Synthesis, structural characterization and electronic properties of 3,3''''-bis(butylsulfanyl)-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene

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Synthesis and NMR, UV–VIS, electrochemical, mobility and X-ray characterization of 3,3''''-bis(butylsulfanyl)-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene are reported. This compound combines the promising properties already observed for 3,3''',3''''-tris(butylsulfanyl)-2,2':5',2'':5:,2''':5''',2'''':5'''',2'''''-sexithiophene with a physical state more suitable for its use in field-effect transistors. In particular, the stability of the oxidized forms, the close packing in the solid state together with the mobility and on/off ratio observed make this sexithiophene of potential interest for organic semiconductors.

Introduction

Oligothiophenes with defined structure are gaining increasing attention as a new class of organic π-electron systems.[1] Among them, α-sexithiophene (α-6T) is a very promising material for field-effect transistors.[2,3]

Optical and electrical properties as well as the processability of these materials can be modulated by adding substituents on the oligothiophene backbone. Recently, interesting methylsulfanyl sexithiophenes with UV maximum absorption wavelengths slightly lower than those of sexithiophene have been reported.[4]

In a recent paper[5] we reported on a tris(butylsulfanyl)sexithiophene showing interesting optical properties and forming a stable radical cation and dication; unfortunately, its physical state does not favor its use as material for a field-effect transistor.

Here, we report on the synthesis and characterization of a new bis(butylsulfanyl)sexithiophene which combines the positive characteristics of the former tris(butylsulfanyl)sexithiophene, mainly due to the substituents in the inner β-position of the two terminal rings, with a favorable physical state.

Results and discussion

Synthesis

There are several approaches for the synthesis of oligothiophenes[1] and among them, the transition metal-catalysed couplings of α-metalated thiophenes with α-halothiophenes are the more useful and popular.[6] The nickel- or palladium-catalyzed cross-coupling reactions of Grignard or organotin reagents with organic halides represent the more direct procedure for the formation of C–C bonds.[7,8] The Kumada reaction[9] and the "Stille" type reaction[10] have been frequently used in the synthesis of oligothiophenes and substituted oligothiophenes.[11–14] In particular, the coupling of the Grignard of 2-bromo-3-alkylthiophene with 5,5'-dibromo-2,2'-bithiophene afforded a quaterthiophene in 56% yield,[11] whereas it is reported by Bäuerle *et al.* that the Kumada coupling between 2-bromo-3-(methylsulfanyl)thiophene and its Grignard reagent[15] failed. On the other hand, the Pd-catalyzed cross-coupling between 2,5-dibromothiophene and 2-(tributylstannyl)thiophene[16] afforded 2,2':5',2''-terthiophene in 59% yield and the coupling of 5,5'-dibromo-3,3'-bis(methylsulfanyl)-2,2'-bithiophene with 2 equivalents of 3-(methylsulfanyl)-2-(trimethylstannyl)thiophene afforded the corresponding quaterthiophene in 40% yield.

The attempt to couple 5,5'-dibromo-2,2'-bithiophene **1** with the Grignard reagent of 2-bromo-3-(butylsulfanyl)thiophene in the presence of NiCl₂(dppp) failed and 3-(butylsulfanyl)thiophene was completely recovered, similarly to the case in ref. 15.

When the Stille[10] type reaction was applied to **1** and **2** in a 1:2 molar ratio in the presence of PdCl₂(PPh₃)₂ as catalyst, the sexithiophene **3** was obtained as the main product (45%) together with 3-(butylsulfanyl)-5''-bromo-2,2':5',2''-terthiophene **4** (17%), the expected 3,3'''-bis(butylsulfanyl)-2,2':5',2'':5'',2'''-quaterthiophene **5** (21%) and 3,3'-bis(butylsulfanyl)-2,2'-bithiophene **6** (17%) (Scheme 1).

The crude material obtained did not contain the starting materials as shown by TLC. From this mixture we were able to isolate pure **3** as a red solid by successive column chromatography. The components were eluted in the following order: bromoderivative **4**, dimer **6**, tetramer **5** and sexithiophene **3**. All the compounds were identified by ¹H NMR spectroscopy and dimer **6** and tetramer **5** are both identical with the authentic samples.[17,18] Sexithiophene **3** and bromoderivative **4** were identified and completely characterized by ¹H and ¹³C NMR spectroscopy. Single crystals suitable for X-ray structure determination were obtained by precipitation of **3** with *n*-pentane from benzene solution.

The obtainment of the hexamer **3** could be due to scrambling processes which exchange the functionalities between the reagents. These processes are possible in metal-catalyzed cross-coupling between an organometallic and a halogenoderivative and are catalyzed by the catalyst through the reversibility of some steps of the catalytic cycle.[19,20]

The proposed mechanism of the reaction is depicted in Scheme 2. The key step of the reaction is the formation of monobromo derivative **4**, which is also found among the reaction products. The presence of homo-coupling derivatives **6** and **3** can be explained on the basis of the formation of more reactive intermediates, like **7** and **8** or their Pd-activated forms, generated by the exchanging of the functionalities between **4** and **2**. These two intermediates probably represent the preferred

path to the obtainment of **5**, even though the coupling of **2** with **4** cannot be excluded. Similar scrambling processes (catalyzed by the catalyst through the reversibility of some steps of the catalytic cycle) are at the origin of the homo-coupling products usually present in metal-catalyzed cross-coupling reactions between an organometallic and a halogenoderivative.[19,20]

NMR structural assignment

The ^{1}H NMR spectra of **3** and **4** display in the aromatic region
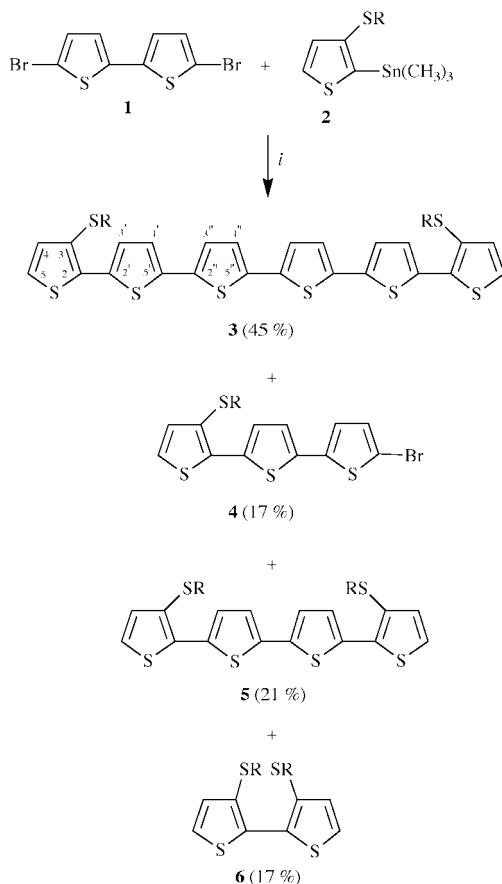
Scheme 1 *Reagents and conditions*: i, [PdCl$_2$(PPh$_3$)$_2$] cat., toluene, 20 h reflux; R=CH$_2$(α)CH$_2$(β)CH$_2$(γ)CH$_3$.
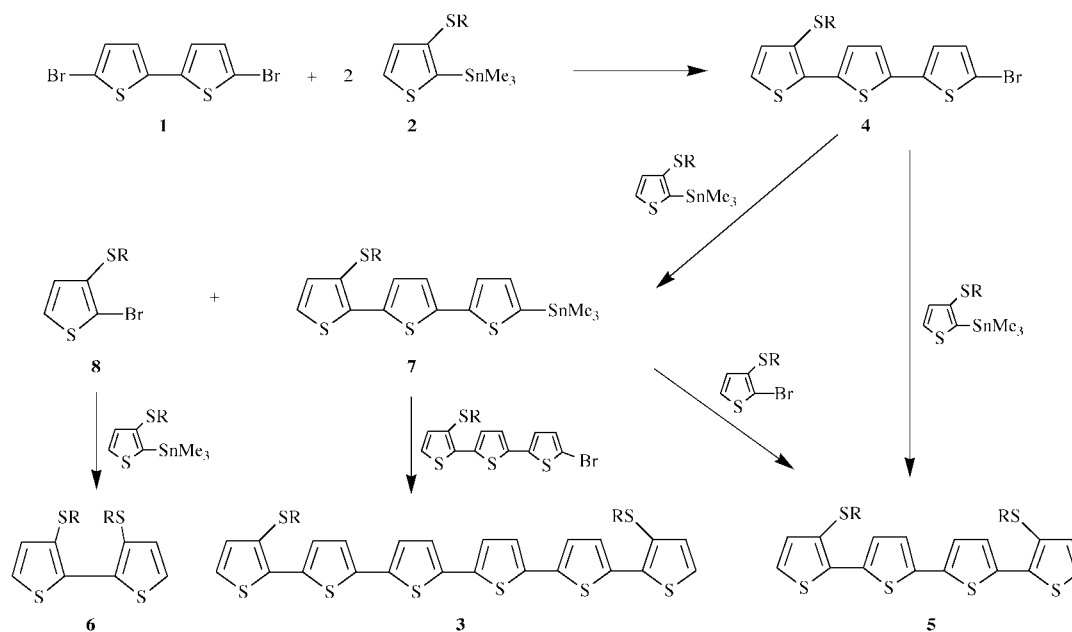
two doublets characterized by a ^3J(H-α,H-β) = 5.2–5.3 Hz (H-4,H-5) coupling and four doublets characterized by a ^3J(H-β,H-β′) = 3.7–3.9 Hz (H-3′,H-4′,H-3″,H-4″) coupling. Only one type of aliphatic chain is found in the proton NMR spectra and CH$_2$(α), CH$_2$(β), CH$_2$(γ) and CH$_3$ signals are readily assigned. Both proton spectra are compatible with the structures of **3** and **4**.

Although the two {^{1}H}-^{13}C NMR spectra consist of 16 resonances (12 in the aromatic and 4 in the aliphatic region, respectively), the chemical shifts of quaternary carbons allow us to distinguish between **3** and **4**. In fact, the presence of a carbon signal at around 110 ppm denotes the presence of a bromine substituent.

The compounds **3** and **4** were characterized through ^{1}H,^{13}C NMR inverse-detection techniques, based on heteronuclear multiple-quantum (HMQC)[21] and multiple-bond (HMBC)[22] coherence 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 measured ^1J(H,C).[23] With the HMBC experiments relayed carbons were assigned on the basis of the values of ^nJ(H,C).[23] These last experiments are of fundamental importance when inter-ring correlations are to be determined. They are based on the existence of inter-ring ^3J(H,C) coupling constants (~3 Hz) and permit derivation of the the whole proton and carbon framework and confirm that compound **3** is a symmetrical sexithiophene and **4** is a brominated trimer. A long-range correlation between CH$_2$(α) protons and the thiophene carbon bearing the butylsulfanyl chains was also detected. The ^{1}H and ^{13}C NMR data are reported in Table 1.

Solution and solid state UV–VIS and photoluminescence spectra

UV–VIS and photoluminescence (PL) spectra of **3** are reported in Fig. 1. Sexithiophene **3** shows a λ_{max}(CHCl$_3$) = 444 nm, similar to that found for tris(butylsulfanyl)sexithiophene,[5] but 12 nm higher than that reported for α-6T[24] and 13–40 nm higher than that reported for methylsulfanylsexithiophenes.[4] A comparison with other oligothiophenes, in which dodecyl chains were present in the β-position on half the thiophene rings, shows that **3** has a λ_{max} intermediate between octi- and dodecithiophene.[14]

The lowering of the optical gap with respect to α-6T and to methylsulfanyl sexithiophenes is probably the consequence of a good balancing between steric and electronic effects. The

Scheme 2 Proposed mechanism for the synthesis of 3,3″″-bis(butylsulfanyl)-2,2′:5′,2″:5″,2‴:5‴,2″″:5″″,2″″′-sexithiophene.

Table 1 ^{1}H and ^{13}C chemical shifts (400 MHz, CDCl$_3$, Me$_4$Si, 300 K) of 3,3$''''$-bis(butylsulfanyl)-2,2$'$: 5$'$,2$''$: 5$''$,2$'''$: 5$'''$,2$''''$: 5$''''$,2$'''''$-sexithiophene **3** and 3-(butylsulfanyl)-5$''$-bromo-2,2$'$: 5$'$,2$''$-terthiophene **4**

a) Compound **3**

Ring	3-H	4-H	5-H	C-2	C-3	C-4	C-5
	—	7.03	7.17	135.64	128.04	132.20	123.71
$'$	7.27	7.08	—	134.72	126.76	123.41	137.14
$''$	7.11	7.07	—	136.16	124.32^a	124.34^a	135.97

Aliphatic	CH$_2$(α)	CH$_2$(β)	CH$_2$(γ)	CH$_3$
δ_H	2.87	1.60	1.41	0.90
δ_C	35.88	31.67	21.85	13.61

^{a} Can be interchanged.

b) Compound **4**

Ring	3-H	4-H	5-H	C-2	C-3	C-4	C-5
	—	7.03	7.18	135.41	128.22	132.17	123.32
$'$	7.25	7.03	—	135.00	126.66	123.66	136.43
$''$	6.95	6.98	—	138.75	123.73	130.65	111.02

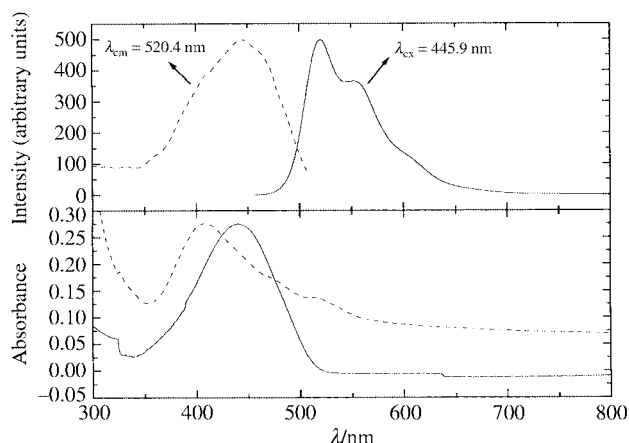| Aliphatic	CH$_2$(α)	CH$_2$(β)	CH$_2$(γ)	CH$_3$
δ_H	2.86	1.60	1.41	0.89
δ_C	35.86	31.64	21.79	13.59

Fig. 1 UV–VIS and PL spectra of sexithiophene **3**. Top: absorption (dashed line) and fluorescence (solid line) spectra of sexithiophene **3**. Bottom: UV–VIS spectra of sexithiophene **3** in solution (CHCl$_3$, solid line) and in the solid state (film cast from CHCl$_3$, dashed line).
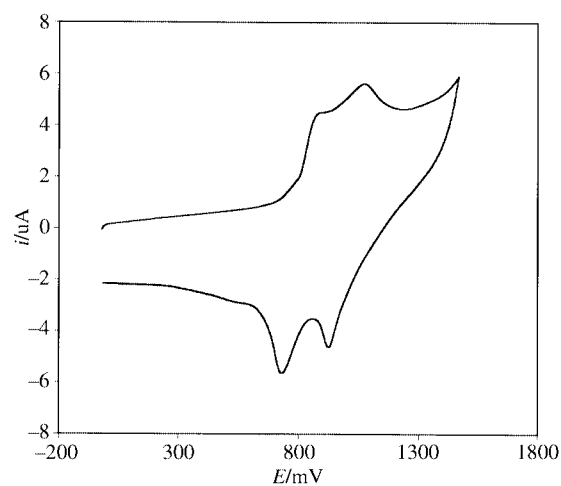

Fig. 2 CV curve of sexithiophene **3**. Scan rate 0.2 V s^{-1}, base electrolyte TBAClO$_4$ 0.1 M.

trum, as usually observed with π-conjugated compounds. The PL spectrum shows a clear shoulder peak at about 552 nm and another shoulder at longer wavelength. Similar structures have been observed with other oligothiophenes.[24–30] Both the excitation spectra monitored at the main peak and the shoulder peak of the photoluminescence give a peak at the same position (446 nm), which is near the λ_{max} position of the absorption band. These results indicate that both the main and shoulder peaks originate from the same electronic excitation.

Mobility measurement

The transport properties of a spin-coated film of the sexithiophene **3** were investigated in metal–insulator–semiconductor field-effect transistors (MISFET). They consist of a highly doped Si substrate, separated by an insulating layer. The insulator of the MISFET devices is SiO$_2$, pre-treated with hexamethyldisilazane (HMDS) before the polymer layer is applied by spin coating from chloroform to improve the interfacial organisation. Two ohmic contacts, the source and the drain, are constructed on the semiconductor layer. The field-effect mobility (μ) of the accumulated charge as a function of gate bias (V_g) may be calculated in the linear regime by eqn. (1), where L is the

$$\mu(V_g) = \left(\frac{L}{ZC_iV_d}\right)\frac{\partial I_{sd}}{\partial V_g}\bigg|_{V_d\to 0} \qquad (1)$$

channel length, Z is the channel width, C_i is the capacitance of the insulator per unit area, V_d is the drain bias and I_{sd} is the source-drain current.

The mobility of the hexamer is about 10^{-4} cm^{2}V^{-1} s^{-1}, with a on/off ratio of about 5×10^4. The mobility was determined from the source current at $V_g = -20$ V and $V_d = -20$ V. The values are in agreement with those reported for other oligothiophenes when deposited *via* spin coating.[31]

Cyclic voltammetry

The voltammogram of sexithiophene **3** shows two couples of peaks (wave I and II) at positive potential values (Fig. 2). E_p and i_p (peak current) were determined by analysing the CV curves with an appropriate deconvolution program developed in our lab. The i_{pa} (anodic peak current) values increase linearly with increasing $v^{1/2}$ (v = scan rate) and sexithiophene concentration above $v > 0.05$ V s^{-1} and using $c < 10^{-4}$ M. This indicates that the process is predominantly diffusion controlled. At higher depolarizer concentration and/or at low scan rate, the linear dependence of i_p on $v^{1/2}$ and c disappears and the peak width of wave I decreases. These facts indicate the appearance of adsorption processes on the electrode surface. The two

conjugation ability of the butylsulfanyl group acts on a π-conjugated system in which the steric hindrance, due to the bulky β-alkylsulfanyl groups, is diluted by the presence of unsubstituted rings. The lone pairs of the two sulfur atoms in the 3- and 3$''''$-positions can be delocalized onto the whole molecular skeleton and determine a λ_{max} longer than that of α-6T.

The solid-state UV–VIS absorption spectrum of **3** film, formed by solvent evaporation on glass from CHCl$_3$, displays a vibronic structure with $\lambda_{max} = 410$ nm with shoulders at 468 and 513 nm. The vibronic structure indicates that the oligomer in the solid state is more planar and more rigid, compared to the chloroform solution, in which we can imagine the oligomer in a "random-coil" conformation. This behaviour is very similar to that observed for other oligothiophenes.[24–30]

The oligomer in a good solvent (CHCl$_3$) exhibits a main photoluminescence peak at 521 nm with a quantum yield φ of 0.22, which agrees with the onset position of the UV–VIS spec-

Table 2 E_p and $E°$ value of wave I and II

	E_{pa}/V	E_{pc}/V	$E°/V$
Wave I	1.068	0.922	0.995
Wave II	0.916	0.732	0.824
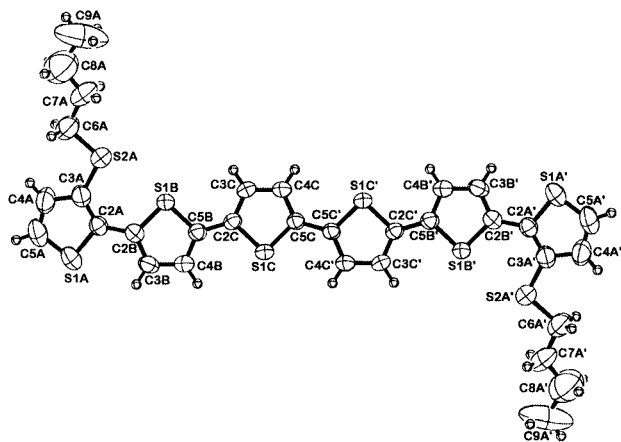
Fig. 3 ORTEP [44] drawing of the molecular structure of sexithiophene **3** showing the atom numbering scheme and thermal motion ellipsoids (50%) for non-H atoms. Primed atoms are related to unprimed ones by an inversion centre at the mid-point of the C5A–C5A′ bond.

electrodic processes are both one electron processes. This has been evaluated by comparing the currents of the present system with the first one-electron reversible wave of anthracene in the same solvent, as reported in ref. 32. The presence of a cathodic counterpart for each anodic peak and the peak to peak separation of the two waves (ranging from 120 to 190 mV, depending on v and c) indicate the occurrence of two quasi-reversible electrochemical processes. In these conditions, the $E°$ values of the two processes can be evaluated as the semisum of the anodic and cathodic peak potentials. Very similar values have been obtained using a convolution method (CONDECON program, PAR). E_p and $E°$ values of the voltammetric signals are reported in Table 2. The shape of wave I and II indicate that the two oxidation processes give rise to a stable radical cation $3^{+•}$ and dication 3^{2+}, respectively. A similar behaviour has already been observed for tris(butylsulfanyl)sexithiophene,[5] although more negative $E°$ values were calculated. It is worthy of note that in the CV curves a new wave appears by repeated cycles. This fact and the current crossover at the positive end of the CV curve, observed starting from the second cycle, suggest the presence of chemical reactions among the oxidation products and perhaps polymerization phenomena on the electrode surface. Further investigations are in progress to verify the possibility of the formation of a polymer film on the electrode surface.

X-Ray molecular structure

X-Ray analysis has been used to find the details of the solid state organization in order to correlate the packing parameters with the mobility parameters. Fig. 3 shows the molecular structure of compound **3**, whereas a crystal packing diagram is presented in Fig. 4. The molecule is centrosymmetric and lies on a crystallographic inversion centre, so that the central thiophene rings are exactly coplanar and their S atoms *trans* with respect to the ring junction. The orientation of the middle thiophene rings (B labelled in Fig. 3) is characterised by S–C–C–S interring torsion angles of ±176.0(2) and ±163.1(2)° with inner (C) and outer (A) rings, respectively. Hence, the whole molecule displays slightly distorted full *anti* conformation, as previously found for the other five sexithiophene derivatives of whose structure we are aware. The deviations of the thiophene rings
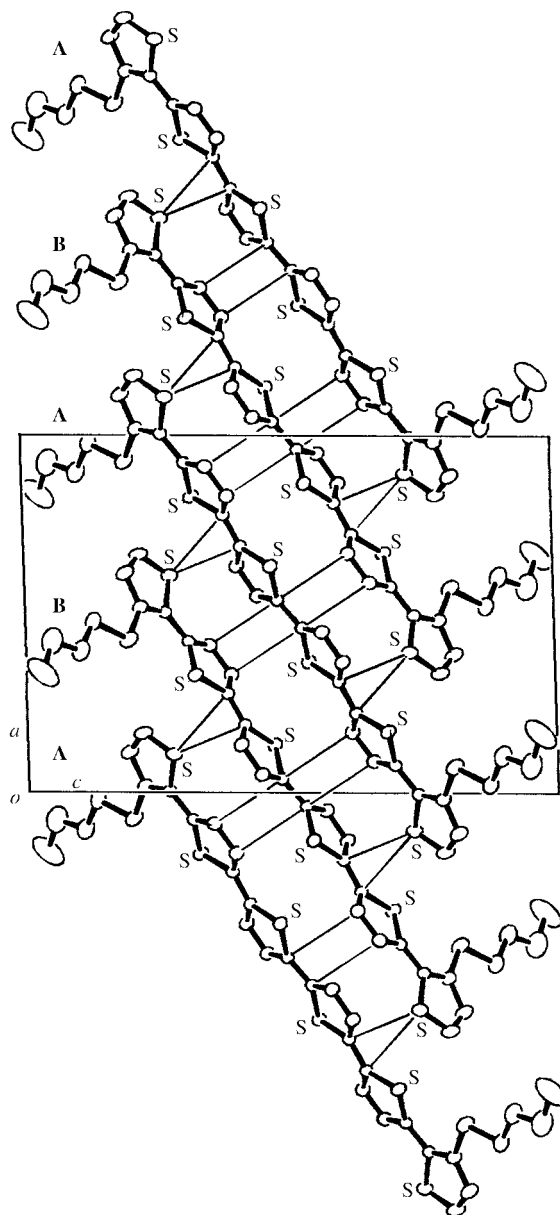
Fig. 4 The molecular packing of sexithiophene **3** as viewed down *b* cell axis. **A** and **B** layers stack along cell axes and are related by a glide plane (and a twofold screw axis). The dihedral angle between their mean planes ("herringbone" angle) is 56.71(6)°. Thin lines represent shortest (<3.60 Å) van der Waals C–S and C–C contacts.

from coplanarity are larger than those observed in the two polymorphic forms of the unsubstituted sexithiophene, both showing quasi-planar *trans* configuration,[33–35] but are close to those reported for two dialkyl sexithiophenes, where the tilt angles between rings range from 5 to 11°.[35] The conformation of the α,ω-bis(triisopropylsilyl)sexithiophene is more distorted, being characterized by tilt angles of ±21.4 and ±37.4°.[36]

The *n*-butylsulfanyl chain displays fully extended *anti* conformation, and the mean plane through its C atoms makes a dihedral angle of 5.5(5)° with that of the bonded ring. It is of interest to note that the same chain conformations and orientations were previously observed either for the *n*-butyl[35] or the *n*-octyl[35] disubstituted sexithiophene, and in the 4,4′-bis-(butylsulfanyl)-2,2′-bithiophene.[37] Nevertheless, in this latter compound the atomic temperature factors of the *n*-butyl-sulfanyl substituent were found to be unusually low, contrary to the present case, in which they are very large, in particular those of terminal carbon atoms. Individual and mean bond distances and angles compare very well with those reported in other sexi- or quaterthiophene derivatives[33–35] and, as a common feature

of oligothienyls, the atoms of all thiophene rings are coplanar within the experimental errors.

The compound exhibits the "herringbone" molecular packing motif typical of planar or quasi-planar oligothiophenes, where the angle between mean planes between coupled molecules normally fall in the 60 and 70° range.[38,39] In the present case we find a significantly smaller herringbone angle of 56.71(6)°. Furthermore, the packing is characterised by some (4) short S···C and C···C van der Waals contacts, quite rarely observed in oligothiophene derivatives.[40] In this case they range from 3.451(4) to 3.503(4) Å, and all occur between herringbone coupled molecules (see Fig. 4). Finally, the shortest intermolecular S···S separations, a parameter of great interest from the point of view of charge transport processes, are in the 3.953(2)–4.038(2) Å range.

Experimental

All air or moisture sensitive reactions were performed under prepurified nitrogen or argon, using dry glassware. Hexane, diethyl ether and toluene were dried prior to use. Other reagents were purchased from Aldrich Chemical Co. and used as received. Melting points and boiling points are uncorrected.

The UV–VIS spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. The PL spectra were recorded on a Perkin-Elmer Luminescence Spectrometer LS 50 B. All emission studies in solution were performed at absorptions between 0.05 and 0.1. Photoluminescence quantum yields were determined relative to fluorescein in 1 M NaOH assuming a quantum yield of 0.93 at an excitation wavelength of 475 nm ($c < 10^{-4}$ M).[41] Quantum yields were calculated using the expression in eqn. (2), where φ is the quantum yield, $\int A_r(v)dv$ is

$$\varphi_x = \varphi_r \left(\frac{\int A_r(v)dv}{\int A_x(v)dv} \right) \left(\frac{n_x^2}{n_r^2} \right) \left(\frac{D_x}{D_r} \right) \qquad (2)$$

the integral over the absorption in the bandwith of excitation, n is the refractive index, and D is the integral over the emission spectrum. The subscripts x and r refer to the sample and the reference solution.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400.13 and 100.61 MHz, respectively, in CDCl$_3$. Chemical shifts, in ppm, are referenced to Me$_4$Si. Coupling constants, J, are given in Hz. HMQC[21] parameters: spectral width (f_2) = 1.3 ppm, 1024 complex points; spectral width (f_1) = 30 ppm, 256 t_1 increments with 16 scans per t_1 value; relaxation and evolution delays = 0.5 s and 2.78 ms, respectively. Zero filling in f_1 and f_2, sine function in f_1 were applied before Fourier transformation. HMBC[22] parameters: spectral width (f_2) = 1.3 or 4 ppm, spectral width (f_1) = 150 ppm, 256 t_1 increments with 64 scans per t_1 value; relaxation delay = 0.5 s and delay for long-range coupling constant evolution = 50 or 100 ms. Zero filling in f_1 and f_2, sine function in f_1 were applied before Fourier transformation.

The transistor characteristics were measured with the Hewlett Packard 4155A semiconductor parameter analyser. The source voltage and the drain voltage are kept constant during the measurements (Vs = 0 V, Vd = −2 or −20 V). A sweep mode is applied to the gate from −20 to +2 or +20 V with a step of 500 mV. The drain current and the source current were measured.

Voltammetric measurements in CH$_2$Cl$_2$ were performed using a PAR 273A Potentiostat/Galvanostat system under an Ar atmosphere. A glassy carbon (GC) electrode was used as working electrode, a Pt sheet as counter and aqueous Ag/AgCl/KCl (4 M) as reference electrode. The diameter of the glassy carbon electrode was 2 mm and the surface was accurately polished and ultrasonically rinsed before each run. The reference electrode was contained in a glassy tube, separated from the solution by a glass frit of medium porosity which was located a few mm from the working electrode. The base electrolyte was tetrabutylammonium perchlorate (TBAClO$_4$) 0.1 M. The voltammetric curves were recorded at scan rates ranging from 0.02 to 2 V s^{-1}. All the potential values were determined with an accuracy of ±5 mV and referenced to aqueous saturated calomel electrode (SCE).

3-Butylsulfanyl-2-(trimethylstannyl)thiophene 2[42]

A solution of n-butyllithium (1.5 M, 7 ml, 10.5 mmol) was added drop by drop into a cooled (−73 °C) solution of 2-bromo-3-(butylsulfanyl)thiophene (2.5 g, 10 mmol) in dry diethyl ether (30 ml) and the reaction was stirred at −73 °C for 15 min. Trimethyltin chloride (2.08 g, 10.4 mmol) in dry diethyl ether (8 ml) was added dropwise (15 min) at a temperature of <−70 °C. After being stirred at −70 °C for 30 min, the reaction mixture was allowed to slowly warm to room temperature overnight and poured onto crushed ice and water. The organic phase was separated and the aqueous phase extracted with ether. The combined organic phases were washed with saturated brine, dried (MgSO$_4$) and evaporated. Distillation of the residue under reduced pressure gave compound **2** (2.28 g, 68%), bp 85–86 °C/0.1 mmHg; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 0.45 [9 H, s with ^{117}Sn and ^{119}Sn satellites, $^2J(^{117}$Sn, Me) 57.2; $^2J(^{119}$Sn, Me) 58.3, SnMe$_3$], 0.93 (3 H, t, CH$_3$), 1.44 (2 H, m, CH$_2(\gamma)$), 1.61 (2 H, m, CH$_2(\beta)$), 2.79, (2 H, t, CH$_2(\alpha)$), 7.25 (1 H, d, $J_{4,5}$ 5.3, $^4J_{H,Sn}$ 5, 4-H), 7.59 (1 H, d, $J_{4,5}$ 5.3, $^4J_{H,Sn}$ 11, 5-H).

5,5′-Dibromo-2,2′-bithiophene 1

The compound was prepared according to the method proposed by Bäuerle[43] in 82% yield, mp 145–146 °C (lit.[43] 146 °C); δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 6.85 (1 H, d, $J_{3,4}$ 3.9), 6.96 (1 H, d, $J_{3,4}$ 3.9).

3,3‴′-Bis(butylsulfanyl)-2,2′:5′,2″:5″,2‴:5‴,2‴′:5‴′,2‴″-sexithiophene 3

5,5′-Dibromo-2,2′-bithiophene **1** (0.24 g, 0.74 mmol) and 3-butylsulfanyl-2-(trimethylstannyl)thiophene **2** (0.5 g, 1.5 mmol) were refluxed in anhydrous toluene (10 mL) under a flow of dry nitrogen in the presence of PdCl$_2$(PPh$_3$)$_2$ (0.052 g, 0.074 mmol). The reaction mixture was stirred (20 h) under reflux until the reagents were consumed as estimated from TLC (SiO$_2$, light petroleum–diethyl ether 2:1). The red mixture was cooled, diluted with CHCl$_3$ (40 mL), washed with water, dried (MgSO$_4$) and the solvent was removed $in\ vacuo$ to yield a brown oil (0.47 g). The crude product was chromatographed on silica gel (neutralized with a 2% triethylamine solution) using light petroleum (bp 40–70 °C) and diethyl ether (2:1) as eluent to give, in order of elution, bromoderivative **4**, dimer **6**, tetramer **5** and a brown solid containing mostly the sexithiophene **3** (from ^{1}H NMR). Compounds **6** and **5** were identical (TLC, ^{1}H NMR, mp) with the authentic samples.[17,18] The brown solid was stirred with n-pentane (20 ml), collected and recrystallized by re-precipitation from n-pentane into toluene to give sexithiophene **3** (0.09 g) as red needles, mp 112–114 °C; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 0.90 (3 H, t, CH$_3$), 1.41 (2 H, m, CH$_2(\gamma)$), 1.60 (2 H, m, CH$_2(\beta)$), 2.87 (2 H, t, CH$_2(\alpha)$), 7.27 (1 H, d, $J_{3',4'}$ 3.9, 3′-H), 7.17 (1 H, d, $J_{4,5}$ 5.3, 5-H), 7.03 (1 H, d, $J_{4,5}$ 5.3, 4-H), 7.08 (1 H, d, $J_{3',4'}$ 3.9, 4′-H), 7.11 (1 H, d, $J_{3'',4''}$ 3.8, 3″-H), 7.07 (1 H, d, $J_{3'',4''}$ 3.8, 4″-H).

Crystal data for compound 3

An orange–red, prismatic crystal of approximate dimensions 0.28 × 0.20 × 0.15 mm, was selected for X-ray data collection. C$_{32}$H$_{30}$S$_8$, M = 671.04. Monoclinic; space group $P2_1/a$, a = 13.684(2), b = 5.827(2), c = 20.132(3) Å, β = 91.76(2)°, V = 1604.5(4) Å^3, Z = 2, μ(Mo-Kα) = 0.579 mm^{-1}. Final R and $wR(F^2)$ 0.0540 and 0.1482 ($I \geq 2\sigma I$).

Data collection, structure analysis and refinement. The measurements were performed at room temperature with an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα radiation, and ω–2θ scan mode. A total of 4116 reflections were collected in the range $2.02 \leq \theta \leq 25.97°$, of which 3140 were independent ($R_{int} = 0.033$), and 1667 had $I \geq 2\sigma I$. An absorption correction based on empirical Ψ scans [45] was applied to intensities. The structure was solved by direct methods (SHELXS86) [46] and refined through full-matrix least-squares based on F^2 (SHELXL93). [47] All non-H atoms were treated anisotropically and H atoms added to the model in calculated positions. Largest difference peak and hole were 0.407 and -0.321 e Å^{-3}, respectively. Scattering factors were from SHELXL93. [47]

CCDC reference number 207/359. See http://www.rsc.org/suppdata/p1/1999/3207 for crystallographic files in .cif format.

Acknowledgements

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