Synthesis of β-Butylsulfanyl α-Oligothiophenes from 3-Butylsulfanyl-2,2'-bithiophene

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β-Butylsulfanyl tetra-, sexa-, and octathiophenes were synthesized by oxidative coupling with iron(III) chloride from 3-butylsulfanyl-2,2'-bithiophene. Tetrathiophene was also generated through coupling reactions. The nmr characterization of oligomers is reported and discussed.

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Introduction.

α-Oligothiophenes with well-defined structure have attracted increasing interest as new materials in field-effect transistors [1], as photoactive materials in photovoltaic devices [2] and as model compounds for the characterization of charge carriers in conjugated chains [3]. The optical and electrical properties as well the processability of oligothiophenes can be modulated by the introduction of substituents in the β-positions.

Some synthetic approaches have been reported about the synthesis of alkylated oligothiophenes. The more widely used are homo-coupling of metalated thiophenes or cross-coupling of α-metalated thiophenes with α-halothiophenes catalyzed by nickel or palladium [4]. The starting point for obtaining longer substituted oligothiophenes is frequently that of the corresponding dimers [5,6].

In a recent communication [7], we described the synthesis in high yield of tris(butylsulfanyl)sexathiophene which shows interesting optical properties and forms a stable radical cation and dication.

In the present paper we report on the synthesis and characterization of oligomers generated from 3-butylsulfanyl-2,2'-bithiophene **3**, by action of iron(III) chloride. Alternative synthetic pathways for the synthesis of quaterthiophene **5** are also investigated.

Synthesis.

The synthetic route to the oligothiophenes prepared in the course of the present study, is outlined in Schemes 1 and 2. The central building blocks of the synthetic pathways are represented by 3-butylsulfanyl-2,2'-bithiophene **3** and by the corresponding 5'-bromo-3-butylsulfanyl-2,2'-bithiophene **4a** and 5'-iodo-3-butylsulfanyl-2,2'-bithiophene **4b**.

Compounds **1-4** were prepared by known methods, suitable for halogenation and Grignard coupling reactions.

2-Bromo-3-(butylsulfanyl)thiophene **2** was obtained from 3-(butylsulfanyl)thiophene **1** [8] in 86% yield of isolated product according to the literature method [9].

The α-conjugated bithiophene **3** was easily obtained in a high yield (90% of isolated product) by Kumada coupling [10] of 2-thienylmagnesium bromide with **2** in refluxing diethyl ether in the presence of nickel(II) bis(diphenylphosphino)propane dichloride as the catalyst.

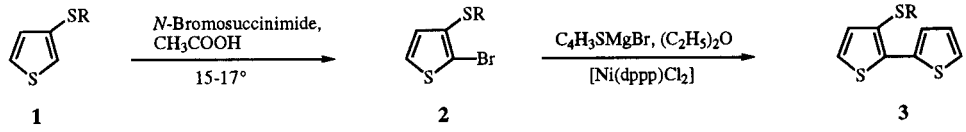
Attempts to synthesize **3** from 3-bromo-2,2'-bithiophene [11] through bromine lithium exchange with butyllithium followed by reaction with an excess (2 mole equivalents) of dibutyl disulfide afforded a complex mixture of products [8]. The low reactivity of the β-position, the vicinal 2-thienyl group and trans-metallation processes are probably the cause of these results.

The bromination of **3** in dimethylformamide with one molar equivalent of *N*-bromosuccinimide at 22-23° afforded the monobromo derivative **4a** with high selectivity and yield (91% of isolated product). This high selectivity, in comparison with bromination of the analogous alkyl derivative, where a mixture of 5- and 5'-monobromobithiophene were obtained [5], is due to the electron-donating effect of the butylsulfanyl group in the β-position of the bithienyl moiety and to the use of a dipolar-aprotic solvent such as dimethylformamide. In fact, the attempts to generate a monobromo derivative in methylene chloride solution under the same experimental conditions afforded a mixture of 60% of 5,5'-dibromo-3-butylsulfanyl-2,2'-bithiophene and 24% of 5'-bromo-3-butylsulfanyl-2,2'-bithiophene.

High selectivity but low yield was obtained by using *N*-iodosuccinimide. The iodination of bithiophene **3** with 1.2 molar equivalents of *N*-iodosuccinimide, carried out at 5° in anhydrous dimethylformamide, gave 40% of compound **4b**. In all the reactions, performed in dimethylformamide, the presence of unreacted bithienyl **3**, as the only by-product, confirms the high selectivity of the reaction. Much more satisfactory yields for **4b** (91% and 87% of isolated product) were obtained with iodine and yellow mercury(II) oxide in benzene (Method A) and with 1.2 molar equivalents of iodine monochloride in methanol (Method B).

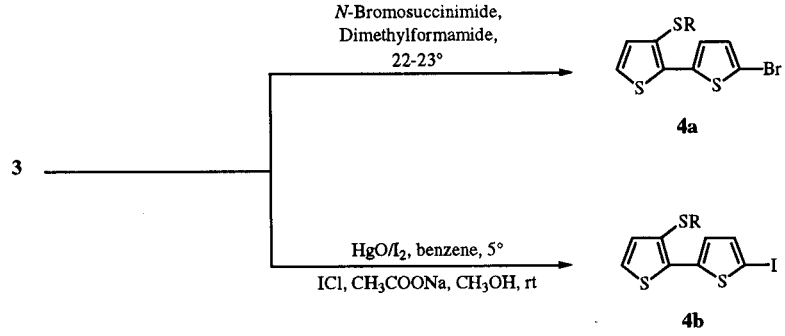
The synthesis of tetramer **5** was performed by oxidative coupling of **3** with iron(III) chloride in chloroform (Method A) and *via* Kumada coupling [10] of the halogenated bithiophenes **4a** or **4b** (Method B).

Scheme 1

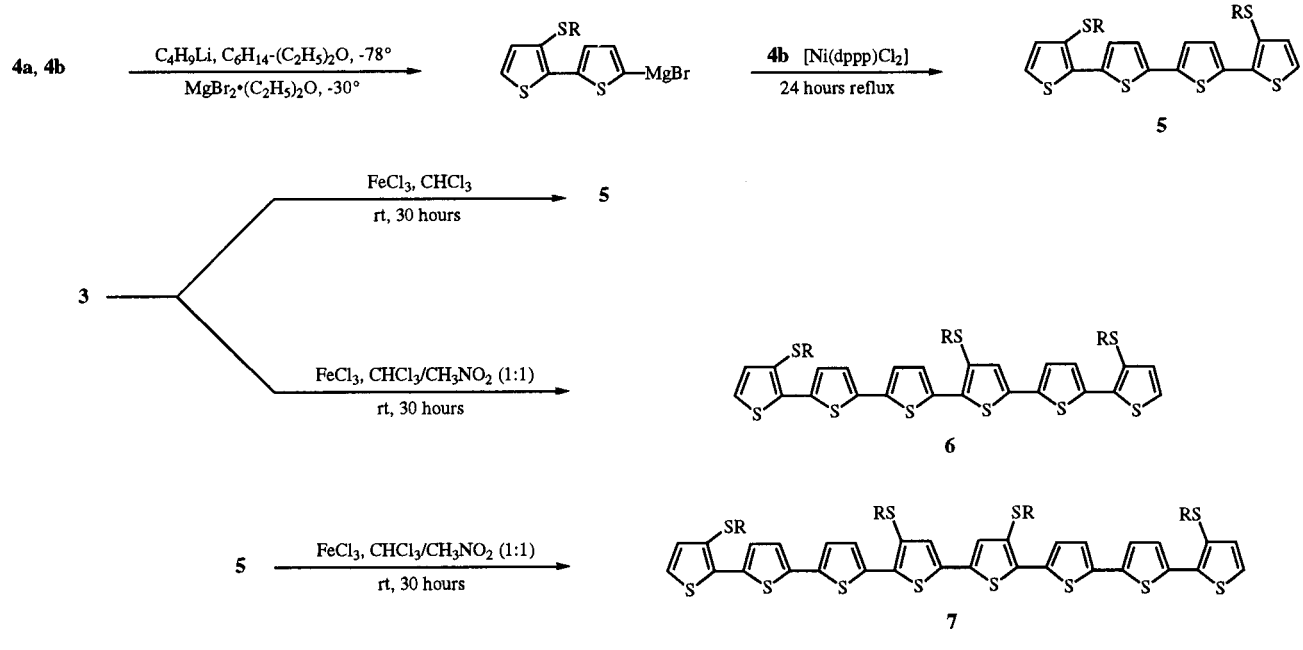


1 2 3

R = $CH_2CH_2CH_2CH_3$



Scheme 2



The reaction of **3** with iron(III) chloride in chloroform afforded a complex mixture of oligomers containing one major compound. This last, although isolated in insufficiently pure form (see Experimental), was identified by ^1H and ^{13}C nmr spectroscopy as 3,3'''-bis(butylsulfanyl)-2,2':5',2'':5'',2'''-quaterthiophene **5**.

Changing the solvent from chloroform to chloroform/nitromethane (1:1), with the aim to improve the yield of the tetramer, we obtained an hexamer in high yield, identified as 3,3''',3''''-tris(butylsulfanyl)-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''-sexathiophene **6** [7].

The wish to obtain the useful tetramer **5** in pure form for the synthesis of higher homologues, required the exploration of other synthetic pathways. The availability of the two monohalobithiophenes suggested that we perform a coupling reaction of the Grignard reagent of monobromo derivative **4a**, or of monoiodo derivative **4b**, with iodo derivative **4b**. Halobithiophenes **4a** and **4b** have low reactivity in affording the corresponding Grignard reagents (<30%) with magnesium in diethyl ether or tetrahydrofuran. The Grignard reagent was easily obtained from **4a** or **4b** by lithiation followed by cation exchange with magnesium bromide. The Kumada coupling of the Grignard reagent with 1.2 equivalents of **4b**, afforded a mixture consisting of tetramer **5**, dimer **3**, derived from hydrolysis of the Grignard reagent, and derivative **4b**, in 6.4:1:2.6 ratio. Column chromatography enabled us to isolate pure quaterthiophene (53% yield of isolated product) with recycling of pure bithiophene **3** and **4b**. Attempts to synthesize **5** by a Stille-type coupling [12] of 5'-stannyl-3-(butylsulfanyl)-2,2'-bithiophene and halogenated bithiophenes **4**, failed because of the difficulty in isolating the appropriate stannyl derivative from a mixture of products derived from the trans-metallation processes. The oxidative coupling with iron(III) chloride afforded a mixture from which it is difficult to isolate compound **5** whereas the Kumada coupling reaction [10] proved to be very effficient in providing **5** in pure form. These results and the possibility of recycling pure **3** and **4b** make this latter route more convenient than the former, even though the oxidative coupling is a one-step reaction and utilizes a less expensive reagent. On the other hand, iron(III) chloride converts, in high yield, bithiophene **3** into tris(butylsulfanyl)sexathiophene **6** when a 1:1 mixture of chloroform/nitromethane is utilized. The prevalence of two major products, **5** and **6**, in the oxidative coupling reaction of **3** with iron(III) chloride is ascribable to the electronic effect of the butylsulfanyl group in the β-position, which deactivates the 5-position of thiophene or bithiophenes [7,13]. The first step of the oxidative coupling is the formation of quaterthiophene **5** that can react with **3** to form **6**. The solvent, chloroform or chloroform/nitromethane, seems to play an important role in directing the reaction pathway towards **5** or **6**. The differences in selectivity could be due to solvation effects together with changes in the oxidation potentials. The above observations suggested to us that the reaction of **5** with iron(III) chloride in the absence of **3** should have generated the octamer **7**. In fact, compound **7** was obtained in satisfactory yield (51% of isolated product) by the action of iron(III) chloride on tetramer **5** by employing the same conditions of oxidation utilized for the generation of sexathiophene.

NMR Spectroscopic Characterization.

All compounds were characterized by ^1H and ^{13}C nmr spectroscopy, mainly by ^1H, ^{13}C nmr inverse-detection techniques, based on heteronuclear multiple-quantum (HMQC) [14] and multiple-bond (HMBC) [15] coherence experiments. The nmr data of **3**, **4a**, **4b** and **5** are reported in Table 1. The nmr data of **6** and **7** are reported in Tables 2 and 3, respectively.

The ^1H nmr spectrum of **3** shows the presence of a disubstituted and a monosubstituted ring. Even though the assignment of the protons of the monosubstituted ring is straightforward, the unambigous assignment of protons of the disubstituted ring is accomplished by the $^1J(C,H)$ coupling constants, obtained by the heteronuclear multiple quantum coherence spectrum.

The proton spectra of compounds **4a**, **4b** and **5** display, in the aromatic region, two doublets, characterized by a coupling constant of 5.3 Hz, attributable to a 2,3-disubstituted ring and two doublets, with a coupling constant of 3.9 Hz, due to a 2,5-disubstituted ring. Although the assignment of H-4 and H-5 is direct (compared with ^1H chemical shifts of **3**), the assignment of the H-3' and H-4' pairs is not trivial and was performed by the H,C multiple-bond correlation experiments. A relative chemical shift inversion between H-3' and H-4' is observed in **4b**. Interesting features are also observed in the ^{13}C nmr spectra. The carbon chemical shifts of the butylsulfanyl substituted ring are similar in the three compounds, whereas marked differences are observed in the second thiophene ring. In **4a** and **4b** the halogen substituent effects are evident and, especially on the directly-bonded carbon, greater than those reported for benzenes or alkenes [16]. The 4'-C and 5'-C chemical shifts of **5** are affected by the junction effect already reported for poly- and oligothiophenes [17].

The ^1H and ^{13}C nmr spectra of **6** confirm that the derivative is a sexathiophene and may confirm its regiochemistry. In the aromatic region of the ^1H nmr spectrum, the presence of four doublets characterized by $^3J_{H\text{-}\alpha,H\text{-}\beta}$ = 5.2-5.3 Hz (H-4, H-5, H-4'''', H-5''''), six doublets characterized by $^3J_{H\text{-}\beta,H\text{-}\beta'}$ = 3.7-3.9 Hz (H-3', H-4', H-3'', H-4'', H-3'''', H-4'''') and a singlet (H-4''') demonstrates that the compound under investigation is actually a sexathio-

Table 1

^1H and ^{13}C Chemical Shifts [a] (ppm) of Derivatives **3**, **4a**, **4b** and **5**

Derivative									
3	H-4	H-5	H-3'	H-4'	H-5'	$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	7.04	7.18	7.38	7.06	7.31	2.85	1.59	1.41	0.89
	C-2	C-3	C-4	C-5		$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	135.6	127.9	131.9	123.1		35.65	31.6	21.8	13.6
	C-2'	C-3'	C-4'	C-5'					
	135.5	126.2	126.9	125.8					
4a	H-4	H-5	H-3'	H-4'		$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	7.01	7.17	7.08	6.98		2.83	1.57	1.41	0.89
	C-2	C-3	C-4	C-5		$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	135.6	128.3	132.3	123.2		36.0	31.6	21.8	13.6
	C-2'	C-3'	C-4'	C-5'					
	137.1	126.0	129.5	113.9					
4b	H-4	H-5	H-3'	H-4'		$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	7.02	7.16	7.01	7.17		2.83	1.58	1.41	0.89
	C-2	C-3	C-4	C-5		$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	135.4	128.4	132.1	123.4		35.9	31.6	21.7	13.6
	C-2'	C-3'	C-4'	C-5'					
	141.5	127.1	136.5	74.9					
5	H-4	H-5	H-3'	H-4'		$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	7.04	7.17	7.29	7.15		2.87	1.61	1.45	0.90
	C-2	C-3	C-4	C-5		$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
	135.7	127.9	132.2	123.1		36.0	31.6	21.8	13.6
	C-2'	C-3'	C-4'	C-5'					
	134.6	126.7	123.4	137.4					

[a] δ values are referred to internal tetramethylsilane.

Table 2

^1H and ^{13}C Chemical Shifts [a] (ppm) of Derivative **6**

ring	H-3	H-4	H-5	C-2	C-3	C-4	C-5	
		7.041	7.18	135.7	128.0	132.23	123.1	
'	7.31	7.15		134.8	126.81	123.5	137.4	
''	7.15	7.30		137.6	123.5	126.77	134.4	
'''		7.14		134.7	128.8	128.2	134.3	
''''	7.11	7.29		136.4	123.7	126.74	135.1	
'''''		7.043	7.19	135.5	128.2	132.20	123.3	
	$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3	$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
3-chain	2.88 [b]	1.62	1.44	0.907 [b]	35.9	31.7	21.8	13.6
3'''-chain	2.92	1.66	1.46	0.92	36.0	31.7	21.8	13.6
3''''-chain	2.87 [b]	1.62	1.44	0.905 [b]	35.9	31.7	21.8	13.6

[a] δ values are referred to internal tetramethylsilane; [b] may be interchanged.

Table 3

^1H and ^{13}C Chemical Shifts [a] (ppm) of Derivative **7**

ring	H-3	H-4	H-5	C-2	C-3	C-4	C-5	
		7.04	7.19	135.7	128.1	132.2	123.2	
'	7.30	7.16		134.9	126.8	123.6	137.3	
''	7.16	7.32		137.8	123.6	126.9	134.2	
'''		7.10		135.0	128.9	128.6	133.3	
	$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3	$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	CH_3
3-chain	2.88	1.61	1.44	0.90	35.9	31.6	21.8	13.6
3'''-chain	2.92	1.66	1.46	0.93	36.0	31.6	21.8	13.6

[a] δ values are referred to internal tetramethylsilane.

phene. That proposed in Scheme 2 is the only structure compatible with the absence of terminal monosubstituted thiophenes. Three distinguished triplets for $CH_2(\alpha)$ are found in the aliphatic region of the proton nmr spectrum, at δ = 2.92, 2.88 and 2.87 ppm. Also two types of triplets, corresponding to the terminal methyls, are found, at 0.92, 0.91 and 0.90 ppm. Signals corresponding to $CH_2(\beta)$ and $CH_2(\gamma)$ are superimposed. The [^{1}H]- ^{13}C nmr spectrum consists of 31 resonances (23 in the aromatic and 8 in the aliphatic region, respectively) out of the required 36. The disentangling of the ^{1}H and ^{13}C nmr spectra was accomplished by the HMQC and HMBC experiments. The coupled HMQC experiment enabled the directly bonded C-H pairs to be found and the Cα-Hα to be distinguished from the Cβ-Hβ fragments, on the basis of the values of the $^1J_{H,C}$ measured [16]. With the HMBC experiments relayed carbons were assigned on the basis of the values of $^nJ_{H,C}$ [16].

The aromatic region of the ^{1}H nmr spectrum of **7** displays two doublets at 7.04 and 7.19 ppm, characterized by a $^3J_{H\text{-}\alpha,H\text{-}\beta}$ = 5.3 Hz (H-4, H-5), four doublets, characterized by $^3J_{H\text{-}\beta,H\text{-}\beta'}$ = 3.9 Hz (H-3', H-4', H-3", H-4"), and one singlet at 7.10 ppm (H-4"'). In the aliphatic region of the proton spectrum, two types of chains are distinguishable. The [^{1}H]- ^{13}C nmr spectrum consists of 24 resonances one for each different carbon (16 in the aromatic and 8 in the aliphatic region, respectively). A HMQC experiment permits us to find directly connected carbons and protons through the modulation of the one-bond coupling constants. The existence of inter-ring $^3J_{H,C}$ coupling constants (~3 Hz) was essential for obtaining ring connectivities and deriving the entire proton and carbon framework of **6** and **7**. In particular, both intra-ring and inter-ring correlations between H-4"' and C-5"' were observed in the case of **7**. Long-range correlations between the $CH_2(\alpha)$ protons and the thiophene carbons bearing the butylsulfanyl chains were also detected and each chain was assigned to the proper ring. Comparing the proton chemical shifts of the aliphatic chains of **5**, **6** and **7** it can be observed that the inner chains are always deshielded with respect to the outer chains.

EXPERIMENTAL

Iron(III) chloride was purchased from Fluka and dried under vacuum. All air- or moisture-sensitive reactions were performed under prepurified nitrogen or argon, using dry glassware. Tetrahydrofuran and diethyl ether were distilled from sodium diphenyl ketyl prior to use. Dimethylformamide, chloroform and nitromethane and all the solvents used in chromatography were dried by standard procedures. Other reagents were purchased from Aldrich Chemical Co., and used as received.

Melting points (Büchi apparatus) and boiling points are uncorrected. Refractive indexes were determined on an Abbe refractometer (Atago). The ir spectra were obtained in Nujol or in tetrachloromethane solutions using a Philips PU 9700 Series IR spectrometer and are reported in ν as cm^{-1}. All uv-vis spectra were taken in 1 x 10^{-4} *M* solutions in chloroform (spectroscopic grade) using a Varian-Cary 3 spectrophotometer.

The ^{1}H and ^{13}C nmr spectra were recorded on a Bruker AMX-400 WB spectrometer at 400.13 and 100.61 MHz, respectively. All nmr spectra were recorded in deuteriochloroform on 0.1 mole dm^{-3} solutions. Chemical shifts are reported in ppm, as δ relative to internal tetramethylsilane at 0.0 ppm. Coupling constants are given in Hz.

The HMQC [14] parameters for aromatic and aliphatic region are: spectral width (f2) = 1 and 4 ppm, 2048 complex points; spectral width (f1) = 50 and 30 ppm, 256 t1 increments with 16 scans per t1 value; relaxation and evolution delays = 0.5-1 s and 2.78-4.00 ms, respectively. Zero filling in f1 and f2, sine function in f1 were applied before Fourier transformation.

The HMBC [15] parameters for aromatic and aliphatic region are: spectral width (f2) = 1 and 4 ppm, spectral width (f1) = 25 and 150 ppm, 256 t1 increments with 64 scans per t1 value; relaxation delay = 0.5 s and delay for long-range coupling constant evolution = 50 and 100 ms, respectively. Zero filling in f1 and f2, sine function in f1 were applied before Fourier transformation.

3-(Butylsulfanyl)thiophene (**1**).

Compound **1** was prepared in high yield (96%) [8] by the method described in the literature [18]; ^{1}H nmr (deuteriochloroform): δ 7.31 (d, $J_{2,5}$ = 3.0, $J_{4,5}$ = 5.0, 1H, H-5), 7.02 (d, $J_{4,5}$ = 5.0, $J_{2,4}$ = 1.3, 1H, H-4), 7.11 (d, $J_{2,4}$ = 1.3, $J_{2,5}$ = 3.0, 1H, H-2), 2.85 (t, 2H, $CH_2(\alpha)$), 1.63 (m, 2H, $CH_2(\beta)$), 1.43 (m, 2H, $CH_2(\gamma)$), 0.92 (t, 3H, CH_3).

Anal. Calcd. for $C_8H_{12}S_2$: C, 55.77; H, 7.02; S, 37.21. Found: C, 55.64; H, 7.22; S, 37.12.

2-Bromo-3-(butylsulfanyl)thiophene (**2**).

To a solution of compound **1** (13 g, 75.4 mmoles) in acetic acid (40 ml) at 15-17° was added portionwise *N*-bromosuccinimide (13.4 g, 75.4 mmoles). The temperature of the reaction was raised to 25° for 2 hours. The crude oily product was distilled under reduced pressure to give compound **2** (16.4 g, 87%), bp 89-90°/0.3 mm Hg; n_D^{22} = 1.5872; uv (chloroform) λ_{max}: 240 nm (ε 9.2 x 10^3 dm^3 mol^{-1} cm^{-1}); ir (Nujol): ν_{max} 3095, 3080 and 960 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.2 (d, $J_{4,5}$ = 5.6, 1H, H-5), 6.9 (d, $J_{4,5}$ = 5.6, 1H, H-4), 2.85 (t, 2H, $CH_2(\alpha)$), 1.59 (m, 2H, $CH_2(\beta)$), 1.41 (m, 2H, $CH_2(\gamma)$), 0.89 (t, 3H, CH_3)

Anal. Calcd. for $C_8H_{11}BrS_2$: C, 38.25; H, 4.41; Br, 31.81; S, 25.53. Found: C, 38.45; H, 4.58; Br, 31.67; S, 25.32.

3-Butylsulfanyl-2,2'-bithiophene (**3**).

The Grignard reagent obtained from 2-bromothiophene (7.8 g, 47.7 mmoles) and magnesium powder (1.2 g, 48 mmoles) in diethyl ether (40 ml) was transferred to the dropping funnel of a second apparatus by means of a cannula and then added dropwise during 1 hour to an ice-cooled solution of 2-bromo-3-(butylsulfanyl)thiophene (10.0 g, 3.98 mmoles) and nickel(II) bis(diphenylphosphino)propane dichloride (0.54 g, 1 mmole) in diethyl ether (25 ml). The mixture was heated at reflux for 20 hours, cooled to room temperature and poured into hydro-

chloric acid-ice water (200 ml). The aqueous layer was extracted with diethyl ether (200 ml). The combined organic phases were washed with aqueous sodium bicarbonate and water, dried (magnesium sulfate) and evaporated. The residue distilled under pressure afforded a yellowish oil (9.0 g, 90%), bp 117-119°/0.05 mm Hg; n_D^{22} = 1.6495; uv (chloroform): λ_{max} 323 nm (ε 1.1 x 10^4 dm^3 mol^{-1} cm^{-1}); ir: ν_{max}: 3100, 3080, 2950, 2920, 2860, 810 and 870 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.38 (dd, $J_{3',4'}$ = 3.7, $J_{3',5}$ = 1.2, 1H, H-3'), 7.31 (dd, $J_{4',5'}$ = 5.2, $J_{3',5}$ = 1.2, 1H, H-5'), 7.06 (dd, $J_{3',4'}$ = 3.7, $J_{4',5}$ = 5.2, 1H, H-4'), 7.18 (d, $J_{4,5}$ = 5.3, 1H, H-5), 7.05 (d, $J_{4,5}$ = 5.3, 1H, H-4), 2.85 (t, 2H, $CH_2(\alpha)$), 1.59 (m, 2H, $CH_2(\beta)$), 1.41 (m, 2H, $CH_2(\gamma)$), 0.89 (t, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{14}S_3$: C, 56.65; H, 5.55; S, 37.80. Found: C, 56.62; H, 5.70; S, 37.62.

5'-Bromo-3-(butylsulfanyl)-2,2'-bithiophene (**4a**).

To a stirred solution of compound **3** (2.0 g, 7.8 mmoles) in anhydrous dimethylformamide (27 ml) was added portionwise during 45 minutes *N*-bromosuccinimide (1.4 g, 7.8 mmoles) at 22-23°. The mixture was stirred for 2 hours, poured into water and extracted with diethyl ether (100 ml). The combined organic layers were washed with water, dried (magnesium sulfate) and the solvent was evaporated to leave a brown oily mixture of **4a** and unreacted **3**. The crude product was chromatographed on silica gel (neutralized with 2% triethylamine solution) with light petroleum (bp 40-70°) as the eluent. Compound **4a** (2.3 g, 91%) was isolated as yellowish oil; uv (chloroform): λ_{max} 335 nm (ε 1.9 x 10^4 dm^3 mol^{-1} cm^{-1}); ir (Nujol): ν_{max} 3095, 3080 and 960 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.17 (d, $J_{4,5}$ = 5.3, 1H, H-5), 7.01 (d, $J_{4,5}$ = 5.3, 1H, H-4), 7.08 (d, $J_{3',4'}$ = 3.9, 1H, H-3'), 6.98 (d, $J_{3',4'}$ = 3.9, 1H, H-4'), 2.83 (t, 2H, $CH_2(\alpha)$), 1.57 (m, 2H, $CH_2(\beta)$), 1.41 (m, 2H, $CH_2(\gamma)$), 0.89 (t, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{13}BrS_3$: C, 43.24; H, 3.93; Br, 23.97; S, 28.86. Found: C, 43.36; H, 3.67; Br, 24.12; S, 29.15.

5'-Iodo-3-(butylsulfanyl)-2,2'-bithiophene (**4b**).

Method A.

To a stirred solution of **3** (7.7 g, 30.3 mmoles) in benzene (150 ml) cooled at 5°, powdered iodine (9.2 g, 36.3 mmoles) and yellow mercury(II) oxide (7.2 g, 33.3 mmoles) were added alternately in small portions over 1 hour. The mixture was stirred at room temperature for 30 minutes and the precipitate was filtered and washed with diethyl ether (50 ml). The combined organic solutions were washed with aqueous sodium thiosulfate, dried over magnesium sulfate and evaporated. The dark oily mixture of **4b** and unchanged **3** was chromatographed on silica gel (neutralized with 2% triethylamine solution) with light petroleum (bp 40-70°) and diethyl ether (98:2) as the eluent. Compound **4b** was isolated as a pure reddish oil (10.5 g, 91%).

Method B.

To a stirred solution of **3** (2.54 g, 10 mmoles) and sodium acetate (0.98 g, 12 mmoles) in metahnol (24 ml) was added dropwise during 1 hour a solution of iodine monochloride (1.94 g, 12 mmoles) in methanol (6 ml) at room temperature. The mixture was stirred for 1 hour and poured onto ice (20 ml) and the aqueous layer was extracted with chloroform (100 ml). The combined organic solutions, worked up as above, were evaporated to give a mixture of **4b** and unreacted **3**. Purification accomplished by column chromatography, provided the compound **4b** (3.3 g, 86%); ^1H nmr (deuteriochloroform): δ 7.16 (d, $J_{4,5}$ = 5.3, 1H, H-5), 7.02 (d, $J_{4,5}$ = 5.3, 1H, H-4), 7.01 (d, $J_{3',4'}$ = 3.9, 1H, H-3'), 7.17 (d, $J_{3'4'}$ = 3.9, 1H, H-4'), 2.83 (t, 2H, $CH_2(\alpha)$), 1.58 (m, 2H, $CH_2(\beta)$), 1.41 (m, 2H, $CH_2(\gamma)$), 0.89 (t, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{13}IS_3$: C, 37.90; H, 3.45; I, 33.37; S, 25.29. Found: C, 37.75; H, 3.62; I, 33.25; S, 25.32.

3,3'''-Bis(butylsulfanyl)-2,2': 5',2'': 5'',2'''-quaterthiophene (**5**).

Method A.

To a stirred solution of anhydrous iron(III) chloride (2.6 g, 16 mmoles) in distilled chloroform (20 ml) was added dropwise for 30 minutes a solution of compound **3** (1.0 g, 4.0 mmoles) in chloroform (20 ml) under a flow of dry nitrogen. The greenish-blue mixture was stirred for 24 hours at room temperature and poured with stirring into methanol (200 ml). The dark precipitate, filtered and washed with methanol (50 ml), was redissolved in chloroform (200 ml). The chloroform solution was filtered to remove insoluble material and refluxed for 20 minutes by stirring with concentrated ammonia (25 ml). The ammonia phase was separated and the procedure was repeated twice. The chloroform solution was finally washed with water and the solvent was evaporated to give a brown oil that was dried under vacuum. The oil was stirred with pentane (200 ml) and the pentane layer was evaporated. The brown residue (0.5 g, 50%) contains compound **5** (90%) difficult to isolate from the other unidentified oligomers.

Method B.

The Grignard reagent, generated from **4b** (2.2 g, 5.7 mmoles), following the procedure reported by Folli *et al.* [19], was slowly added for 30 minutes *via* a cannula to a solution of **4b** (2.0 g, 5.2 mmoles) and nickel(II) bis(diphenylphosphino)propane dichloride (0.07 g, 0.13 mole) in diethyl ether (6 ml) with cooling in an ice-bath. After reflux (20 hours) the mixture was quenched with hydrochloric acid-ice water. The aqueous layer was separated and extracted with diethyl ether (100 ml). The combined organic phases were washed with aqueous sodium bicarbonate, water and evaporated. A brown oil (2.7 g) containing compound **5**, unchanged **4b** and dehalogenated **3** in 6.4:1:2.6 ratio, was recovered. The mixture was chromatographed on silica gel (neutralized with 2% triethylamine solution). Unchanged **4b** (0.7 g) and dehalogenated **3** (0.5 g) were isolated with tetrachloromethane as the eluent. Subsequent elutions with the light petroleum (bp 40-70°) and diethyl ether (2:1) afforded a yellow solid that was stirred with pentane (10 ml) and collected (1.4 g, 53%), mp 54-55°; uv: λ_{max} 409 nm (ε 4.6 x 10^4 dm^3 mol^{-1} cm^{-1}); ir (tetrachloromethane): ν_{max} 3090, 3060, 2950, 2920, 2860, 870 cm^{-1}; ms: EI m/z (70 eV) 510 (4, $[M^+ +4]$), 509 (8, $[M^+ +3]$), 508 (33, $[M^+ +2]$), 507 (32, $[M^+ +1]$), 506 (100, M^+), 449 (25, $[M^+ - C_4H_9]$], 392 (32, $[M^+ -2 \times C_4H_9]$], 360 (43, $[M^+ - C_8H_{18}]$], 328 (17, $[M^+ - S_2C_8H_{18}]$]; ^1H nmr (deuteriochloroform): δ 7.17 (d, $J_{4,5}$ = 5.3, 1H, H-5), 7.04 (d, $J_{4,5}$ = 5.3, 1H, H-4), 7.29 (d, $J_{3',4'}$ = 3.9, 1H, H-3'), 7.15 (d, $J_{3',4'}$ = 3.9, 1H, H-4'), 2.87 (t, 2H, $CH_2(\alpha)$), 1.61 (m, 2H, $CH_2(\beta)$), 1.45 (m, 2H, $CH_2(\gamma)$), 0.90 (t, 3H, CH_3).

Anal. Calcd. for $C_{24}H_{26}S_6$: C, 56.88; H, 5.17; S, 37.95. Found: C, 56.73; H, 5.31; S, 37.72.

The reaction carried out by coupling the Grignard reagent from **4a** (5.7 mmoles) with **4b** (5.2 mmoles) afforded the same compounds in the same molar quantities.

3,3"',3""'-Tris(butylsulfanyl)-2,2':5',2":5",2"':5"',2"":5"",2""'-sexathiophene (**6**).

To a stirred solution of **3** (4.0 g, 15.7 mmoles) in distilled chloroform (240 ml) was added dropwise (2 hours) a solution of anhydrous iron(III) chloride (10.4 g, 64 mmoles) in dry nitromethane (240 ml) under a flow of a dry nitrogen. The greenish-blue mixture, stirred for 30 hours at room temperature, was evaporated and the residue was stirred with a solution of hydrochloric acid-methanol (50 ml). The dark product was allowed to settle and the procedure repeated twice. The addition of methanol led to the formation of a brown solid which was filtered, washed with methanol and redissolved in chloroform (200 ml). The chloroform solution, filtered to remove insoluble material, washed with a 3% hydrazine solution (100 ml) and then with water, was evaporated. The crude oil was washed with pentane (400 ml). The pentane solution was evaporated and the residue was chromatographed on silica gel (neutralized with 2% triethylamine solution) with light petroleum (bp 40-70°) and diethyl ether (9:1) as the eluent. Compound **6** was obtained as a red oil (2.8 g, 70%); uv: λ_{max} 449 nm (ε 7.5 x 10^4 dm^3 mol^{-1} cm^{-1}); ms: EI m/z (70 eV) 762 (10, [M+4]), 761 (15, [M+3]), 760 (41, [M+2]), 759 (43, [M+1]), 758 (100, M+), 506 (18, [M^+-$C_{12}H_{12}S_3$]; ^{1}H nmr (deuteriochloroform): δ 7.31 (d, J = 3.8, 1H, H-4"), 7.30 (d, J = 3.7, 1H, H-3'), 7.29 (d, J = 3.9, 1H, H-4""), 7.19 (d, J = 5.3, 1H, H-5"""), 7.18 (d, J = 5.3, 1H, H-5), 7.15 (d, J = 3.8, 2H, H-4', H-3"), 7.14 (s, 1H, H-4"'), 7.11 (d, J = 3.9, 1H, H-3""), 7.043 (d, J = 5.3, 1H, H-4"""), 7.041 (d, J = 5.3, 1H, H-4), 2.92 (t, 2H, 3"'-CH_2(α)), 2.88 (t, 2H, 3""'-CH_2(α)), 2.87 (t, 2H, 3-CH_2(α)), 1.64 (m, 6H, CH_2(β)), 1.44 (m, 6H, CH_2(γ)), 0.92 (t, 3H, 3"'-CH_3), 0.907 and 0.905 (2 t, 6H, 3-CH_3, 3""'-CH_3).

Anal. Calcd. for $C_{36}H_{38}S_9$: C, 56.95; H, 5.04; S, 38.00. Found: C, 56.73; H, 5.15; S, 37.72.

3,3"',4"",3"""'-Tetra(butylsulfanyl)-2,2':5',2":5",2"':5"',2"":5"",2""':5""',2"""':5""",2"""'-octathiophene (**7**).

The reaction was carried out employing iron(III) chloride and the same procedure reported for **6**. To a stirred solution of **5** (0.6 g, 1.2 mmoles) in chloroform (30 ml), was added dropwise a solution of anhydrous iron(III) chloride (0.78 g, 4.8 mmoles) in dry nitromethane (30 ml) under a flow of a dry nitrogen. After the usual workup with hydrazine, the crude product (0.4 g) was washed with diethyl ether (200 ml) and the solution evaporated. The residue was stirred with pentane and collected to give compound **7** as a red solid (0.31 g, 51%), mp 85-87°; uv: λ_{max} 477 nm (ε 6.0 x 10^4 dm^3 mol^{-1} cm^{-1}); ^{1}H nmr (deuteriochloroform): δ 7.19 (d, $J_{4,5}$ = 5.3, 1H, H-5), 7.04 (d, $J_{4,5}$ = 5.3, 1H, H-4), 7.30 (d, $J_{3',4'}$ = 3.9, 1H, H-3'), 7.16 (d, $J_{3',4'}$ $J_{3"4"}$ = 3.9, 2H, H-4' and H-3"), 7.32 (d, $J_{3"4"}$ = 3.9, 1H, H-4"), 7.10 (s, 1H, H-4"'), 2.88 (t, 2H, 3-CH_2(α)), 1.61 (m, 2H, 3-CH_2(β)), 1.44 (m, 2H, 3-CH_2(γ)), 0.90 (t, 3H, 3-CH_3), 2.92 (t, 2H, 3"'-CH_2(α)), 1.66 (m, 2H, 3"'-CH_2(β)), 1.46 (m, 2H, 3"'-CH_2(γ)), 0.93 (t, 3H, 3"'-CH_3).

Anal. Calcd. for $C_{48}H_{50}S_{12}$: C, 56.95; H, 5.04; S, 38.00. Found: C, 56.9; H, 5.1; S, 37.82.

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