds e. g. **29** (R = H) and **28b** (R = Br). The ring closure of the dibromide **25** to form **26** (not very stable in air) is carried out in tetrahydrofuran/ethanol (1:5) in a nitrogen atmosphere.[18] The sulfide **26** is oxidized with sodium periodate in aqueous ethanol or with *N*-bromosuccinimide in aqueous acetone[19] to the sulfoxide **27**.[20] Compounds **28a, b** are obtained by Knoevenagel-type condensation of the sulfoxide **27** with 2-thiophenecarbaldehydes **6a, b**. The sulfoxide **28a** was reduced to the sulfoxide **29** using 2-chloro-1,3,2-benzodioxaphosphole. **29** is air-stable and soluble in organic solvents like acetonitrile, ethyl acetate, toluene and acetone in the range of $1\text{-}6\cdot10^{-2}$ mol/l.

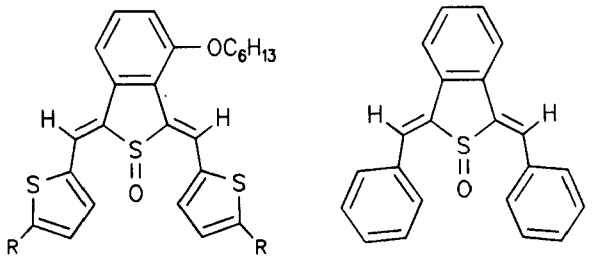


Scheme 5

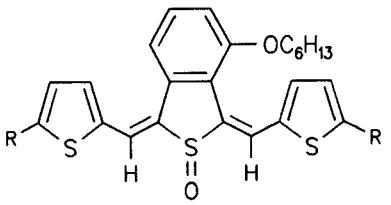
Characteristic for the sulfoxid **27** is the AB-signal in the ^{1}H NMR spectra which shows that the conformation $\mathbf{27}_{ax}$ is preferred.



In the ^{1}H NMR spectra of **28a, b** the methine protons are considerably downfield shifted. This can not be accounted only to electronic effects of the benzene ring. The influence of the ring current effect of the benzene ring on the methine protons must also be considered. Because of this and the high steric demand of the thienyl group compounds **28a, b** exist in the *Z,Z*-configuration. This is confirmed by 2D-NOESY-NMR experiments with 1,3-bis(phenylmethylene) dihydroisothianaphthene 2-oxide (**30**).[21]



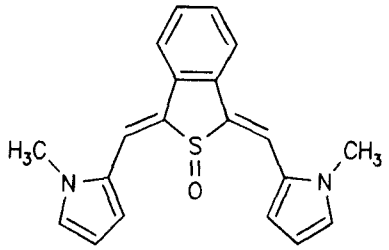
28a,b ***Z,Z*** **30**



28a,b ***E,E***

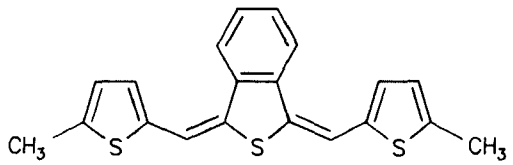
The *Z,Z*-configuration was also proven for 1,3-dihydro-1,3-bis-(2(*N*-methylpyrryl)methylene)isothianaphthene 2-oxide (**31**) by X-ray analysis.[22] Both the *N*-methylpyrrole-rings in **31** are not in the same plane with the almost planar isothianaphthene unit. The configuration of **31** is *Z,Z* in contrast to the X-ray analysis of 2,5-dihydro-2,5-bis(2-thienylmethylene)thiophene 1,1-dioxide (**8**) proving its *E,E*-configuration.

Therefore it must be concluded that in the Knoevenagel-type condensation of ring-annulated 2,5-dihydrothiophene 1-oxides (**9**) or e. g. 2,5-dihydrothiophene 1,1-dioxides (**7**) with 2-thiophenecarbaldehyde (**6a**) and 2-pyrrolecarbaldehyde (**6b**) a stereospecific reaction occurs with the formation of only *Z,Z*-isomers because of the higher steric demand of the annulated benzene rings. This was also proven in the case of the sulfoxide **31** which, according to its crystal structure also has a *Z,Z*-configuration.[14a]

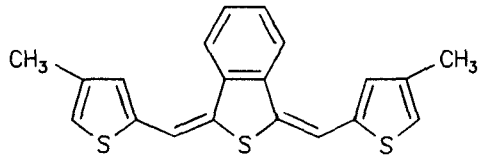


31

The arenemethylenes **32** and **33** containing methylgroups in the α- and ß- positions of the thiophene rings were also synthesized according to Scheme 4 by reacting **9** with 4-methyl- and 5-methyl-2-thiophenecarbaldehyde respectively.[14a]



32



33

As described elsewhere[14a] electrochemical oligomerization is only possible with **33**, whereas **32** does not react under the same conditions. From these observations it was concluded that the electrochemical oligomerization of arenemethylenes **4** (R = H) takes place only in α-position of the thiophene- or pyrrole-ring.

Conclusion

In this feature article we have presented a general route for the synthesis of arene- and hetarenemethylenes **4**, **5**, **20-22** in a large structural variety which will be used as precursors for conducting polymers. Investigations of the electrochemical and chemical oligomerization or polymerization of the precursor molecules described here are in progress.

Experimental

All melting points are uncorrected. - ^1H and ^{13}C NMR spectra: Bruker AC 250 (^1H, 250 MHz; ^{13}C, 62.5 MHz). - FTIR: Bruker IFS 48. - MS: Varian MAT 711 (70 eV). All new compounds gave satisfactory elemental analyses.

Diols 17-19; general procedure:

Bithiophene (1.66 g, 10 mmol) and TMEDA (3.9 mL, 26 mmol) were dissolved in dry THF with exclusion of air and moisture and cooled to -40°C. After slow addition of a 1.6 N solution of BuLi in hexane (16.25 mL, 26 mmol) the mixture was allowed to warm up to r.t. and heated under gentle reflux until the generation of butane was over. The resulting suspension of 5,5'-dilithiobithiophene was transferred to a dropping funnel and slowly added at -40°C to a solution of the corresponding ketone (25 mmol) in dry THF. After warming up to r.t. and heating under reflux for 12 h, the mixture was poured into an ice cold aqueous solution of AcOH. The product was extracted with $CHCl_3$ and the solvent evaporated.

5,5'-Bis[di(2-thienyl)hydroxymethyl]-2,2'-bithiophene (17):

Chromatography on silica gel with $CHCl_3$ as eluent yielded green crystalls, mp 164-166°C (dec.).

IR (KBr): ν = 3436, 3097, 3068, 2987, 2966, 2920, 2866, 2833, 2786, 2709, 1433, 1413, 1230, 1107, 1053, 1037, 1022, 784, 723, 694 cm^{-1}.

^1H NMR: (acetone-d_6): δ = 7.41 (dd, 2 H, J = 4.97, 1.47, 1.41 Hz), 7.34 (s, 1 H), 7.06 (d, 1 H, J = 3.82 Hz), 7.02 - 6.95 (m, 4 H), 6.87 (d,1 H, J = 3.84 Hz).

MS (70 eV): m/z (%) = 554 (M^+, 11), 537 (87), 521 (50), 442 (8), 370 (3), 359 (7.5), 343 (11), 276 (21), 248 (12), 193 (41), 165 (11), 111 (100), 83 (13).

5,5'-Bis[di(phenyl)hydroxymethyl]-2,2'-bithiophene (18):

Recrystallization yielded a white powder, mp 152-154°C.

IR (KBr): ν = 3342, 3060, 3024, 2976, 2873, 1488, 1446, 1205, 1176, 1139, 1047, 1031, 1014, 889, 802, 757, 740, 698, 682, 646 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.4 - 7.38 (m, 10 H), 6.93 (d, 1 H, J = 3.37 Hz), 6.59 (d, 1 H, J = 3.72 Hz), 3.17 (s, 1 H).

MS (70 eV): m/z (%) = 530 (M^+, 7), 513 (2), 496 (3), 453 (7.5) 425 (3.5), 388 (4.7), 347 (10), 311 (6.7), 271 (31), 243 (29), 297 (4), 193 (19), 182 (27), 165 (26), 152 (4.5), 110 (9), 105 (100), 77 (34), 50 (4).

5,5'-Bis[phenyl-*p*-tolylhydroxymethyl]-2,2'-bithiophene (19):

Recrystallization yielded a white powder, mp 86-87°C.

IR (KBr): ν = 3546, 3365, 3082, 3058, 3024, 2974, 2923, 2871, 1508, 1488, 1446, 1380, 1321, 1296, 1205, 1180, 1172, 1139, 1049, 1033, 1022, 1012, 892, 800, 756, 740, 698, 661, 607, 586 cm^{-1}.

^1H NMR (C_6D_6): δ = 7.48 (dd, 2 H, J = 1.37, 1.74, 7.94 Hz), 7.37 (d, 2 H, J = 8.24 Hz), 7.15 - 7.01 (m, 3 H), 6.93 (d, 2 H, J = 8 Hz), 6.80 (d, 1 H, J = 3.71 Hz), 6.52 (d, 1 H, J = 3.72 Hz), 2.96 (s, 1 H), 2.07 (s, 3 H).

MS (FD): m/z (%) = 558 (M^+, 100).

Tetrahydrobithiophenylidenes 20-22; General Procedure:

To a solution of the diol **17-19** in toluene (50 mL) was added a solution of $Na_2S_2O_4$ (10 equiv) in H_2O (10 mL) and 57% HI (10 equiv). The two phase system was rapidly stirred at r.t. for 12 h. After separation of the organic layer the solvent was evaporated and the residue was chromatographed on silica gel with toluene/hexane (1:1) as eluent.

5,5'-Bis[di(2-thienyl)methylene]-2,2',5,5'-tetrahydro-2,2'-bithiophenylidene (20):

Blue microcrystalline compound, mp 174-177°C.

IR (KBr): ν = 3066, 2954, 2923, 2854, 2362, 1731, 1600, 1506, 1458, 1427, 1375, 1350, 1315, 1265, 1230, 1215, 1147, 1122, 1074, 1033, 914, 889, 852, 796, 783, 754, 698, 655, 615, 491 cm^{-1}.

UV ($CHCl_3$): λ_{max} = 580, 380, 330 nm.

^1H NMR (toluene-d_8): δ = 6.76 - 6.63 (m, 6 H), 6.62 (d, 1 H, J = 3.65 Hz), 6.34 (d, 1 H, J = 5.76 Hz).

^{13}C NMR (toluene-d_8): δ = 145.25, 143.43, 142.72, 135.65, 134.54, 132.14, 131.11, 129.43, 128.45, 127.92, 126.94, 126.63, 118.57 ppm.

MS (FD): m/z (%) = 520 (100).

5,5'-Bis[(di(phenyl)methylene]-2,2',5,5'-tetrahydro-2,2'-bithiophenylidene (21):

Blue-violet compound, mp 178-180°C.

IR (KBr): ν = 3055, 3024, 2349, 2293, 1953, 1656, 1649, 1596, 1488, 1319, 1278, 1224, 1205, 1176, 1157, 1130, 1031, 1001, 798, 754, 698, 644.

UV ($CHCl_3$): λ_{max} = 540 nm.

^1H NMR (C_6D_6): δ = 7.09 - 7.00 (m, 10 H), 6.72 (d, 1 H, J = 5.9 Hz), 6.59 (d, 1 H, J = 5.9 Hz).

^{13}C NMR (DMSO-d_6): ν = 148.8, 144.40, 142.53, 141.10, 132.30, 130.00, 129.60, 129.13, 128.68, 128.53, 127.69, 127.077 ppm.

MS (FD): m/z (%) = 496 (M^+, 100).

5,5'-Bis[phenyl-*p*-tolylmethylene]-2,2',5,5'-tetrahydro-2,2'-bithiophenylidene (22):

Violet compound, mp 85-86°C.

IR (KBr): ν = 2957, 2924, 2854, 2362, 2337, 1772, 1733, 1685, 1652, 1575, 1558, 1541, 1506, 1488, 1458, 1446, 1377, 1261, 1101, 804, 752, 698, 667 cm^{-1}.

UV ($CHCl_3$): λ_{max} = 530 nm.

^1H NMR (C_6D_6): δ = 7.5371 (d, 1 H, J = 6.89 Hz), 7.4363 (d, 1 H, J = 7.59 Hz), 7.246 - 6.87 (m, 7 H), 6.81 - 6.74 (dd, 1 H, J = 5.86, 5.79, 5.8 Hz), 2.087 (d, 3 H, J = 10.65 Hz).

^{13}C NMR (C_6D_6) δ = 143.02, 142.33, 140.19, 139.36, 137.56, 137.19, 134.04, 133.94, 133.59, 132.49, 131.80, 131.45, 130.989, 130.08, 129.40, 127.81, 127.57, 21.24 ppm.

MS (FD): m/z (%) = 524 (M^+, 100).

2,3-Dimethylphenyl Hexyl Ether (24):

To a solution of NaOEt in EtOH prepared from Na (5.06 g, 220 mmol) and 95% EtOH (250 mL) was added 2,3-dimethylphenol (26.5 g, 217 mmol). To the resulting mixture was added 1-hexyl bromide (37 mL, 224 mmol) and refluxed for 6 h. Excess of alkyl halide and EtOH was removed by distillation. The residue was taken up in Et_2O,washed with H_2O, 15% NaOH solution and again with H_2O. The organic layer was dried (Na_2SO_4), the solvent evaporated and the residue was purified by chromatography on silica gel. Elution with hexane gave a colorless oil; yield: 37.5 g (84%).

IR (film): ν = 3032, 2955, 2931, 2830, 1585, 1466, 1383, 1259, 1105, 768 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.87 - 0.93 (m, 3 H), 1.3 - 1.37 (m, 4 H), 1.42-1.53 (m, 2 H), 1.73 - 1.89 (m, 2 H), 2.14 (s, 3 H), 2.26 (s, 3 H), 3.92 (t, 2 H, J = 6.4 Hz), 6.68 (d, 1 H, J = 8.19 Hz), 6.74 (d, 1 H, J = 7.55 Hz), 7.02 (t, 1 H, J = 7.86 Hz).

^{13}C NMR ($CDCl_3$): δ = 157.02, 137.68, 125.68, 125.15, 121.95, 108.84, 68.1, 31.61, 29.43, 25.88, 22.63, 20.0, 13.99, 11.51.

1,2-Bisbromomethylphenyl Hexyl Ether (25):

To a solution of 2,3-dimethylphenyl hexyl ether (**24**) (20 g, 97 mmol) in anhydr. CCl_4 (150 mL) was added NBS (34.5 g, 194 mmol) and AIBN (0.1 g). The mixture was refluxed for 3 h, filtered under suction and washed with CCl_4. The solvent was removed under reduced pressure and the crude product was crystallized from MeOH to afford white needles; yield: 16.3 g (46%); mp 44.5-46°C.

IR (KBr): ν = 2955, 2931, 2858, 1583, 1460, 1388, 1273, 1047, 792, 650 cm^{-1}.

^1H NMR (aceton-d_6): δ = 0.85 - 0.95 (m, 3 H), 1.36 - 1.47 (m, 4 H), 1.56 - 1.7 (m, 2 H), 1.84 - 1.93 (m, 2 H), 4.14 (t, 2 H, J = 6.25 Hz), 4.79 (s, 2 H), 4.88 (s, 2 H), 7.05 (dd, 1 H, J = 8.36 Hz, J = 0.9 Hz), 7.11 (dd, 1 H, J = 7.66 Hz, J = 0.9 Hz), 7.35 (t, 1 H, J = 8 Hz).

^{13}C NMR ($CDCl_3$): δ = 157.47, 137.9, 129.97, 125.18, 122.54, 112.27, 68.3, 31.49, 30.06, 29.16, 25.73, 23.84, 22.58, 13.72.

1,3-Dihydro-4-hexyloxyisothianaphthene (26):

A solution of $Na_2S \cdot 9\ H_2O$ (26.4 g, 110 mmol) in THF/EtOH (1:5, 450 mL) was added over a period of 6 h under nitrogen to a solution of **25** (34 g, 93 mmol) under reflux. After 30 min the solvent was removed and then added CH_2Cl_2 (300 mL). The organic layer was washed several times with water, dried (Na_2SO_4) and the crude product was purified by chromatography on silica gel using hexane/toluene (3:1) as eluent. Evaporation of the solvent gave a yellow oil; yield : 17.5g (80%).

IR (film): ν = 3038, 2953, 2930, 2856, 1589, 1464, 1389, 1277, 1070, 766, 731 cm^{-1}.

^1H NMR (aceton-d_6): δ = 0.89 - 0.99 (m, 3 H), 1.34 - 1.45 (m, 4 H), 1.47 - 1.6 (m, 2 H), 1.74 (m, 2 H), 4.06 (t, 2 H, J = 6.49 Hz), 4.17 (d, 2 H, J = 2 Hz), 4.28 (d, 2 H, J = 2 Hz), 6.82 (d, 1 H, J = 8.08 Hz), 6.89 (d, 1 H, J = 7.62 Hz), 7.22 (t, 1 H, J = 7.8 Hz).

^{13}C NMR ($CDCl_3$): δ = 155.6, 142.34, 129.12, 128.3, 116.43, 108.77, 67.99, 38.52, 35.37, 31.52, 29.16, 25.72, 22.56, 13.97.

1,3-Dihydro-4-hexyloxyisothianaphthene 2-Oxide (27):

A solution of **26** (8 g, 34 mmol) in EtOH (50 mL) was added to a solution of $NaIO_4$ (7.7 g, 36 mmol) in H_2O/EtOH (1:1, 180 mL). The mixture was stirred overnight and filtered. After evaporation the residue was treated with water and extracted five times with CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and evaporated to give a dark yellow oil which was recrystallised from hexane/EtOAc (4:1); white crystals; yield: 4.5 g (53%) ; mp 38-39°C.

IR (KBr): ν = 3032, 2955, 2932, 2860, 1587, 1466, 1394, 1277, 1045, 770, 735 cm^{-1}.

^1H NMR (aceton-d_6): δ = 0.88 - 0.94 (m, 2 H), 1.34 - 1.42 (m, 4 H), 1.45 - 1.53 (m, 2 H), 1.75 - 1.86 (m, 2 H), 4.07 (m, 2 H), 3.93 (d, 1 H, J = 16.6 Hz), 3.99 (d, 1 H, J = 16.6 Hz), 4.22 (d, 1 H, J = 16.4 Hz), 4.33 (d, 1 H, J = 16.4 Hz), 6.92 (d, 1 H, J = 8.17 Hz), 6.99 (d, 1 H, J = 7.57 Hz), 7.28 (t, 1 H, J = 7.88 Hz).

^{13}C NMR (DMSO-d_6): δ = 156.77, 136.8, 129.85, 123.37, 117.91, 110.37, 68.14, 59.78, 54.4, 31.46, 29.08, 25.65, 22.49, 13.92.

1,3-Dihydro-4-hexyloxy-1,3-bis(2-thienylmethylene)isothianaphthene 2-Oxide (28a):

To a solution of NaOH (2 g) in MeOH (60 mL) were added **27** (3 g, 12 mmol) and 2-thiophenecarbaldehyde (5.7 g, 52 mmol). After stirring at 40°C for 3 d, the solvent was removed and the crude product purified by chromatography on silica gel. Impurities were removed with Et_2O/hexane (1:2) and the product was eluted with EtOAc. Evaporation of the solvent gave a dark yellow powder, which was recrystallised from EtOAc; yield: 3.1 g (59%); yellow crystals; mp 126-128°C.

IR (KBr): ν = 3063, 2951, 2930, 2858, 1572, 1464, 1416, 1391, 1362, 1277, 1005, 783, 733, 706 cm^{-1}.

^1H NMR (aceton-d_6): δ = 0.85 - 0.95 (m, 3 H), 1.3 - 1.47 (m, 4 H), 1.5 - 1.7 (m, 2 H), 1.9 - 2 (m, 2 H), 4.15 - 4.27 (m, 2 H), 7.04 (dd, 1 H, J = 8.08 Hz, J = 0.7 Hz), 7.22 (dd, 2 H, J = 5.1 Hz, J = 3.75 Hz), 7.34 (t, 1 H, J = 8.08 Hz), 7.44 (dd, 1 H, J = 7.81 Hz, J = 0.7 Hz), 7.54 (dd, 1 H, J = 3.7 Hz, J = 0.9 Hz), 7.65 (dd, 1 H, J = 3.75 Hz, J = 0.85 Hz), 7.87 (dd, 1 H, J = 5.1 Hz, J = 0.85 Hz), 8.03 (s, 1 H), 8.56 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 156.66, 140.15, 139.44, 137.96, 137.71, 137.38, 133.39, 132.31, 132.25, 131.54, 130.98, 128.54, 128.45, 127.4, 125.49, 122.27, 114.01, 112.55, 68.56, 31.25, 28.72, 25.8, 22.33, 14.08.

1,3-Bis(5-bromo-2-thienylmethylene)-1,3-dihydro-4-hexyloxyisothianaphthene 2-Oxide (28b):

To a solution of NaOH (1 g) in MeOH (30 mL) were added **27** (1 g, 4 mmol) and 5-bromo-2-thiophenecarbaldeyde (1.9 g, 10 mmol). After stirring at 40°C for 1 d, the precipitate was filtered, washed with MeOH and crystallised from EtOAc; yield: 850 mg (35%); mp 170-172°C.

IR (KBr): ν = 3071, 2953, 2930, 2868, 1593, 1573, 1479, 1466, 1446, 1412, 1273, 1073, 1013, 966, 793, 781 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 0.83 - 0.93 (m, 3 H), 1.25 - 1.4 (m, 4 H), 1.4 - 1.55 (m, 2 H), 1.76 - 1.91 (m, 2 H), 4.1 - 4.2 (m, 2 H), 7.05 (d, 1 H, J = 7.55 Hz), 7.3 - 7.5 (m, 6 H), 8.1 (s, 1 H), 8.3 (s, 1 H).

1,3-Dihydro-4-hexyloxy-1,3-bis(2-thienylmethylene)isothianaphthene (29):

To a solution of **28a** (1.76 g, 4 mmol) and pyridine (0.5 mL, 6 mmol) in anhydr. toluene (40 mL) was added slowly 2-chloro-1,3,2-benzodioxaphosphole (0.8 mL, 9 mmol). The solution was stirred at r.t. for 2 h. After evaporation of the solvent the mixture was chromatographed on silica gel with hexane/EtOAc (3:1) as eluent. Removal of the solvent and recrystallisation from EtOAc gave violet prisms; yield: 1.4 g (82%) ; mp 93-94°C.

IR (KBr): ν = 3058, 2945, 2923, 2865, 1578, 1566, 1466, 1296, 1275, 1263, 1067, 1047, 775, 692 cm^{-1}.

^1H NMR (aceton-d_6): δ = 0.87 - 0.96 (m, 3 H), 1.33 - 1.5 (m, 4 H), 1.54 - 1.69 (m, 2 H), 1.9 - 2.1 (m, 2 H), 4.19 (t, 2 H, J = 6.18 Hz), 7.0 (d, 1 H, J = 8.01 Hz), 7.18 - 7.22 (m, 2 H), 7.27 - 7.38 (m, 3 H), 7.57 (dd, 1 H, J = 7.99 Hz, J = 0.73 Hz), 7.6 - 7.65 (m, 2 H), 7.75 (s, 1 H), 8.45 (s, 1 H).

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