Pergamon

Tetrahedron Vol. 50, No. 38, pp. 11249-11256, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $7.00+0.00

0040-4020(94)00687-3

Polyhydroxyl Oligothiophenes. I. Regioselective Synthesis of 3,4'- and 3,3'-di(2-hydroxyethyl)-2,2'-bithiophene *via* Palladium Catalyzed Coupling of Thienylstannanes with Thienylbromides.

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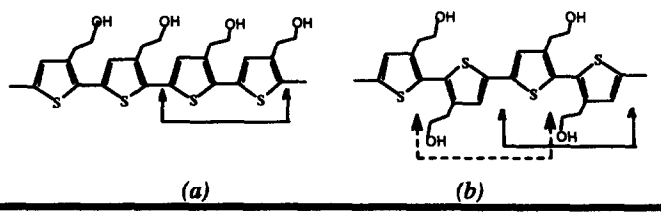
Abstract: The synthesis of 3,4'- and 3,3'-di(2-hydroxyethyl)-2,2'-bithiophene, building blocks for the preparation of regioregular *head-to-tail* and *head-to-head* polyhydroxyl oligothiophenes, is described. The synthesis was achieved through $Pd(PPh_3)_4$ catalyzed cross-coupling of 2- and 5-trimethylstannanes of 3-[2-(tetrahydropyranyloxy)ethyl]thiophene with the corresponding 2-bromo derivative, followed by deprotection of the hydroxyl groups in acidic medium. The synthesis of 3,4'-[2-(tetrahydropyranyloxy)ethyl]-2,2'-bithiophene afforded a non-negligible amount of the 4,4'-regioisomer, arising from the homocoupling reaction of the 5-trimethylstannane. Conversion of 3,3'-di(2-hydroxyethyl)-2,2'-bithiophene to the corresponding sodium sulfonate salt was shown to occur with 55% yield, indicating that polyhydroxyl oligothiophenes are, in fact, useful precursors in the preparation of water soluble 'self-doping' oligothiophenes.

We are currently interested in the synthesis and the properties of regioregular polyhydroxyl oligothiophenes of the type reported in *Scheme* 1, which are possible precursors for the preparation of 'self-doping' oligo and poly(3-thienylalkanesulfonates).[1-3] Water soluble, conducting, poly(3-thienylalkanesulfonates) have been prepared either by electrochemical polymerization of the monomer[1,2] or by chemical polymerization of the monomer in water with ferric chloride as the oxidizing agent.[3]

Scheme 1



Thus far, the synthesis of regioregular oligo(3-thienylalkanesulfonates) has never been performed, although oligothiophenes of sufficient length (six units or more) are expected to show properties similar to those

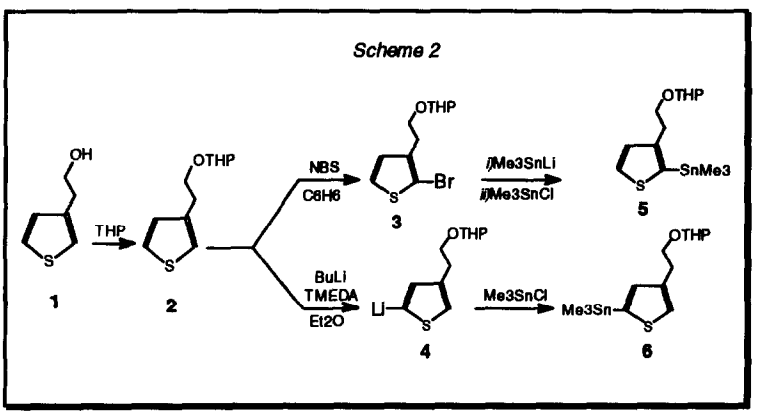
of the corresponding polymer but with a much better defined chemical structure.[4,5] It should also be noted that, in principle, the compounds of *Scheme* 1 - where the 3(2-hydroxyethyl)thiophene units are α,α' linked either *head-to-tail (a)* or *head-to-head (b)* - have also an interest *per se*, owing to their potential capability to self-assemble through H-bonds and to form well defined, possibly chiral, monocrystals.[6]

Oligothiophenes are generally prepared by the Kumada reaction[7], *i.e.* by nickel catalyzed cross coupling of thienylmagnesium bromides with thienyl bromides.[8,9] Recently, the Stille reaction[10] (palladium catalyzed cross coupling of thienylstannanes with thienyl bromides) has been applied with success to the regioselective synthesis of oligothiophenes bearing long β-alkyl chains, for which the Kumada reaction occurs in very poor yields.[11] Currently, there is large interest in Stille reaction due to its compatibility with a variety of functional groups and protecting groups and to the possibility of catalyst tailoring to accellerate the reaction rate.[12,13]

We are now reporting that 3,4'- and 3,3'-di(2-hydroxyethyl)-2,2'-bithiophenes (compounds **7** and **8**), building blocks for the preparation of compounds of type *(a)* and *(b)*, respectively, can be obtained in good yield by the Stille reaction. Specifically, the two regioisomeric bithiophenes were obtained by cross coupling of the 2- and 5-trimethyltin derivatives of 3-[2-(tetrahydropyranyloxy)ethyl]thiophene with the 2-bromo derivative of the same compound, in the presence of $Pd(PPh_3)_4$, followed by action of 0.2 M HCl to deprotect the hydroxyl group. Our attempts to prepare compounds **7** and **8** by the Kumada reaction were unsuccesful. In this paper we will also show that conversion of the hydroxyl functionality to the sodium sulfonate functionality in the 3,3'-dimer - through the pattern followed by Wudl *et al.* for monomer's conversion[1] - occurs in good yield, indicating that polyhydroxyl oligothiophenes are of practical use to obtain water soluble 'self-doping' oligothiophenes.[1-3]

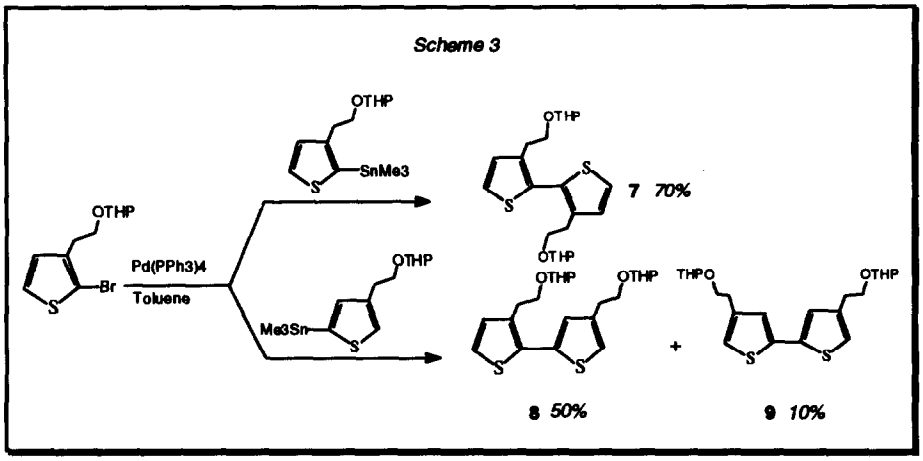
Schemes 2 and 3 show the synthetic pattern followed to obtain the title compounds. The hydroxyl functionality of the starting commercial material, 3(2-hydroxyethyl)thiophene **1**, was protected using the tetrahydropyranyl protecting group (THP).[14] Tetrahydropyranyl is not only one of the most used and less

Scheme 2



expensive protecting groups of the hydroxyl functionality but has also the great advantage, in our case, of giving proton and carbon NMR signals only in the aliphatic region of the spectrum. In consequence, reactions involving the thienyl moieties can easily be monitored by proton NMR. The 2- and 5-trimethylstannanes **5** and **6** were regioselectively obtained from the 2-bromo and the 5-lithio derivatives of 3-[2-

(tetrahydropyranyloxy)ethyl]thiophene **3** and **4**, respectively. The 2-bromo derivative **3** was prepared in good yield (75%) by action of N-bromosuccinimide on 3-[2-(tetrahydropyranyloxy)ethyl]thiophene in chloroform.



The action of butyllithium on **3** did not lead to formation of the 2-lithioderivative **4** by halogen-metal echange. However, **4** could be prepared by reacting the 2-bromo derivative with Me_3SnLi; subsequent quenching with Me_3SnCl afforded the desired 2-trimethylstannane **5** in 71% yield. The 5-trimethylstannane **6** was prepared by quenching of the 5-lithio derivative with Me_3SnCl. Owing to the directing effect of the β-substituent, the 5-lithioderivative was, in turn, obtained by action of BuLi on 3-[2-(tetrahydropyranyloxy)ethyl]thiophene in

Table 1. ^{13}C chemical shifts (ppm/TMS)[a] of compounds **1-3** and **5-12**.

	C2	*C3*	*C4*	*C5*	*CH2(α)*	*CH2(β)*	*THP*
1	121.4	138.9	128.3	125.5	62.6	33.4	
2	121.1	139.4	128.6	125.1	62.2	67.6	98.7; 30.8; 30.7; 25.5; 19.5
3	109.9	138.6	128.8	125.2	62.1	66.3	98.6; 30.6, 30.0; 25.5; 19.4
5	146.5	132.9	(130.6)[b]	(129.7)	62.1	68.4	98.7; 32.6; 30.6; 25.4; 19.4, -8 (Me)
6	126.9	137.0	136.8	140.5	61.9	67.5	98.5; 30.6; 30.3; 25.4; 19.3, -8.5 (Me)
	C2	*C3*	*C4*	*C5*	*CH2(α)*	*CH2(β)*	*THP*
	C2'	*C3'*	*C4'*	*C5'*	*CH2(α)'*	*CH2(β)'*	
7	129.9	139.6	129.5	125.9	62.3	67.5	99.0; 31.1; 29.7; 26.0; 19.9
8	132.4	136.3	(130.6)	124.0	62.2	((67.6))	98.9; 31.3; 31.1; 30.0; 25.4; 19.9; 9.8
	135.8	(128.4)	140.7	121.8	62.2	((67.4))	
9	137.5	125.6	141.0	120.4	62.4	67.5	99.1; 31.0; 30.0; 25.4; 19.9
10	129.8	138.5	128.5	125.9	62.3	31.9	
11	126.1	141.7	131.7	129.6	54.0	26.5[b]	
12	132.4	136.0	(129.9)	124.3	((62.8))	[33.7]	
	135.1	(127.8)	139.4	122.0	((62.7))	[32.3]	

(a) Compounds **1-3**, **5-6**,**10** and **12** in $CDCl_3$, compounds **7-9** in CD_2Cl_2, compound **11** in D_2O.
(b) Values in parentheses could be interchanged.

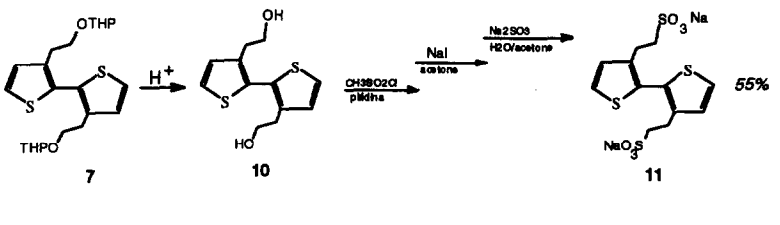
THF, in the presence of TMEDA.[15,16] However, the lithiation at carbon C-5 was not completely selective and after quenching with Me_3SnCl a 70:30 mixture of the 5- and the 2-trimethylstannane was recovered. Distillation of the mixture only led to an enrichement in the 5-isomer (**6**:**5** 80:20). Moreover, several attempts to separate the two stannanes by chromatography were unsuccesful. Thus, in the subsequent steps, we chose to use the mixture of the two stannanes as such, without further attempting their separation. It should be remarked that the 2- and 5- stannanes **5** and **6** are easily identified by ^{13}C NMR, since the presence of the metal leads to a large *deshielding* (15 and 25 ppm) of the bonded carbons. This is shown in Table 1, which gives the carbon chemical shifts of compounds **1-3** and **5-12**. On the other hand, it has already been shown by us[17] and other authors[18] that ^{13}C NMR is the technique of choise for the determination of the regiochemistry and of the purity of oligothiophenes and their intermediates.

As indicated in *Scheme 3*, the yield of formation of the protected 3,3'- dimer **7** (70%) is higher than that for the formation of the 3,4'- counterpart **8** (50%), although in both cases the yield of coupling is reasonably high for these kind of compounds (see, for example, references 8 and 9). In the reaction of the 5-trimethylstannane with the 2-bromo derivative there is also formation of the 4,4'-regioisomer **9** (10%), which is the product of the homocoupling reaction of the 5-trimethylstannane. It should be noted that the homocoupling reaction of the 2-trimethylstannane affords the same product, **7**, as the heterocoupling reaction of the 2-trimethylstannane with the 2-bromo derivative and this is one of the reasons why the yield of formation of **7** is higher than that of **8**. Palladium induced oxidative homocoupling of the arylstannanes has already been observed in the cross coupling reaction of arylstannanes with organic sulphonates.[13]

We were unable to completely separate by chromatography the protected 3,4'- and 4,4'- isomers **8** and **9** and a 85:15 mixture of **8**:**9** was the best we could obtain. However, complete separation of the isomers could be achieved with the deprotected compounds, so that, finally, the pure 3,4'-di(2-hydroxyethyl)-2,2'-bithiophene **12** could be obtained by silicagel chromatography using CH_2Cl_2/THF (80:20) as the eluent. The deprotection reaction of the 3,4- isomer (as well as that of the 3,3'- isomer) occurs quantitatively in dilute HCl and can be monitored by TLC.

Scheme 4 gives the pattern followed for the conversion of the hydroxyl to the sodium sulphonate functionality.

Scheme 4



7 10 11

It implies a series of well known reactions - formation of the mesylate, iodide exchange for mesylate, treatment of the iodide with sodium sulphite[1] - occurring in high yield and affording products which can be isolated, purified and unambiguously identified by ^{13}C NMR (see Table 1). The overall yield for the OH → SO_3Na conversion (55%, to be optimized) is sufficiently high to indicate that polyhydroxyloligothiophenes are convenient precursors for the preparation of regioregular oligo(thienylalkanesulphonates).

We are currently exploring the conditions required for the assembly of the 3,3'- and 3,4'-di(2-hydroxyethyl)-2,2'-bithiophene building blocks to form longer polyhydroxyloligothiophenes.

Experimental

General procedures. n-Butyllithium (2.5 M in hexane), N-bromosuccinimide, 3(2-hydroxyethyl)thiophene and tetrakis(triphenylphosphine)palladium were purchased from Janssen. All solvents used in reactions and chromatographies were dried by standard procedures. Commercially available chemicals were of the best grade and used as delivered. Reactions were carried out under an argon atmosphere. Analytical thin layer chromatography (TLC) was carried out by using 0.2 mm silica gel plates and the visualization accomplished by UV light. Flash chromatographies were carried out on silica gel (230-400 mesh ASTM) or reverse phase RP 18 (230-400 mesh ASTM). UV spectra were obtained in chloroform with a Perkin-Elmer 554 spectrometer. ^1H and ^{13}C NMR spectra were run with a Varian VXR 200 spectrometer working at 200 and 50 MHz, respectively, using $CDCl_3$, CD_2Cl_2 and D_2O as the solvents and TMS or TSP (in water) as the internal standard.

3-[2-(Tetrahydropyranyloxy)ethyl]thiophene (2): 6.88 g (0.082 mol) of 1,4-dihydro-2H-pyran (Aldrich) in 25 ml of EE were added to a solution of 10g (0.078 mol) of 3(2-hydroxyethyl)thiophene in 25 ml EE. Then 0.5 g of p-toluensulfonic acid were added and the mixture was stirred at room temperature for about three hours. Afterwards the solution was washed with 10% K_2CO_3 and with distilled water, dried with $MgSO_4$ and evaporated. The resulting residue was purified by chromatography (CH_2Cl_2-ethyl acetate 3:1). 14.9 g of a white oil were obtained (90 % yield). ^1H ($CDCl_3$ / TMS): 7.25 (m, 1H), 7.02 (m, 2H), 4.62 (t, 1H), 3.7 (m, 4H), 2.95 (m, 2H), 1.7 (m, 6 H) ppm. ^{13}C ($CDCl_3$/ TMS): 139.4, 128.6, 125.1, 121.1, 98.7, 67.6, 62.2, 30.8, 30.7, 25.5, 19.5 ppm.

2-Bromo-3-[2-(tetrahydropyranyloxy)ethyl]thiophene (3): to a solution of 2.12 g (0.01 mol) of **2** in 30 ml benzene were added 1.78 g (0.01 mol) of N-bromosuccinimide stepwise. The solution was stirred for 2 hours, then quenched with water, washed first with 10% KOH and then with distilled water, dried with $MgSO_4$ and evaporated. The resulting residue was purified by flash chromatography (CH_2Cl_2-ethyl acetate 95:5). 2.18 g of a pale yellow oil were obtained (75 % yield). ^1H ($CDCl_3$ / TMS): 7.18 (d, 1H), 6.88 (d, 1H), 4.60 (t, 1H), 3.87 (m, 1H), 3.73(m, 1H), 358 (m, 1H), 3.4 5(m, 1H), 2.88 (t, 2H), 1.7 (m, 6H) ppm. ^{13}C ($CDCl_3$ / TMS): 138.6, 128.8, 125.2, 109.9, 98.6, 66.3, 62.1, 30.6, 30.0, 25.5, 19.4 ppm.

2-Trimethyltin-3-[2-(tetrahydropyranyloxy)ethyl]thiophene (5): to a flask immersed in a bath at - 10°C and containing 0.88 g (0.12 moles) of lithium wire and 10 ml of dry THF, were added dropwise 2.5 g (0.012 mmoles) of trimethyltin chloride dissolved in 40 ml of THF. The mixture was stirred overnight at room temperature. 43 ml (10.7 mmoles) of this trimethyltin lithium solution were added to a solution of 2 g (6.87 mmol) of **3** in 30 ml THF and the mixture was cooled to 0°C. Then 2.73 g (13.74 mmol) of trimethyltin chloride dissolved in 20 ml THF were added dropwise. The solution was allowed to stir at ambient temperature

overnight, then was quenched with a saturated solution of NH_4Cl, treated with ethyl ether, the organic phase separated, washed with brine, dried over $MgSO_4$ and evaporated. The excess of trimethyltin chloride was evaporated under vacuum. 1.83 g of a pale yellow liquid were obtained (71 % yield), which were used without further purification. ^1H ($CDCl_3$ / TMS): 7.53(d, J= 5 Hz, 1H), 7.15(d, J= 5 Hz, 1H), 4.62(t, 2H), 3.92 (m, 1H), 3.80(m, 1H), 3.60(m, 1H), 3.45(m, 1H), 2.95(m, 2H), 1.7(m, 6H), 0.41 (s, 9H) ppm. ^{13}C ($CDCl_3$ / TMS): 146.5, 132.9, 130.6, 129.7, 98.7, 68.4, 62.1, 32.6, 30.6, 25.4, 19.4, -8.0 ppm.

5-Trimethyltin-3-[2-(tetrahydropyranyloxy)ethyl]thiophene 6: to a solution of 5 g (23.58 mmol) of **1** and 3 g (25.94 mmol) of N,N,N',N'-tetramethylenediammine (TMEDA) in 100 ml EE were added 10.38 ml (25.94 mmol) of 2.5 M *n*-butyllithium. The solution was allowed to reflux for one hour, then cooled to 0°C and 5.16 g (25.94 mmol) of trimethyltin chloride dissolved in 20 ml EE were added. The solution was allowed to stir at ambient temperature for two hours, then quenched with a saturated solution of NH_4Cl, treated with ethyl ether, the organic phase separated, washed with brine, dried over Na_2SO_4 and evaporated. The excess of trimethyltin chloride was evaporated under vacuum. 5.3 g were obtained of a mixture which contained 70% of the 5-trimethyltin derivative **6** and 30% of its 2-trimethyltin regioisomer **5**, as measured by ^1H NMR. Distillation only led to an enrichement of the mixture in the **6** isomer (**6**:**5** 80:20). Several attempts to separate the isomers by chromatography were unsuccesful, thus the mixture was used without further purification. NMR of the major component **6**: ^1H ($CDCl_3$ / TMS): 7.32(d, J= 1 Hz, 1H), 7.11 (d, J= 1 Hz, 1H), 4.62(t, 1H), 3.98(m, 1H), 3.80(m, 1H), 3.62(m, 1H), 3.48(m, 1H), 2.98(m, 2H), 1.7(m, 6H), 0.37(s, 9H) ppm. ^{13}C ($CDCl_3$ / TMS): 140.5, 137.0, 136.8, 126.9, 98.5, 67.5, 61.9, 30.6, 30.3, 25.4, 19.3, -8.5 ppm.

3,3'-Di[(2-(tetrahydropyranyloxy)ethyl]-2,2'-bithiophene (7): to a solution of 1.79 g (4.78 mmol) of **5** in 50 ml toluene were added 1.39 g (4.78 mmol) of **3** and 55mg (0.048 mmoles) of tetrakis(triphenylphosphine)palladium dissolved in 30 ml toluene. The reaction was allowed to reflux overnight, after which TLC monitoring showed the complete disappearence of **3**. Then the mixture was hydrolized with 2N HCl, neutralized with $NaHCO_3$, washed twice with brine, dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel with CH_2Cl_2-ethyl acetate 95:5 as eluent. 1.4 g of pure **7** were obtained (69 % yield). ^1H ($CDCl_3$ / TMS): 7.28(d, J=5 Hz, 1H), 7.04(d, J=5Hz), 1H), 4.55(t, 1H), 3.8(m, 2H), 3.5(m, 2H), 2.82 (t, 2H), 1.6(m, 6H) ppm. ^{13}C ($CDCl_3$ / TMS): 139.6, 129.9, 129.5, 125.9, 99.0, 67.5, 62.2, 31.1, 29.7, 26.0, 19.9 ppm. λ_{max} ($CHCl_3$) = 250 nm.

3,4'-Di[(2-(tetrahydropyranyloxy)ethyl]-2,2'-bithiophene (8): to a solution of 1.20 g (3.20 mmoles) of the above described 80:20 mixture of **6**: **5** in 30 ml toluene were added 0.93 g (3.20 mmol) of 2-Bromo-3-[2-(tetrahydropyranyloxy)ethyl]thiophene **3** and 0.03 mmoles of tetrakis(triphenylphosphine)palladium dissolved in 20 ml toluene. The reaction was allowed to reflux overnight, after which TLC monitoring showed the complete disappearence of **3**. Then the mixture was hydrolized with 2N HCl, neutralized with $NaHCO_3$, washed twice with brine, dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography using reverse phase RP 18 silicagel and CH_3OH-H_2O 95:5 as eluent. 0.81g of a mixture of **8** and of its 4,4' regioisomer **9** was obtained. Attempts to separate the two isomers by silicagel or reverse phase silicagel chromatography were unsuccesful and only a 85:15 mixture of **8** and **9** was obtained. Major isomer **8**: ^1H NMR (CD_2Cl_2 / TMS) 7.16(d, J= 5Hz, 1H), 7.09(d, J=1.5 Hz, 1H), 7.02(d, J= 1.5Hz, 1H), 7.00(d, J= 5Hz, 1H), 4.6(m, 1H), 3.95(m, 1H), 3.65(m, 1H), 3.60(m, 1H), 3.45(m, 1H), 3.05(t, 2H), 2.88(t, 2H), 1.6(m, 6H) ppm. ^{13}C ($CDCl_3$ / TMS): 140.7, 136.3, 135.8, 132.4, 130.6, 128.4, 124.0, 121.8, 98.9, 67.6, 67.4, 31.3, 31.1, 30.0,

25.4, 19.9, 9.8. Minor isomer **9**: ^1H ($CDCl_3$ / TMS) of (**9**): 7.07(d, 2H), 6.90(m, 2H), 4.6(t, 1H), 3.95(m, 1H), 3.65(m, 1H), 3.60(m, 1H), 3.45(m, 1H), 3.05(t, 2H), 2.85(t, 2H), 1.6(m, 6H) ppm. ^{13}C ($CDCl_3$ / TMS): 141.0, 137.5, 125.6, 120.4, 62.4, 67.5, 99.1, 31.0, 30.0, 25.4, 19.9.

3,3'-Di(2-hydroxyethyl)-2,2'-bithiophene (10): to a solution of 0.5 g of **7** dissolved in 10 ml THF were added 5 ml of 0.2 N HCl. The solution was allowed to reflux at ambient temperature for three hours and during this time the deprotection reaction was monitored by TLC (CH_2Cl_2-THF 80:20 as eluent). Then the THF was evaporated, the crude product dissolved in CH_2Cl_2, the organic phase isolated, dried over $MgSO_4$ and evaporated. 0.28 g 95% yield) of **10** were obtained. ^1H ($CDCl_3$ / TMS): 7.27 (d, J=5 Hz, 2H), 6.96(d, J=5Hz, 4H), 3.65(t, 2H), 2.98 (broad s, 2H), 2.72 (t, 4H) ppm. ^{13}C ($CDCl_3$ / TMS): 138.5, 129.8, 128.5, 125.9, 62.3, 31.9 ppm. λ_{max} ($CHCl_3$) = 242 nm.

3,3'-Di(2-ethyl-sodium sulphonate)-2,2'-bithiophene (11):

3,3'-di(2-ethyl-methylsulfonate)-2,2'-bithiophene (10a): to a solution of 0.51 g (2.01 mmol) of **10** dissolved in 4.82 ml (60.30 mmoles) of pyridine at -15°C were added 0.51 g (0.34 ml, 4.42 mmoles) of methylsulfonylchloride. The mixture was allowed to stir at room temperature until TLC monitoring (CH_2Cl_2-ethyl acetate 8:2) showed the complete disappearance of the starting material. The mixture was then poured into a beacker containing about 50 g of ice and stirred for about 10 minutes, treated repeatedly with CH_2Cl_2, the organic phase separated and evaporated under vacuum. 0.62 g of *10a* (a white oil) were formed (75 % yield). ^1H($CDCl_3$/TMS): 7.39(d, J=5Hz, 2H), 7.05(d, J=5Hz, 2H), 4.32(t, 4H), 2.99(t, 4H), 2.90(s, 6H) ppm. ^{13}C($CDCl_3$/TMS): 136.4, 130.1, 128.7, 126.8, 69.2, 37.4 , 28.7 ppm.

3,3'-di(2-ethyl-iodide)-2,2'-bithiophene (10b): to a solution of 0.5 g (1.3 mmol) of (*10a)* in 10 ml acetone were slowly added 40 ml of a saturated solution of NaI (about 20 g of sodium iodide in 40 ml). The solution was stirred overnight, then evaporated, the residue redissolved in CH_2Cl_2, washed with water and with brine and evaporated. 0.54 g (88 %) yield of pure *10b* were obtained. ^1H($CDCl_3$/TMS): 7.35(d, J=5Hz, 2H), 7.00(d, J=5Hz, 2H), 3.19(m, 8H) ppm. ^{13}C($CDCl_3$/TMS): 140.4, 129.4, 128.1, 126.4, 33.2, 4.0 ppm.

3,3'-di(2-ethyl-sodium sulphonate)-2,2'-bithiophene (11): to a solution of 0.87 g (6.89 mmol) of Na_2SO_3 in 10 ml H_2O was added dropwise a solution of 0.54 g (1.15 mmoles) of *(10b)* dissolved in 10 ml acetone. Then 30 ml of H_2O were added and the mixture was allowed to reflux overnight. The mixture was treated with CH_2Cl_2, the acqueous phase separated and evaporated under vacuum. The crude product was redissolved with water and a few drops of ethanol were added which led to the formation of a precipitate containing the inorganic salts. The water solution was filtered and evaporated again under vacuum. 0.38 g of the sodium sulfonate **11** (80 % yield) were obtained. ^1H($CDCl_3$/TMS): 7.52(d, J= 6Hz, 2H), 7.14(d, J=6Hz, 2H), 3.0 (m, 8H) ppm. ^{13}C($CDCl_3$/TMS): 141.7, 131.7, 129.6, 126.1, 54.0, 26.5 ppm.

3,4'-Di(2-hydroxyethyl)-2,2'-bithiophene (12): to a solution of 0.8 g of a 80:20 mixture of **8** and **9** dissolved in 15 ml THF were added 5 ml of 0.2 N HCl. The solution was refluxed for three hours and the deprotection reaction monitored by TLC (CH_2Cl_2-THF 80:20 as eluent). Then the THF was evaporated, the crude product dissolved in CH_2Cl_2, the organic phase isolated, dried over $MgSO_4$ and evaporated. 0.43 g (90% yield) of a 80:20 mixture of **12** and its 4,4'-disubstituted isomer were obtained. The mixture was chromatographed on silicagel (CH_2Cl_2/THF 80:20) and 0.24 g (70% yield) of pure **12** were obtained. ^1H ($CDCl_3$ / TMS): 7.19(d, J= 5 Hz, 1H), 7.0(m, 2H), 6.96(d, J=5Hz,1H), 3.85(t, 4H), 3.02(t, 2H), 2.85(t, 2H), 1.9(broad s, 2H) ppm.

^{13}C($CDCl_3$/TMS): 139.4, 136.0, 135.1, 132.4, 129.9, 127.8, 124.3, 122.0, 62.8, 62.7, 33.7, 32.3 ppm. λ_{max} ($CHCl_3$) = 292 nm.

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(*Received in UK* 8 *July* 1994; *revised* 1 *August* 1994; *accepted* 4 *August* 1994)