Synthesis of substituted oligothiophenes and X-ray crystal structures of 3′-methyl-2,2′:5′,2″-terthiophene, 3,3″-dimethyl-2,2′:5′,2″-terthiophene and 5′-(2-thienyl)-2,2′:3′,2″-terthiophene

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A range of substituted oligothiophenes has been prepared and characterised. Crystal structures were determined for three substituted terthiophenes. Both in solution and in the solid state, *syn*-conformers were found to be populated to a greater extent than expected.

Introduction

There is considerable interest in polythiophenes and oligothiophenes because they are conducting when doped, and may be used for third harmonic generation.[1] The structures of a range of substituted and unsubstituted oligothiophenes including bithiophene,[2,3] substituted bithiophenes,[4–8] terthiophene,[9] substituted terthiophenes,[10] tetrathiophenes[11,12] and sexithiophenes[13] have recently been established in diffraction studies. We now report the synthesis and characterisation of some bi- and ter-thiophenes with site-specific substitution of alkyl groups.

Results and discussion

Synthesis of oligothiophenes

The compounds **1**–**11** were prepared by adaptations of known methods (Scheme 1) for bromination and Grignard coupling reactions. Bäuerle's[14] method for bromination of 3-hexylthiophene was the most successful in our hands; use of other solvents resulted in the isolation of considerable amounts of side-chain brominated material. In the preparation of 3-hexylthiophene, varying amounts of dodecane, produced by homocoupling of the Grignard reagent, were detected by GLC in the crude material. The amount of dodecane could be reduced by using an excess of magnesium, and increasing the time for Grignard formation. The products of homocoupling of thienyl Grignard reagents were also detected in the preparations of **7**, **8** and **9**.

Bithiophenes—NMR spectra and conformations; models for higher oligomers

X-Ray diffraction data for oligothiophenes have been sparse until recently, since the compounds do not crystallise well, tend to decompose in the X-ray beam, and structures are frequently disordered. The structure of 2,2′-bithiophene was initially determined in the 1960s by Visser,[15] but was of poor quality. We[2] and Pelletier[3] have recently redetermined the structure, at low temperature. Contrary to conventional wisdom, the structure does not consist exclusively of molecules in the *anti*-conformation **12a**, but contains 15% of the *syn*-conformation **12b**. Disorder in solid-state structures of compounds containing a thiophene ring is relatively common.[16] Substitution in oligothiophenes may cause deviations from coplanarity, unusual proportions of unexpected conformers, and changes in bond lengths. For example, in 5,5′-dibromo-2,2′-bithiophene, bond lengths and angles are slightly altered as a result of the electronic effect of the bromine.[5] In 2,2′-bithiophene-5-carbaldehyde,[8] the main conformation is *syn* with only 20% of molecules adopting the *anti*-conformation. However, crystal structures tell us only a limited amount about solution conformation; for this solution NMR spectroscopy and UV absorption data are more useful.

The ^{1}H NMR spectrum of 3,3′-dimethyl-2,2′-bithiophene **6** shows a singlet for the methyl groups and doublets (J 4.9 Hz) for 4,4′-H (δ 7.01) and 5,5′-H (δ 7.33). The aromatic protons were unambiguously assigned on the basis of an observation of a 2.8% nuclear Overhauser enhancement (NOE) from the methyl group to 4-H. Most of the ^{13}C NMR resonances were assigned from the proton coupled ^{13}C NMR spectrum, with the quaternary carbon atoms assigned by comparison with related data from Barbarella and co-workers.[17]

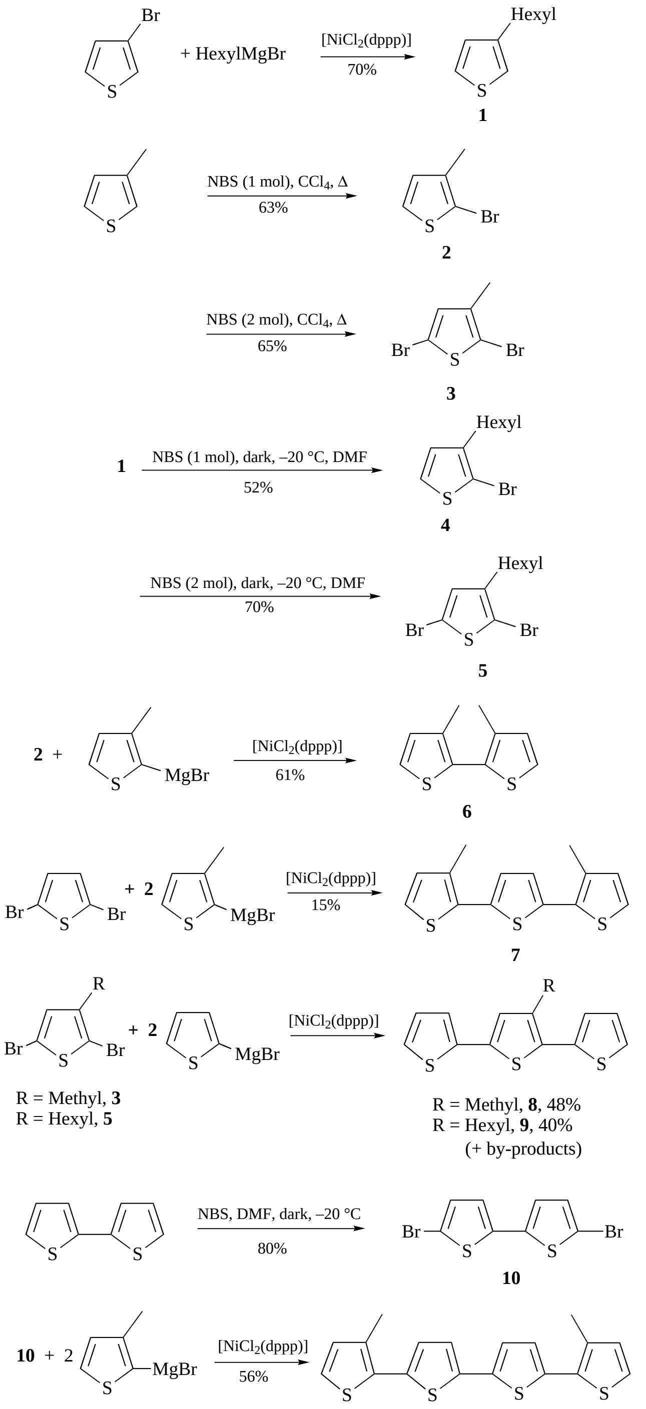
Terthiophenes

The ^{1}H and ^{13}C NMR spectra of terthiophene have been previously assigned,[18] and provide a starting point for the assignment of the spectra of substituted compounds. The structure of terthiophene has been determined, with coplanar, *anti*, rings, as in **13**.[9] The ^{1}H NMR spectrum of 3,3″-dimethyl-2,2′:5′,2″-terthiophene **7** was assigned by a combination of decoupling and NOE experiments. In particular there was a 5.3% NOE between the methyl groups and the 4,4″-hydrogens. More surprisingly there was a 2.7% NOE from the CH_3 to the 3′- and 4′-hydrogens. This suggests that the molecule does not exclusively adopt the all-*anti*-conformation **7a**, but that **7b** and/or **7c** are also significantly populated. Space filling models suggest that **7b** and **7c** are significantly more hindered. The ^{13}C NMR spectrum was assigned by two-dimensional one-bond and long range C−H shift correlations.

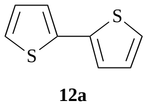
The ^{1}H NMR spectrum of 3′-methyl-2,2′:5′,2″-terthiophene **8** is more complex, due to the lower symmetry. Selective decoupling experiments allowed the grouping of the signals due to 3-H, 4-H and 5-H, and 3″-H, 4″-H and 5″-H, but did not allow us to assign the groups to the appropriate ring. NOEs were again helpful, when all possible conformations were considered (**8a**–**8d**). There is a 4.8% NOE between the methyl group and 4′-H, as expected, but also a 1.5% NOE to 3″-H. This latter is only possible if conformations **8b** or **8d** are populated. There was also a 1.4% NOE between 4′-H and 3-H, possible only in **8c** or **8d**. Again it is clear that *syn*-conformations must be populated in solution. The ^{13}C NMR spectrum was assigned using short and long range two-dimensional C−H correlations.

Similar analyses were applied to the ^{1}H and ^{13}C spectra of 3′-hexyl-2,2′:5′,2″-terthiophene **9**. In this instance the NOE from the α-CH_2 of the hexyl side chain was 5.6% to 4′-H and 2.6% to 3″-H. 4′-H showed an NOE of 2.7% to 3-H.

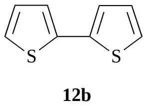
A polymer was prepared from **9** by ferric chloride oxidation. After dedoping the material produced was found to be partially



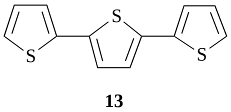
Scheme 1 Synthesis of substituted oligothiophenes



12a



12b



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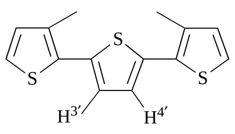
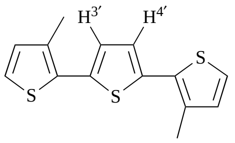
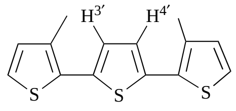


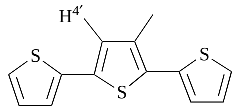
7a



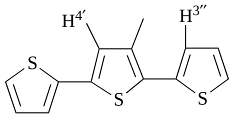
7b



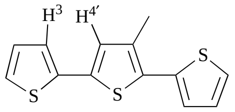
7c



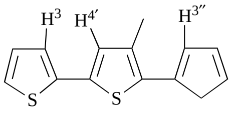
8a all *anti*



8b *anti-syn*

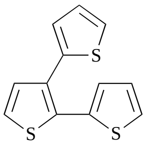


8c *syn-anti*

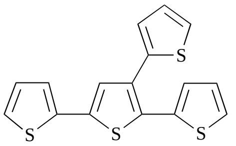


8d all *syn*

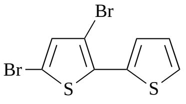
soluble in chloroform suggesting that there was an oligomeric and a polymeric fraction. The most abundant component of the chloroform-soluble material was shown by mass spectrometry and ^{1}H NMR spectroscopy to be a dihexylsexithiophene, although neither spectrum could be fully analysed. Conductivity measurements (4-probe technique on pressed pellets) are given in Table 1 for both fractions, and for poly(3-hexylthiophene) in both doped and undoped states. It is of interest that the oligomeric material is conducting in its doped state, since sexithiophenes have been the subject of much attention as models for polythiophene.[19,20] The chloroform-insoluble fraction was black in both the doped and undoped states, but the soluble fraction underwent a shift in its UV absorption from 454 nm in the undoped state (greenish yellow) to 508 nm in the doped state (blue-black). It was predictable that the polymer derived from hexylterthiophene would be less soluble than that from 3-hexylthiophene, since it is the alkyl groups that confer solubility. Equally its higher conductivity was to be expected, since there are fewer side chains to impede planarity.



14



15



16

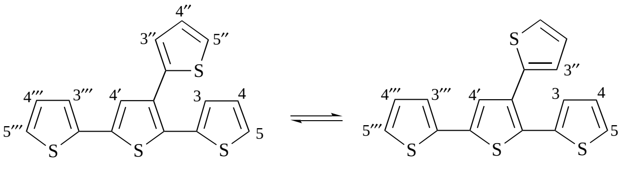
By-products of the synthesis of 3′-hexyl-2,2′:5′,2″-terthiophene 9

The synthesis of **9** involved the coupling of 2-bromomagnesiothiophene with 2,5-dibromo-3-hexylthiophene **5**. The crude material obtained was shown by TLC to contain 2-bromothiophene, 2,5-dibromo-3-hexylthiophene and bithiophene (formed by Grignard homocoupling) as well as three other components with rather similar R_f values. The starting materials and bithiophene were readily removed by chromatography, but the other materials were only fully separated by chromatography on three successive columns. The first compound isolated was **9** and the others were identified by ^{1}H NMR spectroscopy as 2,2′:3′,2″-terthiophene **14**, and 5′-(2-thienyl)-2,2′:3′,2″-terthiophene **15**. The formation of **14** and **15** was surprising. Compound **15** was isolated in reasonable quantity and fully characterised by X-ray diffraction (*vide infra*). Only a small amount of **14** was obtained, and this was characterised by

Table 1 Conductivity measurements on doped and undoped fractions from 3′-hexyl-2,2′:5′,2″-terthiophene polymerisation, and on poly(3-hexythiophene) at 25 °C

Material	Conductivity/S $\mathrm{cm}^{-1\,a}$	
	Undoped	Doped (I_2)
Chloroform-soluble fraction	0	43.5
Chloroform-insoluble fraction	0.0027	446.0
Poly(3-hexylthiophene)	0	239.0

[a] Data given are an average of measurements on five separate pellets.



15a **15b**

Fig. 1 Conformations of 5′-(2-thienyl)-2,2′:3′,2″-terthiophene **15**

^{1}H NMR spectroscopy and mass spectrometry. Control experiments with 2-bromomagnesiothiophene and [$NiCl_2$(dppp)] (dppp = 1,3-bisdiphenylphosphinopropane) or bithiophene and 2-bromomagnesiothiophene did not yield **14** or **15**.

Branched ter- and quater-thiophenes have been previously prepared by Perrine[21] and Kankare[22] from diketones. However, we found it more convenient to prepare an authentic sample of **15** for comparison by reaction of three molar equivalents of 2-bromomagnesiothiophene with 2,3,5-tribromothiophene in the presence of [$NiCl_2$(dppp)]. Compound **15** was obtained in 80% yield after recrystallisation.

Assignment of the ^{1}H and ^{13}C NMR spectra of **15** required selective decoupling, NOE and short- and long-range C–H correlation experiments. A key argument, which also gave information about the conformation of **15** in solution, involves the NOEs from the protons at the 3, 3″ and 3‴ sites (Fig. 1). From coupling constant data it was known that the signals at δ 7.101, 7.152 and 7.223 must be assigned to H-3, H-3″ and H-3‴, but not which was which. Irradiation of H-4′ showed partial saturation of the signal at δ 7.223 and 2.3% NOE to the signal at δ 7.101. This means that the signal at δ 7.101 must be H-3″ or H-3‴; H-3 could not show an NOE to H-4′. This allows us to assign the signal at δ 7.152 to H-3. Irradiation of the signal at δ 7.101 gave a 4.2% NOE to H-4′, and 3.1 and 4.9% NOEs to the signals at δ 7.152 and δ 7.223. This allows its unequivocal identification as H-3″; by rotating ring *D*, this proton may be in proximity to either H-3 or H-3‴ (Fig. 1). Thus the NOE measurements were useful in assigning the spectra, and also showed that some *cisoid* conformations must be populated.

The mechanism of formation of **14** and **15** in the synthesis of **9** remains obscure. The cleavage of the hexyl group may involve a radical–photochemical process, or may involve $MgBr_2$ acting as a source of bromine for *ipso*-substitution of the hexyl group by bromine. If we can postulate the formation of **16**, then **15** could be produced by two further couplings, and **14** by a coupling, Grignard exchange and protonation on work-up. However, since oligomers of these branched materials are likely to be too twisted to be valuable as conductors, we did not pursue the matter further.

Tetrathiophenes

Bromination of bithiophene gave 5,5′-dibromo-2,2′-bithiophene **10** in 80% yield.[14] This was coupled with two molar equivalents of 2-bromomagnesio-3-methylthiophene to give 3,3‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene **11**. The material initially obtained was rather dark in colour, but could be readily decolourised over charcoal, to give, after recrystallisation, a yellow flaky solid.

Table 2 Selected bond lengths and angles for 3,3″-dimethyl-2,2′;5′2″-terthiophene **7**

Bond lengths, *d*/Å		Bond angles, θ/°	
S(3)–C(9)	1.768(3)	C(3)–C(4)–C(5)	128.3(2)
S(3)–C(12)	1.707(4)	C(4)–C(5)–C(6)	128.2(2)
C(9)–C(10)	1.345(4)	S(2)–C(8)–C(9)	123.5(2)
C(11)–C(12)	1.355(4)	C(8)–C(9)–C(10)	134.5(2)
S(3a)–C(9)	1.905(6)	C(9)–C(10)–C(11)	113.5(2)
S(3a)–C(12a)	1.70(3)	C(11)–C(12)–S(3)	111.0(3)
C(9)–C(10a)	1.18(2)	C(9)–C(10a)–C(11a)	116(1)
C(11a)–C(12a)	1.33(2)	C(11a)–C(12a)–S(3a)	115(1)

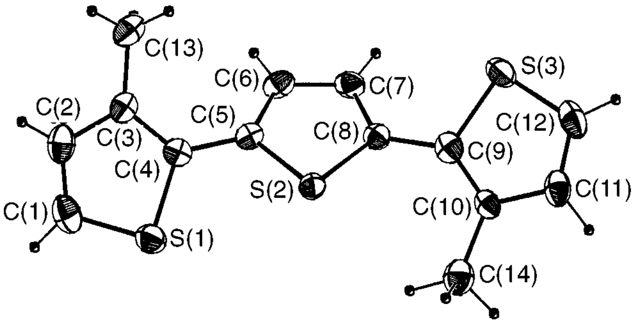


Fig. 2 Structure of 3,3″-dimethyl-2,2′:5′,2″-terthiophene **7**. ORTEP diagram, 50% thermal ellipsoids, H atoms as spheres of arbitrary size.

Most of the ^{1}H NMR spectrum could be assigned by comparison with lower congeners. The assignments were confirmed by the observation of a 4.5% NOE between the methyl groups and H-4 and H-4‴, and of 1.7% between the methyl groups and H-3′ and H-4″ (as before this latter implies population of cisoid conformers). The ^{13}C spectrum was assigned by long and short range C–H correlation experiments.

Crystals which appeared to be satisfactory for an X-ray structure determination were grown from hexane, and a low quality structure was obtained.[23] However, the structure is made up of two independent molecules that are almost related by a non-crystallographic translation of $0.5 + x$, $0.5 + y$, z. The two terminal rings were closely related in this way, but the inner rings had different orientations in the two molecules. Because of the high correlation, the two molecules were refined in alternating cycles of least squares. Three of the carbon atoms became non-positive definite, and were reset isotropic. The final difference map showed residual density at sites corresponding to pseudo-symmetry-related sulfur atoms, and a satisfactory *R* value could not be obtained.

Structure of 3,3″-dimethyl-2,2′:5′,2″-terthiophene 7

Good quality crystals were grown by the slow evaporation of a hexane solution of **7** at room temperature. The structure is shown in Fig. 2, and selected bond lengths and angles in Table 2. The structure contains a single unique molecule which is disordered in the ring containing S(3). The prevailing conformation (85%) is **7b** with 15% of **7a**. The C–S bonds are elongated [1.747(4)–1.768(3) Å] compared with **8** (*vide infra*) or 3,4′,4″-trimethyl-2,2′:5′;2″-terthiophene [1.708(6)–1.744(5) Å],[10] but whether this reflects crowding or disorder is difficult to discern.

Structure of 3′-methyl-2,2′:5′,2″-terthiophene 8

The structure of **8** was determined in an X-ray diffraction study, good quality crystals having been obtained by slow sublimation at atmospheric pressure. Selected bond lengths and angles are given in Table 3. For **8** the diffraction was rather weak (only 1755 significant reflections out of 5105 measured) and did not justify anisotropic refinement of the carbon atoms. Fig. 3 shows the three crystallographically distinct molecules in each unit cell. Two of these (A and B) had the expected geometry with *transoid* ring junctions, and were close to planar

Table 3 Selected bond lengths and angles for 3′-methyl-2,2′:5′,2″-terthiophene **8**

Bond lengths, *d*/Å	Molecule A	B	C	Bond angles, *θ*/°	Molecule A	B	C
S(1)–C(1)	1.70(2)	1.71(2)	1.61(2)	S(1)–C(1)–C(2)	113(1)	112(1)	118(1)
S(1)–C(4)	1.730(5)	1.750(14)	1.67(2)	C(1)–C(2)–C(3)	111(1)	115(1)	118(1)
S(2)–C(5)	1.732(14)	1.732(13)	1.748(15)	S(1)–C(2)–C(3)	108(1)	110(1)	114.4(8)
S(2)–C(8)	1.739(14)	1.714(14)	1.717(13)	S(3)–C(9)–C(10)	111(1)	109(1)	110(1)
S(3)–C(9)	1.721(14)	1.756(14)	1.662(14)	S(3)–C(12)–C(11)	113(1)	114(1)	110(1)
S(3)–C(12)	1.665(15)	1.689(14)	1.66(2)	C(2)–C(3)–C(4)	115(1)	110(1)	95.8(8)
C(2)–C(3)	1.41(2)	1.44(2)	1.57(2)	C(3)–C(4)–C(5)	127(1)	128(1)	121(1)
C(3)–C(4)	1.38(2)	1.41(2)	1.64(2)	S(2)–C(5)–C(4)	118(1)	116.9(9)	120(1)

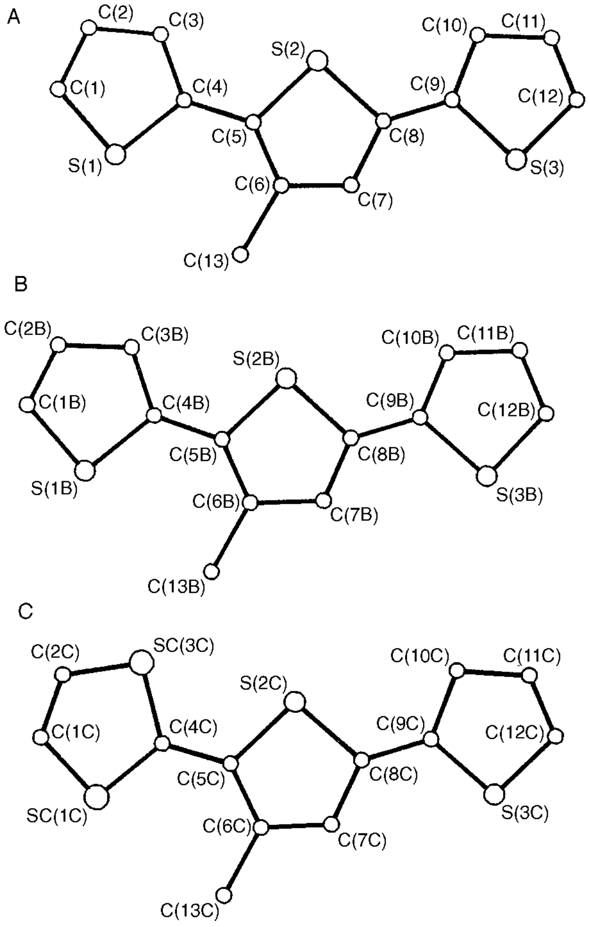


Fig. 3 The three crystallographically distinct molecules in the structure of 3′-methyl-2,2′:5′,2″-terthiophene **8**

with only minor bowing. However, in the third molecule, there is disorder between two orientations related by a 180° rotation about one ring–ring bond, corresponding to conformations **8a** and **8b**. The two sites have equal occupancy and were given an average scattering factor. It is somewhat surprising that the disorder occurs at what seems to be the less likely site, in which one would expect the greatest hindrance between the methyl group and the adjacent C–H. Apparent changes in bond lengths and angles in the outer rings are artefacts created by the averaging over the disorder.

Structure of 5′-(2-thienyl)-2,2′:3′,2″-terthiophene 15

Good quality crystals of **15** were obtained by slow evaporation of an ethanol solution. The structure is shown in Fig. 4 and selected bond lengths and angles are given in Table 4. The molecule is disordered in two of the rings. The ring containing S(2) is disordered 60:40 between the sites labelled S(2) and C(9), and the ring containing S(3) is disordered 72:28 between the sites S(3) and C(3). Thus a range of conformational isomers is present in the solid state. The bond lengths and angles of the trisubstituted ring of **15** compare closely with those in other terthiophenes. However, in this case no ring is coplanar with any other (interplanar angles range from 29 to 88° as was noted with the 3′-aryl and heteroaryl substituted terthiophenes reported by Kankare[22]). Again, apparent peculiarities in bond lengths and angles are artefacts of the disorder.

Table 4 Selected bond lengths and angles for 5′-(2-thienyl)-2,2′:3′,2″-terthiophene **15**

Bond lengths, *d*/Å		Bond angles, *θ*/°	
S(3)–C(1)	1.65(2)	C(1)–S(3)–C(4)	95.6(8)
S(3)–C(4)	1.656(14)	S(3)–C(4)–C(3)	113.2(9)
C(1)–C(2)	1.33(2)	C(1)–C(2)–C(3)	121(2)
C(3)–C(4)	1.58(2)	C(2)–C(3)–C(4)	99.0(9)
C(4)–C(5)	1.50(2)	C(4)–C(5)–C(12)	125(1)
S(2)–C(8)	1.72(2)	C(8)–S(2)–C(11)	92.4(8)
S(2)–C(11)	1.62(2)	S(2)–C(8)–C(9)	115.6(9)
C(8)–C(9)	1.59(2)	C(8)–C(9)–C(10)	96.7(9)
C(10)–C(11)	1.31(2)	C(9)–C(10)–C(11)	117(1)
C(5)–C(12)	1.32(2)	C(6)–C(5)–C(12)	118(1)
C(6)–C(7)	1.42(2)	S(1)–C(7)–C(6)	115(1)

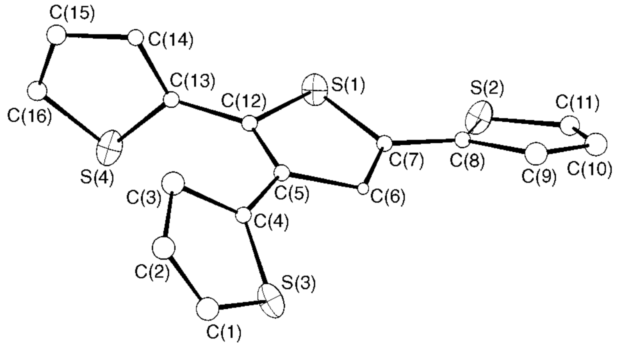


Fig. 4 Structure of 5′-(2-thienyl)-2,2′:3′,2″-terthiophene, **15**. The ORTEP diagram shows the non-H atom as 50% thermal ellipsoids.

UV–VIS spectra

The UV absorption spectra of oligothiophenes[24–26] are generally assigned in terms of the strong absorption band at longer wavelength being associated with the $\pi \longrightarrow \pi^*$ electron transfer of the entire chromophore, and the less intense band with the $\pi \longrightarrow \pi^*$ local excitation of the hetero-nucleus.[27] Our data are given in Table 5, in comparison with the earlier work of van Pham.[28] It is clear that substitution results in a blue shift of the stronger band, relative to the unsubstituted system. This is to be expected, since substitution is likely to result in the greater population of more twisted, and hence less conjugated conformers. One curious effect is that λ_{max} was concentration dependent, particularly for **6** and **7**. For example, for **6**, λ_{max} was 218.5 and 255.5 nm at 0.003 M concentration, but 219.5 and 252.0 nm at 0.0003 M. This concentration dependence may account for the differences between our data and those reported

Table 5 UV–VIS data for oligothiophenes in $CHCl_3$

Compound	λ_{max}/nm (ε) (local excitation)	λ_{max}/nm (ε)
12	243[a]	302[a]
6	219.5	252 (8440) 270[a] (7460)
13	245[a]	355[a]
7	252 276.5 (sh)	343 (17 760) 344[a] (17 340)
8	253 (6390)	352 (13 550) 336[a] (15 980)
9	244 (11 400)	348 (16 100)
15	245 (49 000) 294 (57 100)	352 (47 400)
α-Quaterthiophene	248[a]	390[a]
11	250 (6950)	383 (14 600)

[a] Data taken from ref. 23.

by van Pham. Whilst many organic chromophores do show such dependence, this phenomenon might also be related to stacking effects in solution; we hope to study this further by an examination of the variation of the ^1H NMR spectra with concentration.

Conclusions

Oligothiophenes with a range of substituents at specific sites can be prepared by coupling reactions. Both in the solid state and in solution they adopt a range of conformations, with the 'disfavoured' *syn*-isomers quite highly populated. Both the NOE data in solution, and the prevalence of disorder in the solid-state structures, suggest that the difference in energy between *syn*- and *anti*-conformations is small. As expected, substitution leads to twisting of the oligothiophenes, and shorter conjugation paths.

Experimental

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with $Si(CH_3)_4$ as an external standard, using a Bruker AC250Y (250.13, 62.85 MHz), a Bruker WM360 (360.53, 90.36 MHz) or a Bruker AMX500 (500.73, 125.77 MHz) spectrometer. *J* values are in Hz. Mass spectra were measured on either an MS25 Kratos GC/MS spectrometer or a VG Autospec Fissions instrument using the EI technique. Microanalyses were performed on a Perkin-Elmer 2400 analyser at the University of Sussex, or by Medac Ltd. IR spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer. Data are reported for 10 scans at a resolution of 4 cm^{-1}. UV–VIS spectra were obtained on a Philips PU8720 spectrometer.

2-Bromothiophene and 3-bromothiophene were kindly donated by Synthetic Chemicals Ltd. *N*-Bromosuccinimide (NBS) was recrystallised from nitromethane immediately before use. Solvents were freshly distilled from an appropriate desiccant before use. Reactions were performed under dry nitrogen unless otherwise stated.

$[NiCl_2(dppp)]$ was prepared in 92% yield according to the method of van Hecke.[29]

Synthesis of 3-hexylthiophene 1

Magnesium (5 g, 0.21 mol) was suspended in diethyl ether (100 cm^3) at 0 °C under nitrogen. A solution of 1-bromohexane (29.7 g, 0.18 mol) in diethyl ether (150 cm^3) was added dropwise and the mixture stirred at room temperature for 2 h. The Grignard reagent was then added in portions to 3-bromothiophene (24.25 g, 0.15 mol) and $[NiCl_2(dppp)]$ (0.2 g) in diethyl ether (100 cm^3) and the mixture stirred for 3 h. The reaction mixture was then quenched with water (100 cm^3), the organic phase separated, and the aqueous phase extracted (diethyl ether, 2 × 50 cm^3). The combined organic phases were dried ($MgSO_4$) and the solvent removed under reduced pressure. Fractional distillation gave 3-hexylthiophene (17.6 g, 70%), bp 60–61 °C, 0.77 mmHg (lit.[30] 62–63 °C, 0.7 mmHg). δ_H(360 MHz, $CDCl_3$) 1.13 (3H, t, *J* 6.9, CH_3), 1.56 (6H, m, 3 × CH_2), 1.84 (2H, m, CH_2), 2.84 (2H, t, *J* 7.4, $ArCH_2$) 7.0 (1H, m, 2-H), 7.13 (1H, dd, *J* 1.2, 4.9, 5-H), 7.39 (1H, dd, *J* 2.9, 5.1, 4-H); δ_C(62.5 MHz, $CDCl_3$) 13.92 (CH_3), 22.62 ($\mathit{C}H_2CH_3$), 29.32 ($ArCH_2CH_2\mathit{C}H_2$), 29.67 ($Ar\mathit{C}H_2$), 30.47 ($\mathit{Ar}CH_2CH_2$), 31.4 ($\mathit{C}H_2CH_2CH_3$), 119.73 (5-C), 124.95 (2-C), 128.17 (4-C), 143.11 (3-C).

Synthesis of 2-bromo-3-methylthiophene 2

A mixture of 3-methylthiophene (5 g, 0.05 mol) and NBS (9.08 g, 0.05 mol) in tetrachloromethane (150 cm^3) was heated under reflux for 5 h. The reaction mixture was cooled and filtered and the solvent removed under reduced pressure. Distillation gave **2** as a colourless liquid (5.62 g, 63%), bp 14–16 °C, 0.3 mmHg, (lit.[31] 27 °C, 1.8 mmHg). δ_H(360 MHz, $CDCl_3$) 2.24 (3H, s, CH_3), 6.81 (1 H, d, *J* 5.5, 4-H), 7.19 (1H, d, *J* 5.5, 5-H); δ_C(62.5 MHz, $CDCl_3$) 15.0 (CH_3) 109.2 (2-C), 124.9 (5-C), 129.1 (4-C), 137.0 (3-C).

Synthesis of 2,5-dibromo-3-methylthiophene 3

The same procedure was used as for 2-bromo-3-methylthiophene, except that the quantity of NBS was doubled (18.16 g, 0.1 mol). Distillation gave **3** (8.35 g, 65%) as a colourless liquid, bp 35–37 °C, 0.3 mmHg, (lit.[31] 55 °C, 2 mmHg). δ_H(250 MHz, $CDCl_3$) 2.15 (3 H, d, *J* 0.4, CH_3), 6.74 (1H, d, *J* 0.4, CH); δ_C(62.5 MHz, $CDCl_3$) 15.1 (CH_3), 108.3, 110.1 (2-C, 5-C), 131.7 (4-C), 137.8 (3-C).

Synthesis of 2-bromo-3-hexylthiophene 4

A solution of 3-hexylthiophene (3 g, 0.18 mol) in dimethylformamide (DMF) (50 cm^3) was protected from light and cooled to −20 °C. To this was slowly added a solution of NBS (3.178 g, 0.18 mol) in DMF (50 cm^3). The mixture was stirred at −20 °C for 30 min, and then allowed to warm to room temperature. Stirring was continued for 5 h, and the mixture was poured into ice (50 g) and extracted with dichloromethane (3 × 100 cm^3). The combined organic extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure. Fractional distillation gave **4** (2.31 g, 52%), bp 95–96 °C, 0.1 mmHg, which was used without further purification; δ_H(360 MHz, $CDCl_3$) 0.95 (3H, t, *J* 6.5, CH_3), 1.36 (6H, m, 3 × CH_2), 1.63 (2H, m, CH_2), 2.61 (2H, t, *J* 7.5, $ArCH_2$), 6.83 (1H, d, *J* 5.6, 4-H), 7.20 (1H, d, *J* 5.5, 5-H).

Synthesis of 2,5-dibromo-3-hexylthiophene 5

In the absence of light, NBS (6.36 g, 0.036 mol) dissolved in DMF (30 cm^3) was added in portions to a solution of 3-hexylthiophene (3 g, 0.018 mol) in DMF (50 cm^3) at −20 °C, and the mixture stirred for 5 h while warming to room temperature. The mixture was poured into ice (50 g) and extracted with dichloromethane (3 × 50 cm^3). The combined organic layers were washed with water (2 × 100 cm^3) and dried (Na_2SO_4). Fractional distillation gave the colourless **5** (4.12 g, 70%), bp 142–145 °C, 0.3 mmHg (Found: C, 36.9; H, 4.3. Calc. for $C_{10}H_{14}Br_2S$: 36.8; H, 4.3%); δ_H(250 MHz, $CDCl_3$) 0.91 (3H, t, *J* 7.1, CH_3) 1.28–1.36 (6H, m, 3 × CH_2), 1.54 (2H, m, CH_2), 2.52 (2H, t, *J* 7.2, $ArCH_2$), 6.7 (1H, s, 4-H); δ_C(62.5 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 ($\mathit{C}H_2CH_3$), 28.8, 29.4, 29.5, 31.55 (4 × CH_2), 107.9, 110.3 (2-C, 5-C), 130.9 (4-C), 142.9 (3-C); *m/z* (%) 328 (58, M^+), 326 (100), 324 (56), 255 (46), 177 (79), 175 (77).

Synthesis of 3,3′-dimethyl-2,2′-bithiophene 6

A solution of 2-bromo-3-methylthiophene (5 g, 0.028 mol) in diethyl ether (75 cm^3) was added dropwise over 1 h to magnesium (0.72 g, 0.03 mol) suspended in diethyl ether (25 cm^3). The Grignard reagent was added in small portions to a mixture of 2-bromo-3-methylthiophene (5 g, 0.028 mol) and $[NiCl_2(dppp)]$ (0.1 g) in diethyl ether (100 cm^3) and stirred for

3 h. The reaction was quenched with water (100 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic layers were dried and the solvent removed under reduced pressure. Column chromatography (SiO_2, light petroleum, bp 40–60 °C) gave **6** (3.26 g, 61%) as a colourless liquid, bp 27–29 °C, 0.3 mmHg (Found: C, 62.0; H, 5.1. Calc. for $C_{10}H_{10}S_2$: C, 61.8; H, 5.2%); δ_H(500 MHz, $CDCl_3$) 2.28 (6H, s, CH_3), 7.00 (2H, d, *J* 4.9, 4,4′-H), 7.33 (2H, d, *J* 4.9, 5,5′-H); δ_C(125 MHz, $CDCl_3$) 14.27 (CH_3), 124.9 (5,5′-C), 129.9 (4,4′-C) 129.3 (3.3′-C), 136.3 (2,2′-C); *m/z* (%) 194 (100, M$^+$) 179 (51), 161 (19), 143 (18), 97 (11).

Preparation of 3,3″-dimethyl-2,2′:5′,2″-terthiophene 7

The Grignard derivative of 2-bromo-3-methylthiophene (7.8 g, 0.034 mol) in diethyl ether (150 cm^3) was prepared as before, and added to 2,5-dibromothiophene (18 g, 0.07 mol) and [$NiCl_2$(dppp)] (0.3 g) in diethyl ether (150 cm^3). The mixture was stirred for 3 h at room temperature, before work-up as previously described. TLC indicated a mixture of six compounds. Column chromatography (SiO_2, light petroleum, bp 30–40 °C) allowed the separation of 2,5-dibromothiophene and 2-bromo-3-methylthiophene, as well as **7**. Crystallisation (EtOH) gave pure material (2.8 g, 15%), mp 40–44 °C as a pale yellow opaque solid (Found: C, 60.4; H, 4.55. Calc. for $C_{14}H_{12}S_3$: C, 60.8; H, 4.4%); λ_{max}($CHCl_3$)/nm 276, 344; δ_H(500 MHz, $CDCl_3$) 2.43 (6H, s, CH_3), 6.90 (2H, d, *J* 5.1, 4,4″-H), 7.09 (2H, s, 3′-H, 4′-H), 7.16 (2H, d, *J* 5.1, 5,5″-H); δ_C(125 MHz, $CDCl_3$) 15.43 (CH_3), 123.3 (5,5″-C), 125.7 (3′,4′-C), 130.8 (3,3″-C), 131.4 (4,4″-C), 134.0 (2,2″-C), 136.2 (2′,5′-C); *m/z* (%) 276 (100, M$^+$).

Synthesis of 3′-methyl-2,2′:5′,2″-terthiophene 8

2-Bromomagnesiothiophene was prepared by reacting 2-bromothiophene (6.4 g, 0.039 mol) with Mg (1.87 g, 0.078 mol) in diethyl ether (100 cm^3). This was added to 2,5-dibromo-3-methylthiophene (5 g, 0.019 mol) and [$NiCl_2$(dppp)] (0.1 g) in diethyl ether (100 cm^3), and the mixture stirred for 3 h. The reaction was quenched and worked up as before. Column chromatography (SiO_2, light petroleum, bp 40–60 °C) allowed the successive isolation of 2-bromothiophene, 2,5-dibromo-3-methylthiophene, 2,2′-bithiophene (from Grignard homocoupling) and **8**. On removal of the solvent **8** was initially obtained as a yellow oil, which slowly solidified to long yellow needles, mp 36–37 °C (2.4 g, 48%) (Found: C, 59.8; H, 3.9. Calc. for $C_{13}H_{10}S_3$: C, 59.5; H, 3.8%); λ_{max}($CHCl_3$)/nm 353; δ_H(500 MHz, $CDCl_3$) 2.79 (3H, s, CH_3), 6.99 (1 H, s, 4′-H), 7.02 (1 H, dd, $J_{4'',5''}$ 5.1, $J_{3'',4''}$ 3.5, 4″-H), 7.08 (1H, dd, $J_{4,5}$ 5.1, $J_{3,4}$ 3.5, 4-H), 7.16 (1H, dd, $J_{3,5}$ 1.2, $J_{3,4}$ 3.5, 3-H), 7.17 (1H, dd, $J_{3'',5''}$ 1.1, $J_{3'',4''}$ 3.5, 3″-H), 7.22 (1H, dd, $J_{3'',5''}$ 1.1, $J_{4'',5''}$ 5.1, 5″-H), 7.31 (1H, dd, $J_{3,5}$ 1.1, $J_{4,5}$ 5.1, 5-H); δ_C(125 MHz, $CDCl_3$) 15.5 (CH_3), 123.6 (3″-C), 124.2 (5″-C), 125.0 (5-C), 125.3 (3-C), 127.3 (4-C), 127.91, 127.93 (4′,4″-C), 129.95 (5′-C), 134.5 (3′-C), 134.6 (2′-C), 136.2 (2-C), 137.1 (2″-C) ppm; *m/z* (%) 262 (100, M$^+$), 229 (14), 217 (8), 203 (5), 184 (10), 171 (7).

Synthesis of 3′-hexyl-2,2′:5′,2″-terthiophene 9

2-Bromomagnesiothiophene was prepared as before from 2-bromothiophene (8.18 g, 0.05 mol) and magnesium (1.3 g, 0.054 mol) in diethyl ether (100 cm^3). The solution was added in portions to a mixture of 2,5-dibromo-3-hexylthiophene (8.15 g, 0.025 mol) and [$NiCl_2$(dppp)] (0.2 g) in diethyl ether (150 cm^3). The mixture was stirred for 3 h, then quenched with water (200 cm^3). the organic phase was separated and the aqueous phase extracted with diethyl ether (3 × 50 cm^3). The organic fractions were combined and dried (Na_2SO_4), and the solvent removed under reduced pressure to give a brown oil (8.83 g). Column chromatography (SiO_2, light petroleum, bp 30–40 °C) allowed separation of a mixture of 2-bromothiophene and 2,5-dibromo-3-hexylthiophene (2.08 g), 2,2′-bithiophene (1.16 g, from Grignard homocoupling) and a mixture of three other components. Further chromatography of this mixture (SiO_2, light petroleum, bp 30–40 °C) gave **9** as a viscous green oil (3.32 g, 40%), 2,2′:3′,2″-terthiophene **14** (0.137 g) and 5′-(2-thienyl)-2,2′:3′,2″-terthiophene **15** (1.05 g) the latter two components being identified spectroscopically (*vide infra*) (Found: C, 65.5; H, 6.1. Calc. for $C_{18}H_{20}S_3$: C, 65.0; H, 6.1%); δ_H(500 MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.2, CH_3), 1.31 (4H, m, 2 × CH_2), 1.38 (2H, m, CH_2), 1.66 (2H, m, CH_2), 2.74 (2H, t, *J* 7.9, ArCH_2) 7.04 (1H, dd, $J_{3,4}$ 3.6, $J_{4,5}$ 5.1, 4-H), 7.05 (1H, s, 4′-H), 7.09 (1H, dd, $J_{4'',5''}$ 5.1, $J_{3'',4''}$ 3.6, 4″-H), 7.16 (1H, dd, $J_{3'',5''}$ 1.1, $J_{3'',4''}$ 3.5, 3″-H) 7.19 (1H, dd, $J_{3,5}$ 1.1, $J_{3,4}$ 3.5, 3-H) 7.23 (1H, dd, $J_{3,5}$ 1.1, $J_{4,5}$ 5.1, 5-H), 7.33 (1H, dd, $J_{3'',5''}$ 1.1, $J_{4'',5''}$ 5.1, 5″-H); δ_C(125 MHz, $CDCl_3$) 14.0 (CH_3), 22.6 ($\mathit{C}H_2CH_3$), 29.2 (Ar$\mathit{C}H_2$), 29.3 (Ar$CH_2CH_2\mathit{C}H_2$), 30.5 (Ar$CH_2\mathit{C}H_2$), 31.6 ($\mathit{C}H_2CH_2CH_3$) 123.4 (3″-C), 124.2 (5″-C), 125.2 (5-C), 125.7 (3-C), 126.4 (4′-C), 127.3 (4-C), 127.7 (4″-C), 129.4 (2-C), 135.0 (5′-C), 135.8 (2-C), 137.1 (2″-C), 140.1 (3′-C); *m/z* (%) 332 (100, M$^+$), 261 (55), 227 (15).

2,2′:3′,2″-Terthiophene 14. δ_H(500 MHz, $CDCl_3$) 7.004 (1H, dd, *J* 3.6, 5.2, 4-H or 4″-H), 7.028 (1H, dd, *J* 3.6, 5.1, 4-H or 4″-H), 7.053 (1H, dd, *J* 1.3, 3.6, 3-H or 3″-H), 7.130 (1H, dd, *J* 1.1, 3.6, 3-H or 3″-H), 7.180 (1H, d, *J* 5.3, 4′-H or 5′-H), 7.267 (1H, dd, *J* 1.2, 5.3, 5-H or 5″-H), 7.290 (1H, d, *J* 5.3, 4′-H or 5′-H), 7.324 (1H, dd, *J* 1.2, 5.1, 5-H or 5″-H); *m/z* (%) 248 (M$^+$, 100), 203 (53), 171 (15), 69 (25).

Synthesis of 5′-(2-thienyl)-2,2′:3′,2″-terthiophene 15

2-Bromothiophene (22.57 g, 0.138 mol) in diethyl ether (100 cm^3) was added dropwise to magnesium (3.35 g, 0.138 mol) suspended in diethyl ether (50 cm^3) and stirred under nitrogen for 1 h. The Grignard reagent was added in portions to 2,3,5-tribromothiophene (14.8 g, 0.046 mol) and [$NiCl_2$(dppp)] (0.1 g) in diethyl ether (100 cm^3) and stirred for 3 h. The reaction was then quenched with water (100 cm^3) and the organic phase separated. The aqueous phase was extracted with diethyl ether (3 × 50 cm^3). The combined organic phases were dried (Na_2SO_4), decolourised over charcoal, and the solvent removed under reduced pressure. The product was purified by column chromatography (SiO_2, light petroleum, bp 40–60 °C) and recrystallised from ethanol (12.1 g, 80%), mp 57–58 °C (Found: C, 58.1; H, 3.0. Calc. for $C_{16}H_{10}S_4$: C, 58.15; H, 3.05%); δ_H(500 MHz, $CDCl_3$) 7.029 (1H, dd, $J_{3,4}$ 3.6, $J_{4,5}$ 5.1, 4-H), 7.034 (1H, dd, $J_{3'',4''}$ 3.6, $J_{4'',5''}$ 5.1, 4″-H), 7.055 (1H, dd, $J_{3''',4'''}$ 3.6, $J_{4''',5'''}$ 5.1, 4‴-H), 7.101 (1H, dd, $J_{3'',4''}$ 3.6, $J_{3'',5''}$ 1.2, 3″-H), 7.152 (1H, dd, $J_{3,4}$ 3.6, $J_{3,5}$ 1.2, 3-H), 7.223 (1H, dd, $J_{3''',4'''}$ 3.6, $J_{3''',5'''}$ 1.2, 3‴-H), 7.24 (1H, s, 4′-H), 7.266 (1H, dd, $J_{4''',5'''}$ 5.1, $J_{3''',5'''}$ 1.2, 5‴-H), 7.307 (1H, dd, $J_{4'',5''}$ 5.1, $J_{3'',5''}$ 1,2, 5″-H), 7.317 (1H, dd, $J_{4,5}$ 5.1, $J_{3,5}$ 1.2, 5-H); δ_C(125 MHz, $CDCl_3$) 124.1 (3‴-C), 124.9 (5‴C), 125.7 (5″-C), 126.3 (4′-C), 126.7 (5-C), 126.8 (3″-C), 127.1 (4″-C), 127.2 (4-C), 127.7 (3-C), 127.8 (4‴-C), 130.5 (2′-C), 132.5 (2″-C), 134.7 (2-C), 135.8 (5′-C), 136.5 (2‴-C), 137.0 (3′-C); *m/z* (%) 330 (M$^+$, 100), 296 (18), 285 (33).

Synthesis of 5,5′-dibromo-2,2′-bithiophene 10

In the dark, under an atmosphere of nitrogen, NBS (8.58 g, 0.48 mol) in DMF (50 cm^3) was added in portions to a solution of 2,2′-bithiophene (5 g, 0.024 mol) in DMF (100 cm^3) at −20 °C, and the mixture stirred for 4 h. The mixture was poured onto ice (100 g) and the precipitate collected by filtration and washed with water. Drying over P_2O_5 and recrystallisation (EtOH–hexane) gave 5,5′-dibromo-2,2′-bithiophene **10** as a pale green solid (6.2 g, 80%), mp 145–146 °C (lit.[14] 146 °C); δ_H(500 MHz, $CDCl_3$) 6.85 (2H, d, *J* 3.8, 4-H, 4′-H), 6.96 (2H, d, *J* 3.8, 3-H, 3′-H); *m/z* (%) 326 (61), 324 (100), 322 (55).

Synthesis of 3,3‴-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene 11

2-Bromomagnesio-3-methylthiophene was prepared from 2-bromo-3-methylthiophene (10.9 g, 0.062 mol) as previously described. The Grignard reagent was then added dropwise to a solution of 5,5′-dibromo-2,2′-bithiophene (10 g, 0.031 mol)

Table 6 Crystallographic data for compounds **7**, **8** and **15**[2]

Crystal data	**7**	**8**	**15**
Molecular formula	$C_{14}H_{12}S_3$	$C_{13}H_9S_3$	$C_{16}H_{10}S_4$
M	276.4	261.4	330.5
Crystal system	monoclinic	monoclinic	monoclinic
a/Å	8.072(3)	5.653(6)	15.823(7)
b/Å	14.023(3)	36.977(8)	5.637(2)
c/Å	12.058(2)	17.645(5)	16.373(8)
β/°	107.52(2)	94.54(5)	96.63(4)
V/Å^3	1301.6	3676	1457.3
Parameters for cell determination	25 reflections $8 < \theta < 10°$	25 reflections $8 < \theta < 9°$	25 reflections $7 < \theta < 10°$
λ/Å	0.710 69	0.710 69	0.710 69
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	12	4
D_x/g cm^{-3}	1.41	1.42	1.51
Appearance	Yellow blocks	Pale yellow needles	Yellow needles
Crystal dimensions/mm	0.3 × 0.2 × 0.2 cut from block	0.6 × 0.1 × 0.08 cut from needle	0.4 × 0.1 × 0.05
μ(Mo-Kα)/cm^{-1}	5.5	5.5	6.1
Data collection and processing			
Diffractometer type	CAD4	CAD4	CAD4
Collection method	θ–2θ	θ–2θ	θ–2θ
Radiation	Graphite monochromated Mo-Kα	Graphite monochromated Mo-Kα	Graphite monochromated Mo-Kα
Reflections measured	3475	5105	2059
Independent reflections	3272	4568	1992
R_{int}	0.02	0.04	0.06
Observed reflections	2237	1755	1001
Criterion for observed	$\lvert F^2\rvert > 2\sigma(F^2)$	$\lvert F^2\rvert > 2\sigma(F^2)$	$\lvert F^2\rvert > 2\sigma(F^2)$
h	0→10	0→5	0→16
k	0→18	0→39	0→5
l	−15→15	−18→18	−17→17
$\theta_{min,max}$/°	2, 28	2, 22	2, 22
Max. change in standard reflections (%)	−0.2	−0.6	−0.7
Decay correction	No	No	No
Absorption correction	No	DIFABS[32] max, min 1.29, 0.75	No
T/K	173	293	173
Structure analysis and refinement			
Method, program	Direct, SHELXS-86[33] Enraf-Nonius MolEN[34]	Direct, SHELXS-86[33] Enraf-Nonius MolEN[34]	Direct, SHELXS-86[33] Enraf-Nonius MolEN[34]
Weighting scheme	$\sigma(F^2) = [\sigma^2(I) + 0.04I^2]^{\frac{1}{2}}/Lp$ $w = \sigma^{-2}(F)$ $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ minimised	$\sigma(F^2) = [\sigma^2(I) + 0.04I^2]^{\frac{1}{2}}/Lp$ $w = \sigma^{-2}(F)$ $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ minimised	$\sigma(F^2) = [\sigma^2(I) + 0.04I^2]^{\frac{1}{2}}/Lp$ $w = \sigma^{-2}(F)$ $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ minimised
R	0.041	0.074	0.103
R'	0.045	0.085	0.102
S	1.2	1.8	2.1
Variables	222	243	101
$(\Delta/\sigma)_{max}$	0.01	0.01	0.02
$(\Delta\rho)_{max,min}$/e Å^{-3}	+0.36, −0.14	+0.52, −0.20	+0.96, −0.74

and [$NiCl_2$(dppp)] (0.1 g) in tetrahydrofuran–diethyl ether (1 : 1; 100 cm^3). The reaction mixture was stirred at 23 °C for 3 h, then quenched with water (200 cm^3) and worked up in the usual manner. Removal of the solvent under reduced pressure, followed by charcoal decolourisation, gave **11** (6.2 g, 56%) as a yellow solid, mp 108–109 °C (from hexane) (Found: C, 60.45; H, 3.9; S, 35.95. Calc. for $C_{18}H_{14}S_4$: C, 60.3; H, 3.9; S, 35.8%); δ_H(500 MHz, $CDCl_3$) 2.44 (6H, s, CH_3), 6.90 (2H, d, *J* 5.1, 4-H, 4‴-H), 7.05 (2H, d, *J* 3.7, 4′-H, 3″-H), 7.16 (2H, d, *J* 5.1, 5-H, 5‴-H), 7.14 (2H, d, *J* 3.7, 3′-H, 4″-H); δ_C(125 MHz, $CDCl_3$) 15.49 (CH_3), 123.4 (5-C, 5‴-C), 123.8 (4′-C, 3″-C), 126.0 (3′-C, 4″-C), 130.8 (2-C, 2‴-C), 131.5 (4-C, 4‴-C), 134.1 (3-C, 3‴-C), 135.6 (5′-C, 2″-C), 136.5 (2′-C, 5″-C); *m/z* (%) 358 (M^+, 100).

Polymerisation of 3′-hexyl-2,2′ : 5′,2″-terthiophene 9

3′-Hexyl-2,2′ : 5′,2″-terthiophene (1.6 g, 0.005 mol) in tetrachloromethane (10 cm^3) was added to a suspension of iron(III) chloride (3.12 g, 0.019 mol) in tetrachloromethane (150 cm^3) and stirred for 4 h. The mixture was poured into methanol (500 cm^3), and the precipitate collected. This was extracted with methanol in a Soxhlet apparatus for 52 h. The material was then extracted with chloroform, and choloroform-soluble and -insoluble fractions dried under reduced pressure. For conductivity measurements the materials were pressed into pellets and doped by exposure to iodine under ambient conditions.

Synthesis of poly(3-hexylthiophene)

The method described above was used with 3-hexylthiophene (1 g, 0.006 mol) and iron(III) chloride (4 g, 0.025 mol). After removal of iron(II) chloride, the polymer was dried under reduced pressure to give pristine undoped poly(3-hexylthiophene) (0.69 g, 69%) as a black powder.

Structure of 3,3″-dimethyl-2,2′ : 5′,2″-terthiophene 7

Good quality crystals were obtained by slow evaporation of a hexane solution of **7** at room temperature. Data are given in Table 6. Non-H atoms were refined anisotropically except the lower occupancy sites, which were refined isotropically. H atoms were freely refined isotropically except for the lower occupancy sites, which were omitted. The five-membered ring containing S(3) had 85% occupancy in the orientation shown in

Fig. 2 and 15% occupancy in the orientation related by a 180° rotation about the C(8)–C(9) bond.†

Structure of 3′-methyl-2,2′:5′,2″-terthiophene 8

Good quality crystals were obtained by slow sublimation at atmospheric pressure. Data are given in Table 6. Refinement of sulfur was anisotropic and carbon isotropic. The weakness of the data did not justify anisotropic refinement of C atoms. Hydrogen atoms were fixed at calculated positions with $U_{\mathrm{iso}} = 1.3U_{\mathrm{eq}}$ for parent atom. There are three independent molecules in the asymmetric unit. They have similar geometry except that in molecule C one ring is disordered equally between two orientations related by a 180° rotation about the ring–ring bond. The two sites having 50:50 S/C occupancy were given an average scattering factor and the H-atom involved was omitted.†

Structure of 5′-(2-thienyl)-2,2′:3′,2″-terthiophene 15

Good quality crystals were obtained by slow evaporation from a saturated solution in ethanol. Refinement of sulfur was anisotropic and carbon isotropic. Hydrogen atoms were fixed at calculated positions with $U_{\mathrm{iso}} = 1.3U_{\mathrm{eq}}$ for parent atom. There is disorder in two of the rings. S(2) is disordered 0.6:0.4 between the sites labelled S(2) and C(9), and S(3) is disordered 0.72:0.28 between sites labelled S(3) and C(3). The atoms at these sites were given an average scattering factor, and hydrogen atoms were included at the sites attached to C(3) and C(9) at appropriate occupancies. Because of the disorder, attempts to refine C atoms with anisotropic thermal vibrations resulted in many non-positive definite values.†

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† Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/74.

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