One-step synthesis of tris(butylsulfanyl)sexithiophene from 3-butylsulfanyl-2,2′-bithiophene

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$FeCl_3$ converts, in high yield, 3-butylsulfanyl-2,2′-bithiophene into a tris(butylsulfanyl)sexithiophene, which shows interesting optical properties and forms a stable radical cation and dication.

Oligothiophenes with defined structure are gaining increasing attention as a new class of organic π-electron systems. Among them, α-sexithiophene (α-6T) is a very promising material for field-effect transistors.[1] The optical and electrical properties as well as the processability of these materials can be modulated by adding substituents on the oligothiophene backbone. Recently, interesting methylsulfanylsexithiophenes with UV maximum absorption wavelengths near to, but lower than, those of sexithiophene have been reported.[2] Among alkylsulfanyl groups, butylsulfanyl shows interesting solubility and structural properties in poly(3-butylsulfanyl)thiophene[3] and in 4,4′-bis(butylsulfanyl)-2,2′-bithiophene.[4] To minimize the steric effect due to the bulky substituent we chose to build a sexithiophene from 3-butylsulfanylbithiophene.

Here, we report preliminary results on 3,3‴,3‴″-tris(butylsulfanyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴″-sexithiophene **1**, obtained by oxidative coupling of 3-butylsulfanyl-2,2′-bithiophene with $FeCl_3$ in $CHCl_3$–$MeNO_2$ (Scheme 1).† The product was identified by ^1H and ^{13}C NMR, mass and UV spectra. Mass analysis confirmed a molecular formula of $C_{36}H_{38}S_9$: *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, $[M^+ - C_{12}H_{12}S_3]$).

^1H NMR data enabled the regiochemistry of **1** to be determined. In the aromatic region of the ^1H NMR spectrum (Fig. 1), the presence of four doublets characterized by ^3J(H-α,H-β) 5.2–5.3 Hz (H-4, H-5, H-4‴″ H-5‴″), six doublets characterized by ^3J(H-β, H-β′) 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 sexithiophene. Compound **1** proposed in Scheme 1 is the only structure compatible with the absence of monosubstituted terminal thiophenes. Three distinguishable 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. Two further triplets, corresponding to the terminal methyls, are found at δ 0.92 (double intensity) and 0.90. Signals corresponding to $CH_2(\beta)$ and $CH_2(\gamma)$ are superimposed. Complete NMR characterization was achieved through ^1H and ^{13}C NMR inverse-detection techniques, HMQC[5] and HMBC.[6]

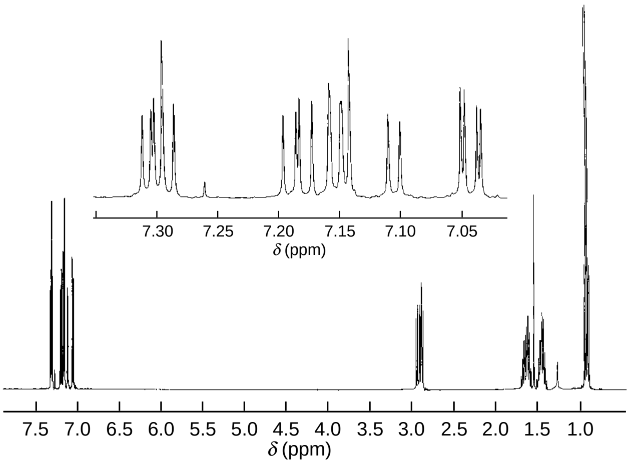
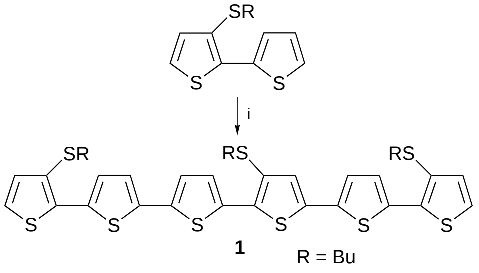


Fig 1 ^1H NMR spectrum of sexithiophene **1**. The upper trace shows the expanded aromatic region.

The formation of the regioisomer **1**, out of the possible four that could in principle derive from the starting bithiophene, can be explained by considering the deactivation effect of the 3-methylsulfanyl group on the 5-position of thiophene or bithiophenes in oxidative coupling reactions with $FeCl_3$.[7] Another important result is the high reaction yield (70% of pure product) probably due to the stability of radical cation $1^{+\bullet}$ in the reaction conditions. This stability was confirmed by a cyclic voltammetry investigation (Fig. 2) which showed the presence of two reversible oxidation peaks at 0.89 and 1.02 V (0.1 M Bu_4NBF_4–CH_2Cl_2, glassy carbon electrode, scan rate 100 mV s^{-1}, SCE) corresponding to the formation of the cation radical $1^{+\bullet}$ and the dication 1^{2+}. Compound **1** shows $\lambda_{max}(CHCl_3)$ 449 nm, 17 nm higher than that reported for α-6T[8] and 19–43 nm higher than that reported for methylsulfanylsexithiophenes.[2] A further 19 nm bathochromic effect is observed in CS_2. In fact, λ_{max} changes from 443 in MeOH, to 446 in MeCN, to 449 in $CHCl_3$ and to 468 nm in CS_2. The lowering of the optical gap with respect to α-6T and to methylsulfanylsexithiophenes is probably the consequence of a good balance between steric and



Scheme 1 *Reagents and conditions*: i, $FeCl_3$, $CHCl_3$–$MeNO_2$ 1 : 1, room temp., 30 h

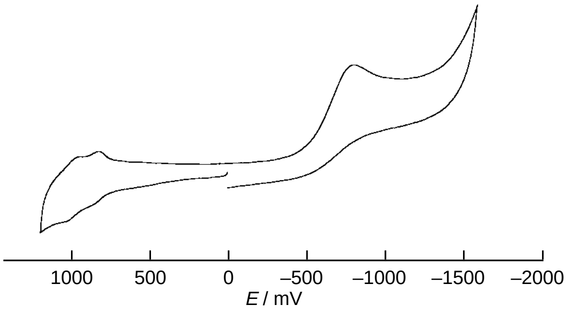


Fig. 2 Cyclic voltammogram of sexithiophene **1**

electronic effects. The conjugational 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 regiochemistry of substitution should play a fundamental role in determining the optical characteristics of **1**. In fact, the lone pairs of the two sulfur atoms in the 3- and 3″‴-positions can be delocalized onto the whole molecular skeleton. The sulfur lone pair could not exert the same conjugative effect if the outer butylsulfanyl groups were placed in the 4- and 4″‴-positions. The 3‴-butylsulfanyl group can only give rise to a less extended conjugation pattern (over four rings). In conclusion, through the accurate choice of the starting monomer we were able to synthesize a substituted sexithiophene with butylsulfanyl groups on the 3-, 3‴- and 3″‴-positions, having a $\lambda_{\max}$ at a longer wavelength than that of α-6T and forming a stable radical cation and dication.

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Footnotes and References

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† *Preparative details*: A solution of anhydrous $\mathrm{FeCl_3}$ (10.4 g, 64 mmol) in dry nitromethane (240 ml) was added dropwise over a period of 2 h to a solution of 3-butylsulfanyl-2,2′-bithiophene (4.0 g, 15.7 mmol) in distilled $\mathrm{CHCl_3}$ (240 ml) under a flow of dry nitrogen. The reaction mixture, stirred 30 h at room temperature, was evaporated and the residue was stirred with a solution of HCl acidified methanol (100 ml). The filtered dark product was washed with methanol (40 ml) and dissolved in $\mathrm{CHCl_3}$ (150 ml). The chloroform solution was washed with a 3% hydrazine solution (100 ml) and then with water, and evaporated. The crude red oil was washed with pentane (400 ml). The pentane solution was evaporated and the product (3.7 g) chromatographed on silica gel (neutralized with a 2% solution of triethylamine) using light petroleum (bp 40–70 °C)–diethyl ether (90 : 10) as the eluent. The compound isolated (2.8 g, 70%) is a red oil identified as 3,3‴,3″‴-tris(butylsulfanyl)-2,2′ : 5′,2″ : 5″,2‴ : 5‴,2⁗, : 5″″,2″‴-sexithiophene **1**.

‡ *NMR data* for **1**: δ_{H} (400 MHz, $\mathrm{CDCl_3}$, 27 °C, $\mathrm{Me_4Si}$, J/Hz) 7.31 [d, ^3J(H,H) 3.8, 1 H, H-4″], 7.30 [d, ^3J(H,H) 3.7, 1 H, H-3′], 7.29 [d, ^3J(H,H) 3.9, 1 H, H-4⁗], 7.19 [d, ^3J(H,H) 5.3, 1 H, H-5″‴] 7.18 [d, ^3J(H,H) 5.3, 1 H, H-5], 7.15 [d, ^3J(H,H) 3.8, 2 H, H-4′, H-3″], 7.14 (s, 1 H, H-4‴), 7.11 [d, ^3J(H,H) 3.9, 1 H, H-3⁗], 7.043 [d, ^3J(H,H) 5.3, 1 H, H-4″‴] 7.041 [d, ^3J(H,H) 5.3, 1 H, H-4], 2.92 [t, 2 H, 3‴-$\mathrm{CH_2}$(α)], 2.88 [t, 2 H, 3″‴-$\mathrm{CH_2}$(α)], 2.87 [t, 2 H, 3-$\mathrm{CH_2}$(α)], 1.64 [m, 6 H, $\mathrm{CH_2}$(β)], 1.44 [m, 6 H, $\mathrm{CH_2}$(γ)], 0.92 (t, 6 H, 3-$\mathrm{CH_3}$, 3″‴-$\mathrm{CH_3}$), 0.90 (t, 3 H, 3‴-$\mathrm{CH_3}$); δ_{C} 137.61, 136.73, 137.36, 136.42, 135.50, 135.13, 134.67, 134.60, 134.39, 134.27, 132.23, 132.20, 128.76, 128.24, 128.02, 126.81, 126.77, 126.74, 123.72, 123.49, 123.48, 123.31, 123.13, 36.00, 35.89, 35.88, 31.66, 31.65, 21.86, 21.83, 13.58; $\lambda_{\max}$/nm ($\mathrm{CHCl_3}$) 449 (ε/dm^3 mol^{-1} cm^{-1} 75 000); *m/z* (70 eV) 762 (10%, [$\mathrm{M^+}$ + 4]), 761 (15, [$\mathrm{M^+}$ + 3]), 760 (41, [$\mathrm{M^+}$ + 2]), 759 (43, [$\mathrm{M^+}$ + 1]), 758 (100, [$\mathrm{M^+}$]), 506 (18, [$\mathrm{M^+} - \mathrm{C_{12}H_{12}S_3}$]).

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