Synthesis of 3,4′-dibromo-2,2′-bithiophene: a useful intermediate for 3,4′-disubstituted 2,2′-bithiophenes. X-Ray molecular structure of 3,4′-dibromo-2,2′-bithiophene

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The first synthesis of 3,4′-dibromo-2,2′-bithiophene *via* metal-catalysed cross-coupling between a metallated and a halogenated thiophene derivative is described. An X-ray crystal structure of 3,4′-dibromo-2,2′-bithiophene is reported. 3,4′-Dibromo-2,2′-bithiophene was converted into corresponding bis(alkylsulfanyl) derivatives through bromine–lithium exchange, followed by reaction with two dialkyl disulfides (Me_2S_2 or Bu_2S_2). The ^1H and ^{13}C NMR data are discussed.

Introduction

β-Substituted oligo- and poly-thiophenes have aroused interest thanks to their electrical[1] and optical[2] properties, and can be utilized as electronic semiconducting materials,[3,4] non-linear optical materials,[5] highly ordered molecular assemblies[6] and in biological studies.[7,8] In recent years, β-substituted oligothiophenes have attracted increased attention owing to their well defined structures, enhanced solubility, better processability and easier characterizability with respect to the related polymers.[9,10]

β-Substituted bithiophenes can be utilized as starting materials for chemical and electrochemical polymerization, for the step-by-step synthesis of longer oligomers and as model compounds for the interpretation of related polymers.[11]

Whereas alkylated oligo-[12] and poly-thiophenes[13] have been widely studied, less attention has been paid to derivatives bearing electroactive groups. Thus an alkylsulfanyl group should lead to materials whose electronic structure and properties are strongly influenced by the electron-donating features of the substituent.[8]

The starting point for obtaining longer substituted oligothiophenes is frequently that of the corresponding dimers.[9,12] The synthesis of disubstituted bithiophenes usually follows two routes: (a) oxidative homo-coupling of metallated thiophenes,[14] (b) cross coupling of α-metallated thiophenes with α-halogenothiophenes.[15,16] The syntheses of symmetrical dimers *via* coupling reactions have been successfully carried out, regardless of the type of substituent.[15–17] However, in the case of the *head-to-tail* dimer, 3,4′-bis(methylsulfanyl)-2,2′-bithiophene, this route has not proved to be entirely satisfactory.[16] In fact, difficulties arise during the formation and purification of the suitable substituted starting monomers, and poorly separable isomeric by-products are formed in the coupling reaction.

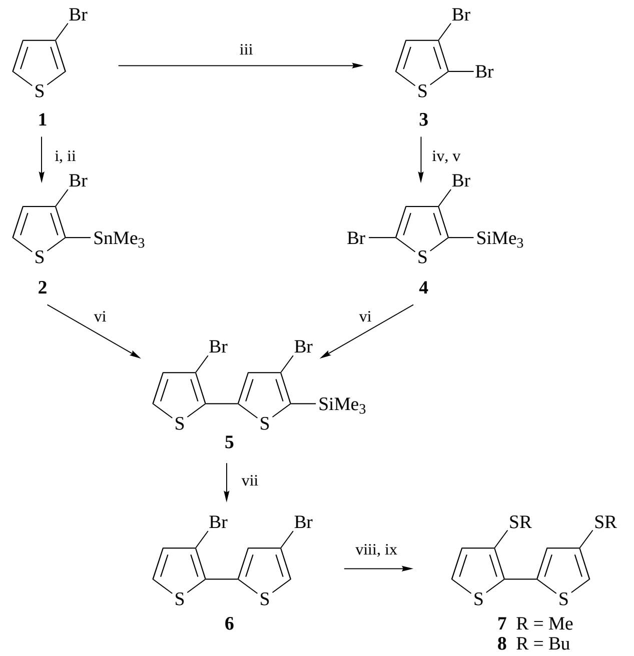
In recent papers, it has been established that 3,3′- and 4,4′-dibromo-2,2′-bithiophenes are convenient precursors for the synthesis of the corresponding *head-to-head* and *tail-to-tail* dimers.[17–19]

The present work reports the synthesis and characterization of 3,4′-dibromo-2,2′-bithiophene. By analogy with 3-bromothiophene,[20] this compound can be considered as an intermediate for electrophilic or nucleophilic (through lithium–bromine exchange) substitution in the preparation of a great variety of 3,4′-disubstituted-2,2′-bithiophenes. With our background in the field of this type of organic materials, we used this derivative as an intermediate to obtain 3,4′-bis(alkylsulfanyl)-2,2′-bithiophenes *via* bromo substitution. The described method suggests an alternative route to the coupling reaction[16] for the functionalization of the 3,4′ positions of 2,2′-bithiophene.

Results and discussion

Synthesis

3-Bromo-2-(trimethylstannyl)thiophene **2** was obtained from 3-bromothiophene **1**[21] in 75% yield (Scheme 1). Reaction of substrate **1** with Br_2 gave 2,3-dibromothiophene **3**.[21] 3,5-Dibromo-2-(trimethylsilyl)thiophene **4** was prepared by lithiation of dibromide **3**, followed by treatment with trimethylsilyl chloride (TMSCl).[22,23] When both reagents were added in one portion, the palladium-catalysed cross-coupling of compounds **2** and **4** gave a complex mixture containing only a small percentage of 3,4′-dibromo-5′-(trimethylsilyl)-2,2′-bithiophene **5**. Optimal results in the formation of target molecule **5** were obtained by slow addition of dibromide **4** into a solution of the stannane **2**.



Scheme 1 *Reagents, conditions and yields* (*in parentheses*): i, LDA, THF, −78 °C; ii, Me_3SnCl (75%); iii, Br_2, HOAc, overnight (83%); iv, LDA, THF, −70 °C; v, Me_3SiCl (73%); vi, $Pd(PPh_3)_4$, toluene, 105 °C (40%); vii, aq. HI, benzene, room temp., 36 h (93%); viii, BuLi, THF, −75 °C; ix, Me_2S_2 (47% **7**) or Bu_2S_2 (55% **8**)

3,4′-Dibromo-5′-(trimethylsilyl)-2,2′-bithiophene **5** was obtained in the presence of the unchanged reagents. The crude product was purified by chromatography and afforded pure compound **5** in 40% yield.

3,4′-Dibromo-2,2′-bithiophene **6** was prepared in high yield (93%) by a desilylation process with hydroiodic acid.

Lithiation of compound **6** followed by reaction with the appropriate dialkyl disulfide should produce the corresponding alkylsulfanyl derivative. However, when the butyllithium solution was added dropwise to a cold solution of compound **6**, transmetallation occurs.[18,24] On the other hand, dropwise addition of a solution of dibromide **6** to the cold butyllithium solution avoids the transmetallation process. The 3,4′-dilithium derivative was quenched with a 20% excess of dialkyl disulfide at relatively high temperature (−20 °C). Under these conditions maximum yields are obtained. This procedure was applied to generate 3,4′-bis(methylsulfanyl)- **7** and 3,4′-bis(butylsulfanyl)-2,2′-bithiophene **8**, in 47 and 55% yield, respectively.

The Ni- or Pd-catalysed cross-coupling reactions of organotin reagents with organic halides provide a general route to carbon–carbon bond formation.[25,26] Pd complexes are reported to be more compatible with various functional groups and more chemo- and regio-selective than are the corresponding Ni complexes.[25]

Nickel-catalysed coupling of Grignard reagents, previously applied in our group for the synthesis of 3,4′-bis(alkylsulfanyl)-2,2′-bithiophenes,[16] could, in theory, be a way of synthesizing 3,4′-dibromo-2,2′-bithiophene from 2,3-dibromothiophene and 2,4-dibromothiophene. Unfortunately, the nickel-catalysed coupling of the Grignard reagent of 2,3-dibromothiophene with 2,4-dibromothiophene in Et$_2$O gave a mixture of 2,4-dibromothiophene and 3-bromothiophene (arising from hydrolysis of the Grignard reagent).

Palladium-catalysed coupling of 2,4-dibromothiophene with 3-bromo-2-(trimethylstannyl)thiophene in toluene at 105 °C yielded a mixture of the three possible dibromo-2,2′-bithiophenes (3,4′-, 4,4′- and 3,3′-: 83; 7.5; 4.5%, respectively) and 2,4-dibromothiophene (5%) (total: 64% conversion). Complete purification of the product gave the 3,4′-derivative (containing 1–2% of the 4,4′-isomer) (25% yield). However, the results could not be reproduced during several attempts to optimize the reaction conditions; this might be due to impurities.

On account of its β-carbocation stabilization and its easy elimination, the trimethylsilyl group[27–29] was introduced in order to enhance the reactivity of the 2,4-dibromo derivative in the α-position and to achieve a higher regioselectivity in the Stille-type coupling. Since the trimethylsilyl group can undergo electrophilic substitution with the dialkyl disulfide,[28] 3,4′-dibromo-5′-(trimethylsilyl)-2,2′-bithiophene has to be desilylated before the final steps in the synthetic pathway. By comparison with the cross-coupling reaction[16] this synthetic route affords compounds **7** and **8** of higher purity and avoids the presence of poorly isolable isomeric by-products.

X-Ray molecular structure

The molecular structure of dibromide **6** is presented in Fig. 1, along with bond distances and ring bond angles (Table 1). The unit-cell contains one crystallographically independent molecule, which exhibits a slightly bent *anti* conformation, characterized by an S(1a)–C(2a)–C(2b)–S(1b) torsion angle of 175.0(3)°. It is of interest to note that all but one of the symmetrically disubstituted 2,2′-dithienyls of known structure have a crystallographic inversion centre at the mid-point of the inter-ring bond, which makes the molecules exactly coplanar; the only exception of which we are aware is 3,3′-bis(hydroxyethyl)-2,2′-bithiophene, which exhibits 2-fold symmetry and a strongly twisted *anti* conformation.[30]

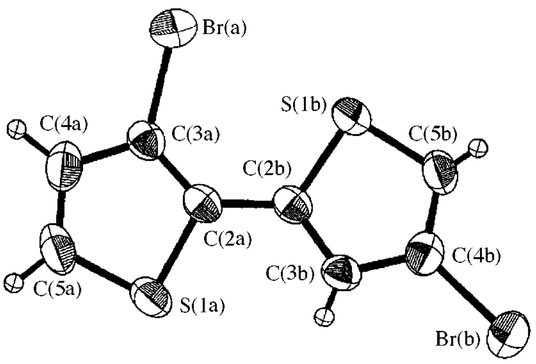


Fig. 1 The molecular structure of 3,4′-dibromo-2,2′-bithiophene **6** showing the atom-numbering scheme and thermal motion ellipsoids (40%). Ring bond lengths and selected bond angles are reported in Table 1.

Table 1 Ring bond lengths (Å) and selected bond angles (°) of compound **6**

Br(a)–C(3a)	1.878	Br(b)–C(4b)	1.896
S(1a)–C(2a)	1.734	S(1b)–C(2b)	1.729
C(2a)–C(3a)	1.363	C(2b)–C(3b)	1.362
C(3a)–C(4a)	1.413	C(3b)–C(4b)	1.386
C(4a)–C(5a)	1.338	C(4b)–C(5b)	1.341
S(1a)–C(5a)	1.713	S(1b)–C(5b)	1.708
C(2a)–C(2b)	1.455		
C(5a)–S(1a)–C(2a)	91.8	C(5b)–S(1b)–C(2b)	91.8
S(1a)–C(2a)–C(3a)	109.4	S(1b)–C(2b)–C(3b)	110.1
C(2a)–C(3a)–C(4a)	114.4	C(2b)–C(3b)–C(4b)	113.0
C(3a)–C(4a)–C(5a)	111.9	C(3b)–C(4b)–C(5b)	114.2
C(4a)–C(5a)–S(1a)	112.5	C(4b)–C(5b)–S(1b)	111.0

Bond distances and angles compare well with those observed in other oligothiophene derivatives.[30–32] We observed widening of the intra-ring bond angles at the substituted C atoms, they being about 2–3° wider than those reported for methyl-substituted thienyl carbons.[31] This effect has also been observed in the 5,5′-[33] and 4,4′-dibromo[34] analogues.

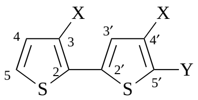
The compound exhibits a typical herringbone packing motif, commonly reported for crystals of planar or quasi-planar oligothiophenes.[35] The molecules are stacked in parallel layers along the shortest *b* cell axis at an interplanar distance of 3.633 Å. The angle between mean planes of glide-plane-related molecules (herringbone angle) is 52.0°, significantly smaller than those reported for planar thiophene oligomers. It is of interest to note that the molecular packing contains some very short van der Waals contacts involving Br, S and C atoms. The shortest ones [Br(1)···C(5b) = 3.542(6) Å; Br(1)···Br(2) = 3.580(1) Å; S(1a)···C(3b) = 3.551(5) Å; Br(1)···S(1b) = 3.677(2) Å] occur between glide-plane-related molecules, but not between the stacked layers. It may also be pointed out that the lack of short van der Waals interactions appears to be a common feature of the molecular packing of thiophene oligomers.[31]

NMR Structural assignment

^{1}H and ^{13}C NMR chemical shifts of derivatives **5**, **6** and **8** are reported in Tables 2 and 3. In derivatives **5**, **6** and **8**, the two types of thiophene ring are easily recognized by the proton–proton coupling constants (5.3 and 1.3 Hz for 2,3- and 2,4-disubstituted thiophenes). The assignment of the H,C directly and long-range-bonded pairs was achieved through inverse-detected heteronuclear multiple-quantum coherence (HMQC)[36] and inverse-detected heteronuclear multiple-bond correlation (HMBC)[37] experiments.

The assignment of the C(α)–H(α) and C(β)–H(β) pairs was based on the different value of the corresponding ^1J(C,H) values (~190 and 170 Hz, respectively).[38]

In derivative **8**, two different types of butylsulfanyl chains are present. By exploiting the presence of a long-range coupling constant between the protons of S–CH$_2$(α) and the thiophene carbon bearing the substituent we performed an HMBC



5 X = Br, Y = SiMe$_3$
6 X = Br, Y = H

Table 2 ^{1}H and ^{13}C chemical shifts (δ, ppm) of compounds **5** and **6**

Compound		C-2	C-3	4-H/C-4	5-H/C-5	C-2′	3′-H/C-3′	C-4′	5′-H/C-5′	Si(CH$_3$)$_3$
5	δ_H			7.02	7.21		7.41			0.43
5	δ_C	130.9	108.5	131.9	125.0	140.0	131.3	117.3	135.5	−0.78
6	δ_H			7.02	7.22		7.32		7.24	
6	δ_C	130.8	108.8	132.0	125.1	135.7	128.8	110.2	123.2	

Table 3 ^{1}H and ^{13}C chemical shifts (δ, ppm) of compound **8**

	C-2	C-3	4-H/C-4	5-H/C-5		C-2′	3′-H/C-3′	C-4′	5′-H/C-5′
δ_H			7.02	7.18			7.27		7.08
δ_C	134.93	128.55	132.01	123.45		136.2	128.38	132.36	123.37
3-chain	CH$_2$(α)	CH$_2$(β)	CH$_2$(γ)	CH$_3$	4′-chain	CH$_2$(α)	CH$_2$(β)	CH$_2$(γ)	CH$_3$
δ_H	2.84	1.57	1.41	0.88		2.88	1.64	1.45	0.93
δ_C	35.74	31.61	21.82	13.62		34.96	31.47	21.82	13.58

experiment (modulation of the coupling constant of 5 Hz) and assigned each chain to the proper ring. The ^{1}H and ^{13}C parameters of compound **8** can be used for the regiochemical characterization of related oligomers and polymers. The 3′-H signal in the *head-to-tail* dimer is strongly deshielded with respect to the corresponding *tail-to-tail* and *head-to-head* dimers.[18] Similar behaviour has already been observed for 3,4′-bis(methylsulfanyl)-2,2′-bithiophene.[16] The C-2, C-2′, C-3, C-3′ and the S–CH$_2$(α) signals show a regiochemical dependence. A comparison with the NMR data reported for the *head-to-head* and the *tail-to-tail* dimers,[16,18] reveals that C-2 and C-2′, in the *head-to-tail* derivative, are intermediate with respect to those of the two symmetric dimers, C-3 in the *head-to-tail* dimer is shielded with respect to C-3 in the *head-to-head* one, and C-3′ is deshielded with respect to C-3′ in the *tail-to-tail* one.

The dimer **8** represents a model compound for poly-[3-(butylsulfanyl)thiophene],[39] taking into account the regiochemical dependence of the chemical shifts of 3′-H, C-2 and C-2′, -3 and -3′.

Experimental

All air- or moisture-sensitive reactions were performed under prepurified nitrogen or argon, using dry glassware. Tetrahydrofuran (THF) was distilled from sodium diphenyl ketyl prior to use. Toluene was distilled from sodium and diisopropylamine from KOH. Other reagents were purchased from Aldrich Chemical Co. and used as received.

Mps (Büchi apparatus) and bps are uncorrected. Refractive indexes were determined on an Abbe refractometer (Atago). IR spectra were obtained in CCl$_4$ solutions using a Philips PU 9700 Series IR spectrometer and are reported in ν_{max}-values as cm^{-1}. All UV–visible spectra were taken on 1×10^{-4} M solutions in CHCl$_3$ (spectroscopic grade) using a Varian-Cary 3 spectrophotometer. The purity of all compounds was monitored by HPLC (HP 1090 Liquid Chromatograph; UV detector; Merck prepared column RT 250-4) and TLC (Merck TLC plates 10 × 20 cm, silica gel 60 F$_{254}$). Preparative column chromatography (PCC) was performed using glass columns of different size, packed with silica gel RS, grain size 0.05–0.20 mm (Carlo Erba). Light petroleum refers to the fraction with distillation range 30–50 °C.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 WB at 400.13 and 100.61 MHz, respectively, on 0.1 mol dm^{-3} solutions in CDCl$_3$. Chemical shifts, in ppm, refer to internal Me$_4$Si. Coupling constants, *J*, are given in Hz.

HMQC[36] parameters for aromatic and aliphatic region: spectral width ($f2$) = 1–4 ppm, 2048 complex points; spectral width ($f1$) = 50–30 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.

HMBC[37] parameters: spectral width ($f2$) = 1–4 ppm, spectral width ($f1$) = 150 ppm, 256 $t1$ increments with 64 scans per $t1$ value; relaxation delay = 0.5 s and delay for long-range coupling constant evolution = 100 ms. Zero filling in $f1$ and $f2$, sine function in $f1$ were applied before Fourier transformation.

3-Bromo-2-(trimethylstannyl)thiophene 2

To a solution of butyllithium (1.6 M; 85.3 ml, 0.14 mol) in dry THF (85.0 ml) at −70 °C was added a solution of diisopropylamine (16.07 g, 0.16 mol) in THF (15.0 ml). The temperature was raised to −60 °C for 10 min and the mixture was then recooled to −70 °C before a solution of compound **1** (18.48 g, 0.11 mol) in dry THF (5.0 ml) was rapidly added to the reaction mixture. The mixture was stirred for 30 min at this temperature, then a solution of trimethyltin chloride (36.15 g, 0.18 mol) dissolved in dry THF (37.0 ml) was added dropwise, the temperature being maintained between −40 and −30 °C. The mixture was allowed to warm to ambient temperature overnight, was then poured onto ice, the phases were separated, and the aqueous layer was extracted with diethyl ether (200 ml). The combined organic phases were dried over MgSO$_4$ and evaporated. Distillation of the residue under reduced pressure gave compound **2** (27.86 g, 75%), bp 77–78 °C/0.9 mmHg; n_D^{20} 1.5799; λ_{max}/nm 249 (ε/dm^3 mol^{-1} cm^{-1} 6800); ν_{max}/cm^{-1} 3100, 3080, 2980 and 1070; δ_H(400 MHz; CDCl$_3$) 0.47 (9 H, s, 3 × CH$_3$), 7.13 (1 H, d, *J* 4.8) and 7.50 (1 H, d, *J* 4.8).

2,3-Dibromothiophene 3

The procedure of Gronowitz *et al.*[21a] gave compound **3** (83%), bp 88–90 °C/6.5 mmHg; n_D^{21} 1.6306; λ_{max}/nm 240 (ε/dm^3 mol^{-1} cm^{-1} 8300); ν_{max}/cm^{-1} 3100, 3080 and 1080; δ_H(400 MHz; CDCl$_3$) 6.92 (1 H, d, *J* 5.7) and 7.26 (1 H, d, *J* 5.7).

3,5-Dibromo-2-(trimethylsilyl)thiophene 4

To a solution of butyllithium (1.5 M; 5 ml, 7.4 mmol) in dry THF (22 ml) at −70 °C was added a solution of diisopropyl amine (0.81 g, 8.1 mmol) in dry THF (8 ml). The temperature was raised to −60 °C for 10 min. To the reaction mixture, cooled to −78 °C, was added rapidly a solution of compound **3** (1.5 g, 6.2 mmol) in dry THF (8 ml), and stirring was continued for 30 min at the same temperature. The intermediate thus formed was trapped by slow addition of a solution of TMSCl (0.67 g, 6.2 mmol) in dry THF (4 ml), and stirring was continued for 30 min at −80 °C. The mixture was then poured into 1 M aq. HCl (40 ml), extracted with Et_2O (80 ml) and the organic extract was washed with water (15 ml) and dried over $MgSO_4$. The solvent was removed, and the residue was distilled under reduced pressure to give compound **4** (1.42 g, 73%), bp 88–89 °C/1.2 mmHg; n_D^{20} 1.5684; λ_{max}/nm 247 (ε/dm^3 mol^{-1} cm^{-1} 9100); ν_{max}/cm^{-1} 3100, 2950 and 1245; δ_H(400 MHz; $CDCl_3$) 0.39 (9 H, s, 3 × CH_3) and 7.03 (1 H, s, 4-H).

3,4′-Dibromo-5′-(trimethylsilyl)-2,2′-bithiophene 5

A solution of compound **4** (1.44 g, 4.60 mmol) in dry toluene (10 ml) was added dropwise (4 h) to a stirred solution of stannane **2** (1.50 g, 4.60 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.42 g, 0.36 mmol) in dry toluene (4 ml) at 105 °C. The reaction mixture was stirred for 3 days at this temperature. After cooling, the reaction mixture was transferred into a separatory funnel, diluted with Et_2O (40 ml) and washed successively with saturated aq. $NaHCO_3$ (15 ml) and water (15 ml). The organic phase was dried over $MgSO_4$ and evaporated. The dark oily product was chromatographed (SiO_2; light petroleum) to give compound **5** (0.72 g, 40%); δ_H(400 MHz; $CDCl_3$) 7.02 (1 H, d, $J_{4,5}$ 5.5, 4-H), 7.21 (1 H, d, $J_{4,5}$ 5.5, 5-H) and 7.41 (1 H, s, 3′-H).

3,4′-Dibromo-2,2′-bithiophene 6

A solution of hydroiodic acid (10.4 M; 0.93 ml, 9.7 mmol) and water (0.17 ml) were added dropwise to a stirred solution of compound **5** (1.70 g, 4.3 mmol) in benzene (102.5 ml) at room temperature. The mixture was stirred for 15 h at room temperature, then a second portion of hydroiodic acid (10.4 M; 0.93 ml, 9.7 mmol) was added and stirring was continued at ambient temperature for 20 h. The mixture was poured into water and extracted with Et_2O (4 × 10 ml). The combined organic extracts were washed successively with 1 M aq. NaOH (15 ml) and brine (15 ml) and dried over $MgSO_4$. The volatile materials were removed under reduced pressure and the residue was purified by column chromatography (SiO_2; light petroleum) to give compound **6** (1.29 g, 93%) as a solid, mp 49–51 °C. Crystals suitable for X-ray diffraction were obtained by recrystallization from propan-2-ol; λ_{max}/nm 307 (ε/dm^3 mol^{-1} cm^{-1} 11 000); ν_{max}/cm^{-1} 3105, 3090 and 1145; δ_H(400 MHz; $CDCl_3$) 7.02 (1 H, d, $J_{4,5}$ 5.4, 4-H), 7.22 (1 H, d, $J_{4,5}$ 5.4, 5-H), 7.24 (1 H, d, $J_{3',5'}$ 1.4, 5′-H) and 7.31 (1 H, d, $J_{3',5'}$ 1.4, 3′-H).

3,4′-Bis(methylsulfanyl)-2,2′-bithiophene 7

Butyllithium (1.4 M; 4.8 ml, 6.8 mmol) was added to THF (5 ml) at −70 °C. A solution of compound **6** (1.00 g, 3.1 mmol) in THF (3 ml) was added dropwise (5 min) to this stirred solution at −75 °C and the reaction mixture was stirred for 40 min at this temperature. Then dimethyl disulfide (0.69 g, 7.4 mmol) was added in one portion, and the temperature was allowed to rise to −20 °C. This temperature was maintained for 40 min before water (20 ml) was added. The mixture was extracted with Et_2O (4 × 10 ml). The combined organic extracts were washed successively with 10% aq. NaOH (15 ml) and water (15 ml) and dried over $MgSO_4$. The volatile materials were carefully removed under reduced pressure and the oil was purified[16] by chromatography (SiO_2; light petroleum) to give compound **7** (0.58 g, 47%), λ_{max}/nm 328 (ε/dm^3 mol^{-1} cm^{-1} 8300); ν_{max}/cm^{-1} 3100, 3080, 2980, 2920 and 1180; δ_H(400 MHz; $CDCl_3$) 2.46 (3 H, s, CH_3), 2.50 (3 H, s, CH_3), 6.96 (1 H, d, $J_{3',5'}$ 1.5, 5′-H), 7.03 (1 H, d, $J_{4,5}$ 5.3, 4-H), 7.21 (1 H, d, $J_{4,5}$ 5.3, 5-H) and 7.23 (1 H, d, $J_{3',5'}$ 1.5, 3′-H).

3,4′-Bis(butylsulfanyl)-2,2′-bithiophene 8

Using the procedure as described above, compound **8** was obtained from dibromide **6** as an oil (55%). The product was purified by chromatography (SiO_2; light petroleum): n_D^{20} 1.6212; λ_{max}/nm 330 (ε/dm^3 mol^{-1} cm^{-1} 9800); ν_{max}/cm^{-1} 3100, 3080, 2940, 2920 and 1180; δ_H(400 MHz; $CDCl_3$) 0.88 (3 H, t, CH_3), 0.93 (3 H, t, CH_3), 1.54 [8 H, m, $CH_2(\beta)$-$CH_2(\gamma)$], 2.84 [2 H, t, $CH_2(\alpha)$], 2.88 [2 H, t, $CH_2(\alpha)$], 7.02 (1 H, d, $J_{4,5}$ 5.3, 4-H), 7.08 (1 H, d, $J_{3',5'}$ 1.4, 5′-H), 7.18 (1 H, d, $J_{4,5}$ 5.3, 5-H) and 7.27 (1 H, d, $J_{3',5'}$ 1.4, 3′-H).

Crystal data for compound 6

$C_8H_4Br_2S_2$, $M = 324.05$. Monoclinic, $a = 12.009(1)$, $b = 4.0423(8)$, $c = 20.384(3)$ Å, $\beta = 102.768(9)°$, $V = 965.1(2)$ Å^3 (by least-squares refinement on diffractometer angles for 30 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/n$, $Z = 4$, $D_x = 2.230$ g cm^{-3}, $F(000) = 616$. Plates, crystal dimensions 0.33 × 0.20 × 0.08 mm, μ(Mo-Kα) = 87.69 cm^{-1}.

Data collection and processing

Siemens P4RA-M18X diffractometer, room temperature, graphite-monochromated Mo-Kα radiation (45 kV, 50 mA), $\omega/2\theta$ scan mode, 3690 reflections measured ($2.05 \leqslant \theta \leqslant 27.97°$, $-15 \leqslant h \leqslant 15$, $-1 \leqslant k \leqslant 5$, $-1 \leqslant l \leqslant 26$), of which 1449 with $I > 2\sigma(I)$ were unique [merging $R = 0.017$ after absorption correction based on ψ scans] and were retained for structure analysis. No crystal decay was observed during collection.

Structural analysis and refinement

Direct methods (SHELXS86)[40] (all non-H-atoms) followed by full-matrix least squares (SHELXL93).[41] Non-H-atoms anisotropic and H-atoms (located in ΔF maps) isotropic. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0528\ P)^2 + 0.9379\ P]$, with $P = (F_o^2 + 2\ F_c^2)/3$, gave satisfactory agreement analyses. Final R and $wR(F^2)$ were 0.034 and 0.089 for 125 parameters, $S = 1.09$. Maximum and minimum features in ΔF synthesis were 0.67 and −0.47 e Å^{-3}, respectively. Scattering factors were from SHELXL93.[41] Most of the calculations were carried out on a Digital Alpha 3000/800 computer. Tables of final fractional coordinates and full lists of bond distances and bond angles for compound **6** have been deposited at the Cambridge Crystallographic Data Centre.†

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References

1 J. Roncali, *Chem. Rev.*, 1992, **92**, 711.
2 M. R. Andersson, M. Berggren, O. Inganäs, G. Gustafsson, J. C. Gustafsson-Carlberg, D. Selse, T. Hjertberg and O. Wennerström, *Macromolecules*, 1995, **28**, 7525.
3 N. Noma, T. Tsuzuki and Y. Shirota, *Adv. Mater.*, 1995, **7**, 647.
4 G. Horowitz, F. Garnier, A. Yassar, R. Hajlaoui and F. Kouki, *Adv. Mater.*, 1996, **8**, 52.
5 H. Higuchi, H. Koyama, H. Yokota and J. Ojima, *Tetrahedron Lett.*, 1996, **37**, 1617; C. Branger, M. Lequan, R. M. Lequan, M. Barzoukas and A. Fort, *J. Mater. Chem.*, 1996, **6**, 555.
6 Z. Gao, K. S. Siow and H. S. O. Chan, *Synth. Met.*, 1995, **75**, 5.
7 R. Rossi, A. Carpita, M. Ciofalo and J. L. Houben, *Gazz. Chim. Ital.*, 1990, **120**, 793; A. MacEachern, C. Soucy, L. C. Leitch, J. T. Arnason and P. Morand, *Tetrahedron*, 1988, **44**, 2403.
8 P. Bäuerle, G. Götz, A. Synowczyk and J. Heinze, *Liebigs Ann. Chem.*, 1996, 279.

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† For details of the CCDC deposition scheme, see ‘Instructions for Authors’, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/114.

9 L. L. Miller and Y. Yu, *J. Org. Chem.*, 1995, **60**, 6813.

10 P. Bäuerle, F. Pfau, H. Schlupp, F. Würthner, K.-U. Gaudl, M. Balparda Caro and P. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1993, 489.

11 G. Zotti, M. C. Gallazzi, G. Zerbi and S. V. Meille, *Synth. Met.*, 1995, **73**, 217; F. Demanze, A. Yassar and F. Garnier, *Synth. Met.*, 1996, **76**, 269; P. Bäuerle, G. Gotz, U. Segelbacher, D. Huttenlocher and M. Mehring, *Synth. Met.*, 1993, **55–57**, 4768; G. Horowitz, P. Delannoy, H. Bouchriha, F. Deloffre, J.-L. Fave, F. Garnier, R. Hajlaoui, M. Heyman, F. Kouki, P. Valat, V. Wintgens and A. Yassar, *Adv. Mater.*, 1994, **6**, 752.

12 P. Bäuerle, T. Fisher, B. Bidlingmeier, A. Stabel and J. P. Rabe, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 303; H. Higuchi, T. Nakayama, H. Koyama, J. Ojima, T. Wada and H. Sasabe, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2363; J. M. Tour and R. Wu, *Macromolecules*, 1992, **25**, 1901.

13 T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233; M. D. McClain, D. A. Whittington, D. J. Mitchell and M. D. Curtis, *J. Am. Chem. Soc.*, 1995, **117**, 3887; R. D. McCullough, S. P. Williams, S. Tristam-Nagle, M. Jayaraman, P. C. Ewbank and L. Miller, *Synth. Met.*, 1995, **69**, 279; Y. Miyazaki and T. Yamamoto, *Synth. Met.*, 1994, **64**, 69.

14 M. J. Marsella, P. J. Carroll and T. M. Swager, *J. Am. Chem. Soc.*, 1994, **116**, 9347.

15 C. Arbizzani, G. Barbarella, A. Bongini, M. Mastragostino and M. Zambianchi, *Synth. Met.*, 1992, **52**, 329.

16 U. Folli, D. Iarossi, M. Montorsi, A. Mucci and L. Schenetti, *J. Chem. Soc., Perkin Trans. 1*, 1995, 537.

17 K. Faïd, R. Cloutier and M. Leclerc, *Macromolecules*, 1993, **26**, 2501.

18 U. Folli, F. Goldoni, D. Iarossi, A. Mucci and L. Schenetti, *J. Chem. Res.* (*S*), 1996, 69.

19 E. Khor, S. C. Ng, H. C. Li and S. Chai, *Heterocycles*, 1991, **32**, 1805.

20 E. Schulz, K. Fahmi and M. Lemaire, *Acros Organics Acta*, 1995, **1**, 10.

21 (*a*) S. Gronowitz, Y. Zhang and A.-B. Hörnfeldt, *Acta Chem. Scand.*, 1992, **46**, 654; (*b*) M. J. Naujan, V. Kannappan and R. Z. Ganesan, *Phys. Chem.*, 1981, **127**, 13.

22 F. Sauter, H. Fröhlich and W. Kalt, *Synthesis*, 1989, 771.

23 H. Fröhlich and W. Kalt, *J. Org. Chem.*, 1990, **55**, 2993.

24 L. Brandsma and H. D. Verkruijsse, *Preparative Polar Organometallic Chemistry*, Springer-Verlag, Berlin, 1987, vol. 1, pp. 123 and 160.

25 E. Negishi, T. Takahashi and A. O. King, *Org. Synth.*, 1988, **66**, 67 and references therein.

26 J. K. Stille, *Pure Appl. Chem.*, 1985, **57**, 1771.

27 E. W. Colvin, *Chem. Soc. Rev.*, 1978, **7**, 15.

28 T. H. Chan and I. Fleming, *Synthesis*, 1979, 761.

29 D. Habich and F. Effenberger, *Synthesis*, 1979, 841.

30 G. Barbarella, M. Zambianchi, A. Bongini and L. Antolini, *J. Org. Chem.*, 1996, **61**, 4708.

31 G. Barbarella, M. Zambianchi, A. Bongini and L. Antolini, *Adv. Mater.*, 1993, **5**, 834.

32 S. Hotta and K. Waragai, *Adv. Mater.*, 1993, **5**, 896.

33 G. J. Pyrka, Q. Fernando, M. B. Inoue, M. Inoue and E. Velazquez, *Acta Crystallogr., Sect. C*, 1988, **44**, 562.

34 L. Antolini, unpublished results.

35 W. Porzio, S. Destri, M. Mascherpa and S. Brükner, *Acta Polym.*, 1993, **44**, 266.

36 A. Bax, R. H. Griffey and B. L. Hawkins, *J. Magn. Reson.*, 1983**, 55**, 301.

37 A. Bax and M. F. Summers, *J. Am. Chem. Soc.*, 1986, **108**, 2093.

38 F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*, Heyden, Bristol, 1978.

39 F. Goldoni, D. Iarossi, A. Mucci, L. Schenetti and M. Zambianchi, *J. Mater. Chem.*, 1997, **7**, 593.

40 G. M. Sheldrick, SHELXS86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

41 G. M. Sheldrick, SHELXL93: Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.

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