

Formation of Radical Cation and Dication of 1,3,4,6-Tetrakis(isopropylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophene and their Reactions with Nucleophiles

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1,3,4,6-Tetrakis(isopropylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophene **1** formed the complex **2** with I₂ in hexane at -30 °C. The ESR spectrum of the complex **2** in MeCN solution showed that the spin densities in the π-electron system are large in the 1-, 3-, 4- and 6-positions. The complex **2** reacted with amines in MeCN to give the C-C coupling products **4a-c** in high yields. The oxidation of **1** with I₂ in the presence of aniline in benzene gave the thiophene derivative **5** in a high yield by hydrogen abstraction at the 3-position. The compound **1** was oxidised to its dication by NOBF₄. The dication reacted with amines, alcohols and water to give the ring-opening products **10-14** and with thiols and NaBH₄ to give the adducts **23-25**.

2λ⁴δ²-Thieno[3,4-*c*]thiophenes¹⁻⁸ are novel heterocyclic compounds which have a nonclassical structure with 10π-electrons. The elucidation of these physical and chemical properties is an interesting subject. However, the information about the reactivity of this system has been insufficient, since the isolable derivatives have been limited to the 1,3,4,6-tetraphenyl⁴⁻ and 1,3,4,6-tetrathienyl⁶⁻-substituted compounds owing to the lability in the air. Recently we have developed a synthetic method for preparing 1,3,4,6-tetrakis(alkylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophenes⁷ in a stable form, and reported the reactions with electrophiles such as trifluoroacetic acid and Vilsmeier reagent.⁸ Furthermore, we have disclosed that 1,3,4,6-tetrakis(isopropylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophene **1** undergoes one- and two-electron oxidation electrochemically in acetonitrile (MeCN) ($E_{\frac{1}{2}}^1 = +0.19$ V and $E_{\frac{1}{2}}^2 = +0.54$ V vs. saturated calomel electrode)⁹ and is more electron-donating than tetrathiafulvalene.⁹ On the other hand, it has been reported that 1,3,4,6-tetraphenyl-2λ⁴δ²-thieno[3,4-*c*]thiophene is oxidised to 2,5-diphenyl-3,4-dibenzoylthiophene by chromic acid⁴ or by irradiation in the presence of oxygen⁴ and to its cation radical by AlCl₃.¹⁰

To elucidate the physical and chemical properties of an oxidised form of 2λ⁴δ²-thieno[3,4-*c*]thiophenes, we investigated the oxidation of compound **1** by I₂ and nitrosonium tetrafluoroborate (NOBF₄). In this paper, we report that these reactions lead to formation of a radical cation by I₂ and a dication by NOBF₄ and these species react with nucleophiles at the 1-, 3-, 4- or 6-position to lead to the formation of various thiophene derivatives in high yields. The dication of **1** is of interest as the first example of a sulphur analogue of pentalene with 8π-electrons. A part of this study has been reported in our preliminary paper.¹¹

Results and Discussion

Radical Cation of 1,3,4,6-Tetrakis(isopropylthio)-2λ⁴δ²-thieno[3,4-*c*]thiophene.—The reaction of the 2λ⁴δ²-thieno[3,4-*c*]thiophene **1** with I₂ (2 equiv.) under nitrogen in hexane at -30 °C gave the complex **2** (1:I₂ = 1:2) as a black green solid in 97% yield (Scheme 1). The complex **2** was reduced by *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) to regenerate **1** in 75% yield, accompanied by the formation of TMPD^{•+} which was detected by UV-VIS spectroscopy. The ESR spectrum of this complex in MeCN solution at room temperature showed a signal which consisted of five lines due to four equivalent methine protons of the isopropylthio groups, as

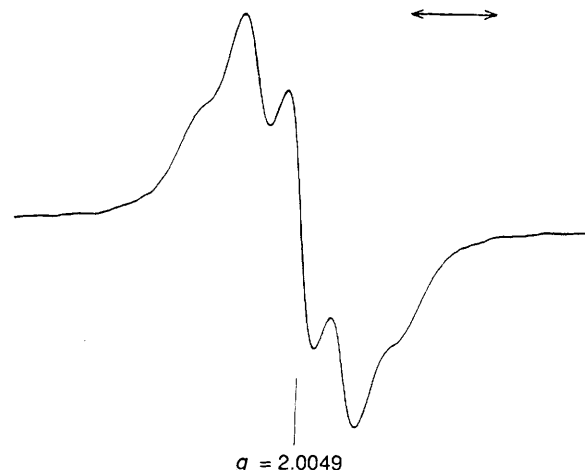
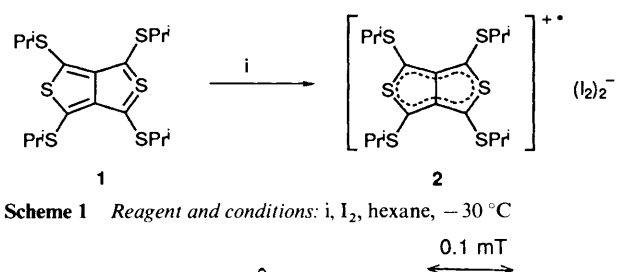
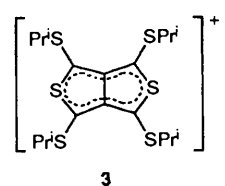


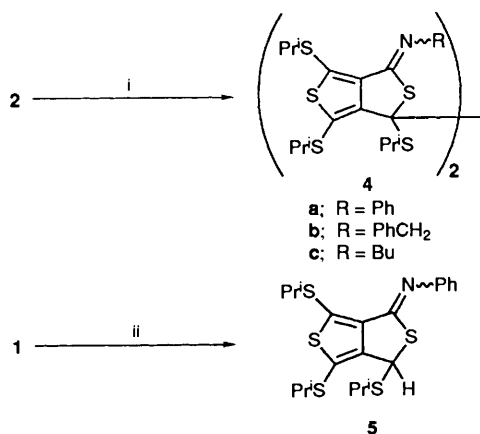
Fig. 1 ESR spectrum of the complex **2** in MeCN solution (room temp.)



shown in Fig. 1. This spectrum was also observed when **1** was added to a solution of I₂ (1 equiv.) or AgClO₄ (1 equiv.) in MeCN, thus indicating the formation of the radical cation **3**. The *g*-value and the hyperfine splitting constant (*a_H*) calculated from the signal were 2.0049 and 0.056 mT respectively. The *g*-value becomes smaller as compared with those of the radical cations of other sulphur-containing π-electron systems, for example, 2,5-bis(methylthio)thiophene (2.00065),¹² thianthrene (2.0081)¹³ and tetrathiafulvalene (2.00838).¹⁴ The hyperfine

splitting constant (a_{SR} , mT) also is smaller than those of the alkylthio-substituted compounds such as 2,5-bis(isopropylthio)thiophene (0.25),¹² 1,4-bis-(methylthio)benzene (0.456)¹⁵ and 1,4- and 2,6-bis(methylthio)naphthalene (0.365 and 0.220 respectively).¹⁶ This result demonstrates that the spin densities of the radical cation **3** are relatively small on the sulphur atoms in the 2- and 5-positions and large on the carbon atoms in the 1-, 3-, 4- and 6-positions. Furthermore, the spin densities of the radical cation **3** were estimated from the HOMO coefficients of **1** to be 0.19 in the 1-, 3-, 4- and 6-positions and zero in the 2- and 5-positions,¹⁷ thus corresponding to those from the ESR spectrum. The UV-VIS spectrum of the complex **2** in dichloromethane solution at room temperature showed the absorptions at λ/nm 291, 360 and 730. The absorption at 730 nm was shifted to a longer wavelength as compared with that of the longest wavelength of **1** (λ/nm 513).

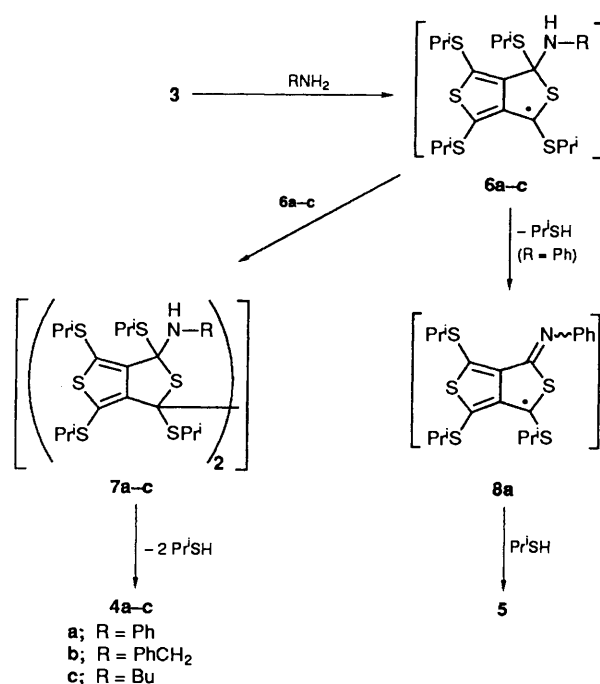
Reaction of Radical Cation with Amines.—The reaction of the complex **2** with aniline, benzylamine and butylamine in MeCN at -30°C gave the thiophene derivatives **4a-c** in 83% yields in all cases (Scheme 2). The formation of **4a-c** indicates that nucleophilic addition of amines to the radical cation **3** occurs at the 1-position and carbon-carbon coupling at the 3-position. Thus, it was found that there is a remarkable difference in reactivity between the radical cations of **1** and sulphur-containing compounds, such as thianthrene,¹⁸ phenoxathiin¹⁹ and phenothiazines,²⁰ in that radical cations react with nucleophiles at the sulphur atom. In relation to this fact, we carried out the reaction of **1** with I_2 in the presence of aniline, benzylamine or butylamine in dry benzene: a solution of I_2 (0.5 equiv.) in benzene was slowly added to a solution of a mixture of **1** and amines (2 equiv.) in benzene at room temperature. In the case of aniline, the thiophene derivative **5** was obtained in quantitative yield without the formation of **4a** (Scheme 2). The



Scheme 2 Reagents and conditions: i, RNH_2 (R = Ph, PhCH₂, Bu), MeCN, -30°C ; ii, PhNH₂, I_2 , C₆H₆, room temp.

¹H NMR spectrum of **5** showed a singlet at δ 5.67 for 3-H. On the other hand, the oxidation of **1** by I_2 did not occur in the presence of benzylamine and butylamine, but **1** was recovered unchanged, since these amines formed a complex with I_2 . The formation of **5** indicates that the attack of amines on the radical cation **3** occurs at the 1-position and the resulting radical species undergoes hydrogen abstraction at the 3-position.

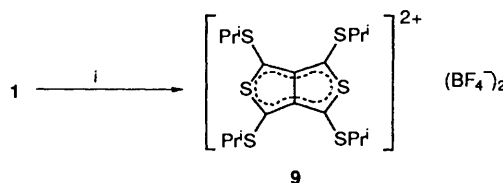
A possible pathway for the formation of **4a-c** and **5** is proposed in Scheme 3. The radical cation **3**, generated by the oxidation of **1** with I_2 , reacts with amines to form the intermediate radicals **6a-c**. The coupling of **6a-c** to form intermediates **7a-c**, followed by elimination of propane-2-thiol, leads to the formation of **4a-c**. When the elimination of propane-2-thiol from **6a** occurs in preference to the C-C coupling probably



Scheme 3

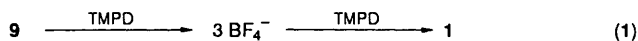
owing to low concentration of **6a**, **5** is considered to be produced from **8a** by the abstraction of hydrogen from the eliminated propane-2-thiol.

Dication of 1,3,4,6-Tetrakis(isopropylthio)-2λ⁴δ²-thieno[3,4-c]thiophene.—The reaction of **1** with NOBF_4 was carried out under nitrogen at -30°C : a solution of NOBF_4 (2 equiv.) in MeCN was added under nitrogen to a suspension of **1** in MeCN. As the reaction proceeded, the reaction mixture became homogeneous. When ether was added to this solution, 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-c]thiophenium bis(tetrafluoroborate) **9** was obtained as a reddish purple solid in 84% yield (Scheme 4). The dication **9** was quite stable under dry

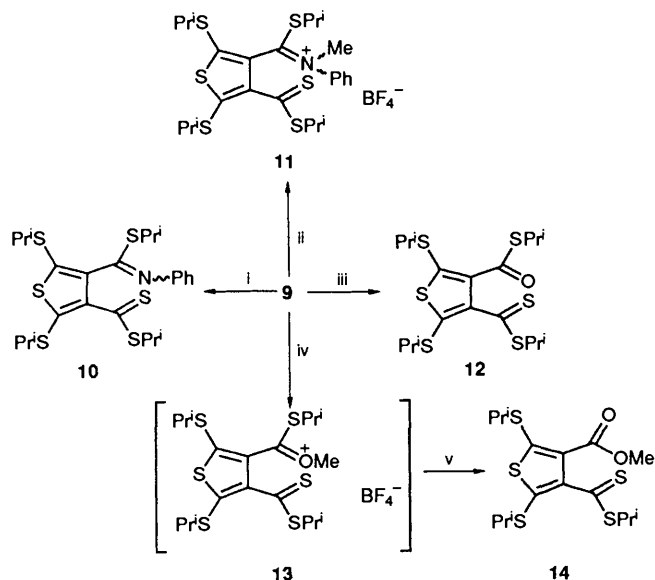


Scheme 4 Reagent and conditions: i, NOBF_4 (2 equiv.), MeCN, -30°C

nitrogen at room temp. The reduction of **9** with TMPD (2 equiv.) in MeCN gave **1** in 73% yield along with $\text{TMPD}^{+\cdot}$. The use of an equimolar amount of TMPD resulted in the formation of the radical cation **3**, which was confirmed by measuring the UV-VIS spectrum of the reaction mixture. The ¹H NMR spectrum of **9** at -30°C exhibited a doublet at δ 1.71 for methyl



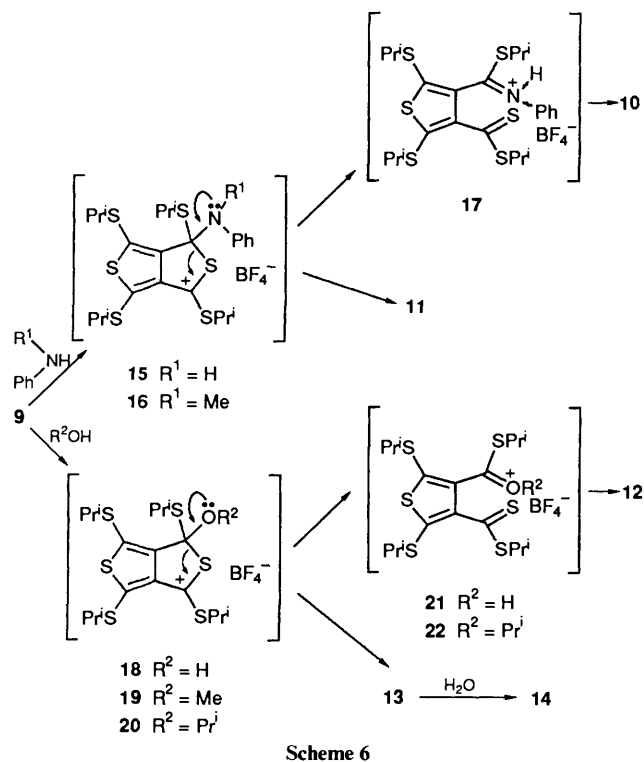
protons and a septet at δ 4.26 for methine protons. Thus, both peaks appeared to lower field compared with those of **1** by 0.42 and 0.82 ppm respectively. Furthermore, the ¹³C NMR spectrum of **9** at -30°C exhibited peaks due to the ring carbons at δ 139.5 for C-1, C-3, C-4 and C-6 and at δ 176.2 for C-3a and C-6a, which were shifted to lower field compared with those of **1** by 23.1 and 25.0 ppm respectively. These downfield shifts are attributable to the delocalization of the positive charge in the π -electron system of **9**. The absorption at the longest wavelength



Scheme 5 Reagents: i, PhNH_2 ; ii, PhNHMe ; iii, Pr^iOH or H_2O ; iv, MeOH ; v, H_2O

in the UV-VIS spectrum of **9** in MeCN solution appeared at λ 579 nm which was intermediate between those of **1** and its radical cation.

Reaction of Dication with Nucleophiles.—Amines, alcohols, water, thiols and NaBH_4 were used as the nucleophiles. The reactions were carried out, under nitrogen, by adding the nucleophiles to a solution of **9** in MeCN at -30°C . After completion of the reaction, MeCN was removed and the products were isolated by the usual method. The reactions with aniline and *N*-methylaniline gave the thiophene derivatives **10** and **11** in 88 and 100% yields, respectively, by ring opening (Scheme 5). The use of isopropyl alcohol and water resulted in the formation of the thiophene derivative **12** in 75 and 98% yields respectively. The reaction with methanol gave the

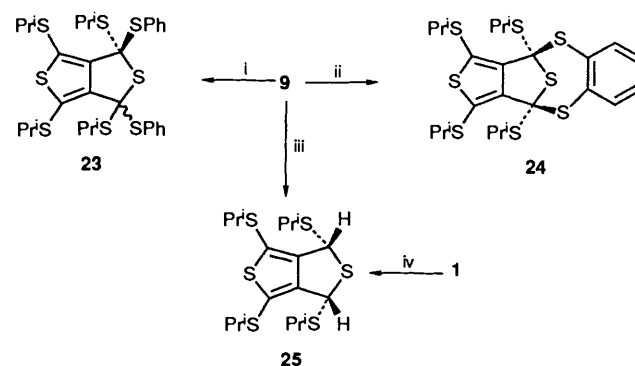


Scheme 6

thiophene derivative **13** in a quantitative yield. The structure of **13** was established by the fact that its ^1H NMR spectrum exhibited three doublets at δ 1.28 (12 H), 1.43 (6 H) and 1.71 (6 H) for non-equivalent methyl protons of four isopropylthio groups, three septets at δ 3.51 (2 H), 3.80 (1 H) and 4.13 (1 H) for non-equivalent methine protons of four isopropylthio groups and a singlet at δ 3.57 for the methyl protons of the methoxy group.

Furthermore, it was confirmed that compound **13** was converted into the thiophene derivative **14** in quantitative yield by treatment with water. Thus, the dication **9** reacted with amines, alcohols and water to bring about the ring opening. The reaction is explained in terms of nucleophilic attack of amines, alcohols and water on the 1-position to form **15**, **16** and **18–20**, followed by the fission of the C(1)–S bond to give **17**, **11**, **21**, **13** and **22**, respectively, as shown in Scheme 6. The intermediates **17** and **21** are converted into **10** and **12**, respectively, by deprotonation, and **22** into **12** by elimination of the isopropyl cation. The reaction of **13** with water leads to the formation of **14**.

On the other hand, the reaction of **9** with benzenethiol,



Scheme 7 Reagents and conditions: i, PhSH ; ii, benzene-1,2-dithiol; iii, NaBH_4 ; iv, $\text{H}_2/\text{Pd-C}$

benzene-1,2-dithiol and NaBH_4 gave the adducts **23**, **24** and **25** in 95, 63 and 95% yields respectively (Scheme 7). The adduct **23** was a 1:1 mixture of *cis* and *trans* isomers, of which the molar ratio was determined by measuring the integral values of the peaks due to the methine protons of the isopropylthio groups in the ^1H NMR spectrum of the isomers. The *cis* configuration of **25** was assigned on the basis of the fact that the ^1H NMR spectrum of **25** agreed with that of the product obtained by the hydrogenation of **1** over Pd-C .⁴ Thus, the C(1)–S bond was not cleaved by the addition of thiols and hydride to the 1-position. This result coincides with that shown for the addition of a proton to **1**.⁸

Conclusions.—Compound **1** is oxidised to the radical cation **3** and the dication **9** by I_2 and NOBF_4 respectively. The radical cation **3** reacts with amines at the 1-position, where there are large spin densities, and the resulting radical species undergo C–C coupling and hydrogen abstraction at the 3-position. On the other hand, the dication **9** reacts with amines, alcohols and water at the 1-position to bring about the fission of the C(1)–S bond, although the reactions with thiols and NaBH_4 lead to the formation of the adducts in the 1- and 3-positions.

Experimental

M.p.s were determined on a Yanaco MP-S3 melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 215 Spectrometer. UV-VIS spectra were obtained on a Shimadzu UV-160 spectrophotometer. ^1H and ^{13}C NMR spectra are recorded on a JEOL JNM-GX270 FT NMR

spectrometer with tetramethylsilane as internal standard; J values are in Hz. Mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 70 eV by a direct-inlet system. ESR spectra were obtained on a JEOL JES-RE2X spectrometer. Column chromatography and preparative TLC (PLC) were carried out with Wacogel C-300 and Merck Kieselgel 60 GF₂₅₄ respectively. All solvents were dried and purified by the usual methods. Aniline, *N*-methylaniline, benzylamine, butylamine and benzenethiol were distilled under reduced pressure. Methanol and isopropyl alcohol were distilled over calcium hydride. Iodine was purified by sublimation. NOBF₄, benzene-1,2-dithiol and NaBH₄ were obtained from a commercial source and were special grade. Compound **1** was prepared according to the method described previously.⁷

1,3,4,6-Tetrakis(isopropylthio)-2λ⁴δ²-thieno[3,4-c]thiophene-Iodine Complex 2.—A solution of I₂ (64 mg, 0.25 mmol) in hexane (50 cm³) was added under nitrogen to a solution of **1** (50 mg, 0.11 mmol) in hexane (150 cm³) at -30 °C and the mixture was stirred for 0.5 h. The precipitate was collected by filtration, washed with hexane and dried *in vacuo* to give the complex **2** (105 mg, 97%) as a black green solid, m.p. 38 °C (decomp.) (Found: C, 23.1; H, 2.95. C₁₈H₂₈I₄S₆ requires C, 22.8; H, 2.9%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2950 (CH), 1500, 1420, 1370, 1305, 1245, 1205, 1155, 1110, 1050, 1010, 950, 875, 830, 810, 730 and 670; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 291 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.92), 363 (4.55) and 730 (4.11).

Reduction of Complex 2 with TMPD.—TMPD (tetramethyl-*p*-phenylenediamine) (87 mg, 0.53 mmol) was directly added under nitrogen to a solution of the complex **2** (50 mg, 0.053 mmol) in MeCN (5 cm³) at room temperature and the mixture was stirred for 0.5 h. The precipitate was collected by filtration, washed with MeCN and dried *in vacuo* to give **1** (17 mg, 75%). Compound **1** was identified by comparison with the ¹H NMR spectrum of an authentic sample. The UV-VIS spectrum of the filtrate showed absorption at λ/nm 526, 563 and 613 which was assigned to TMPD^{•+}.

ESR Spectrum of Complex 2 in MeCN Solution.—Complex **2** (1 mg) was dissolved under argon in degassed MeCN (1 cm³) at -30 °C and the spectrum was measured at room temperature. The g -value and the hyperfine splitting constant were determined by comparison with those of 1,1-diphenyl-2-picrylhydrazyl and potassium nitrosodisulphonate. The ESR spectrum of **1** in MeCN solution containing I₂ or AgClO₄ was measured as follows. I₂ (0.6 mg, 0.002 mmol) or AgClO₄ (0.5 mg, 0.002 mmol) was added under argon to a suspension of **1** (1 mg, 0.002 mmol) in degassed MeCN (1 cm³) at -30 °C. The spectrum of this solution was measured at room temperature. The spectrum was the same as that of complex **2** in MeCN solution.

Reaction of Complex 2 with Amines.—**General procedure.** Aniline (50 mg, 0.54 mmol), benzylamine (41 mg, 0.13 mmol) or butylamine (38 mg, 0.083 mmol) was added under nitrogen to a solution of complex **2** (44 mg, 0.054 mmol) in MeCN (6 cm³) at -30 °C. After being stirred for 4 h, the mixture was evaporated to dryness under reduced pressure. The residue was separated by PLC [dichloromethane-hexane (2:3)] to give the thiophene derivatives **4a-c**.

***N,N'*-Diphenyl-1,1',4,4',6,6'-hexakis(isopropylthio)[1,1'-bithieno[3,4-c]thiophene]-3,3'(1H,1'H)-diimine 4a** (30 mg, 83%): pale yellow oil, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3050, 2960 and 2855 (CH), 1620 (C=N), 1585, 1510, 1485, 1440, 1380, 1365, 1265, 1240, 1215, 1150, 1050, 1030, 990, 845, 760 and 730; $\lambda_{\max}(\text{hexane})/\text{nm}$ 253 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.52) and 350sh (4.11); $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.15 (6 H, d, J 6.7, 2 × SCHMeMe), 1.29 (6 H, d, J 6.7,

2 × SCHMeMe), 1.39 and 1.40 (each 12 H, d, J 6.7, 2 × SCHMe₂), 3.03, 3.49 and 3.56 (each 2 H, sep, J 6.7, 2 × SCHMe₂) and 6.90–7.34 (10 H, m, 2 × Ph); $\delta_{\text{C}}(270 \text{ MHz}; \text{CDCl}_3)$ 14.12, 22.65, 23.16, 23.38, 23.44, 23.62, 23.91, 24.59, 31.59, 39.43, 40.16, 40.85, 81.31, 120.67, 124.47, 128.98, 151.20 and 157.24; m/z 453 [(M⁺/2) + 1] (Found: C, 55.8; H, 5.9; N, 3.0. C₄₂H₅₂N₂S₁₀ requires C, 55.7; H, 5.7; N, 3.0%).

***N,N'*-Dibenzyl-1,1',4,4',6,6'-hexakis(isopropylthio)[1,1'-bithieno[3,4-c]thiophene]-3,3'(1H,1'H)-diimine 4b** (41 mg, 83%): pale yellow oil, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3070–2860 (CH), 1627 (C=N), 1513, 1496, 1380, 1362, 1238, 1150, 1035, 720 and 695; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 247 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 5.00) and 346 (4.07); $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.22, 1.27, 1.28, 1.31, 1.33 and 1.39 (each 6 H, d, J 6.7, 2 × SCHMeMe), 2.99, 3.59 and 3.61 (each 2 H, sep, J 6.7, 2 × SCHMe₂), 4.48–4.56 (4 H, br dd, 2 × CH₂Ph) and 7.18–7.44 (10 H, m, 2 × Ph); m/z 467 [(M⁺/2) + 1] (Found: C, 56.3; H, 6.0; N, 2.7. C₄₄H₅₆N₂S₁₀ requires C, 56.6; H, 6.05; N, 3.0%).

***N,N'*-Dibutyl-1,1',4,4',6,6'-hexakis(isopropylthio)[1,1'-bithieno[3,4-c]thiophene]-3,3'(1H,1'H)-diimine 4c** (38 mg, 83 mmol): pale yellow oil, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2960–2855 (CH), 1625 (C=N), 1510, 1445, 1380, 1360, 1240, 1150, 1050, 1030, 995 and 950; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 247 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.48) and 342 (4.01); $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 0.93 (6 H, t, J 7.3, 2 × Me), 1.14–1.48 (44 H, m, 6 × SCHMe₂ and 2 × CH₂CH₂), 1.57–1.72 (4 H, m, 2 × =NCH₂) and 2.91–3.08, 3.20–3.35 and 3.56 (each 2 H, br sep, J 6.7, 2 × SCHMe₂); m/z 433 [(M⁺/2) + 1] (Found: C, 52.9; H, 7.1; N, 3.3. C₃₈H₆₀N₂S₁₀ requires C, 52.7; H, 6.9; N, 3.2%).

Reaction of 1 with I₂ in the Presence of Aniline.—A solution of I₂ (17 mg, 0.068 mmol) in dry benzene (5 cm³) was added under nitrogen to a solution of a mixture of **1** (50 mg, 0.11 mmol) and aniline (21 mg, 0.23 mmol) in benzene (10 cm³) at room temperature. The mixture was stirred for 1 h and the solvent was evaporated under reduced pressure. The residue was separated by PLC [dichloromethane-hexane (2:3)] to give *N*-phenyl-1,4,6-tris(isopropylthio)thieno[3,4-c]thiophene-3(1H)-imine **5** as pale yellow oil (52 mg, 100%), $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3050, 2960, 2910 and 2855 (CH), 1620 (C=N), 1580, 1520, 1485, 1440, 1380, 1365, 1240, 1220, 1150, 1050, 1015, 990, 905, 840, 765 and 725; $\lambda_{\max}(\text{hexane})/\text{nm}$ 253 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.42) and 335 (4.00); $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.21, 1.33, 1.34, 1.35, 1.45 and 1.51 (each 3 H, d, J 6.7, SCHMeMe), 3.15, 3.35 and 3.62 (1 H, sep, J 6.7, SCHMe₂), 5.67 (1 H, s, 1-H) and 7.06–7.38 (5 H, m, Ph); $\delta_{\text{C}}(270 \text{ MHz}; \text{CDCl}_3)$ 22.67, 23.08, 23.22, 23.56, 23.64, 23.72, 36.50, 40.06, 42.20, 49.46, 120.49, 124.74, 125.38, 129.02, 137.84, 138.95, 150.89, 151.42 and 157.77; m/z 453 (M⁺) (Found: C, 55.8; H, 6.3; N, 3.1. C₂₁H₂₇NS₅ requires C, 55.5; H, 6.0; N, 3.0%).

1,3,4,6-Tetrakis(isopropylthio)thieno[3,4-c]thiophenium Bis-(tetrafluoroborate) 9.—A solution of NOBF₄ (177 mg, 1.51 mmol) in MeCN (20 cm³) was added under nitrogen to a suspension of **1** (300 mg, 0.688 mmol) in MeCN (7.5 cm³) at -30 °C. A blue-purple colour appeared and the mixture became homogeneous. After being stirred for 1 h at -30 °C, dry ether (200 cm³) was added to the reaction mixture. The precipitate was collected by filtration, washed with MeCN and dried *in vacuo* to give the dication **9** as a reddish purple solid (350 mg, 84%); m.p. 147–148 °C (decomp.) (Found: C, 35.2; H, 4.7. C₁₈H₂₈B₂F₈S₆ requires C, 35.4; H, 4.6%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2975, 2925 and 2860 (CH), 1470, 1375, 1310, 1250, 1100–1000 and 980; $\lambda_{\max}(\text{MeCN})/\text{nm}$ 274 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.34), 295 (4.45), 418 (4.24) and 579 (4.51); $\delta_{\text{H}}(270 \text{ MHz}; \text{CD}_3\text{CN}; -30 \text{ }^\circ\text{C})$ 1.71 (24 H, d, J 6.7, 4 × SCHMe₂) and 4.26 (4 H, br sep, J 6.7, 4 × SCHMe₂); $\delta_{\text{C}}(270 \text{ MHz}; \text{CD}_3\text{CN}; -30 \text{ }^\circ\text{C})$ 22.42, 51.25, 139.49 and 176.24.

Reduction of the Dication 9 with TMPD.—TMPD (29 mg, 0.18 mmol) was added under nitrogen to a solution of **9** (50 mg, 0.082 mmol) in MeCN (5 cm³) at -30 °C and the mixture was stirred for 0.5 h. The precipitate was collected by filtration, washed with MeCN and dried *in vacuo* to give **1** as a red solid (26 mg, 73%). When equimolar amount of TMPD was used, **1** did not precipitate under similar conditions. The UV-VIS spectrum of this reaction mixture exhibited absorption due to the radical cation **3** at 730 nm.

Reaction of the Dication 9 with Amines.—Aniline (149 mg, 1.6 mmol) or *N*-methylaniline (176 mg, 1.6 mmol) was added under nitrogen to a solution of **9** (100 mg, 0.16 mmol) in MeCN (10 cm³) at -30 °C and the mixture was stirred for 0.5 h. The solvent was evaporated to dryness under reduced pressure. The crude products **10** and **11** were purified by column chromatography on silica gel with dichloromethane-hexane (1:1) and dichloromethane-methanol (10:1) as eluent respectively.

Isopropyl 2,5-bis(isopropylthio)-4-(isopropylthio)-*N*-phenyliminomethylthiophene-3-carbodithioate 10 (74 mg, 88%): pale yellow oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3060, 2975, 2925 and 2875 (CH), 1600 (C=N), 1490, 1470, 1390, 1370, 1250, 1220, 1185, 1160, 1115, 1090, 1055, 1000, 950, 905, 880, 845, 825, 765 and 740; $\lambda_{\max}(\text{MeCN})/\text{nm}$ 275 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.00) and 300 (3.92); $\delta_{\text{H}}[270 \text{ MHz}; (\text{CD}_3)_2\text{SO}; 100^\circ\text{C}]$ 1.21–1.27 (18 H, br m, 3 \times SCHMe₂), 1.42 (6 H, d, *J* 6.7, SCHMe₂), 3.32 (2 H, sep, *J* 6.7, 2 \times SCHMe₂), 3.4–3.6 (1 H, br sep, *J* 6.7, SCHMe₂), 4.01 (1 H, sep, *J* 6.7, SCHMe₂) and 6.84–7.20 (5 H, m, Ph); *m/z* 527 (M⁺) (Found: C, 54.9; H, 6.4; N, 2.8. C₂₄H₃₃NS₆ requires C, 54.6; H, 6.3; N, 2.7%).

***N*-{[Isopropylthio]-[2,5-bis(isopropylthio)-4-isopropylthio-(thiocarbonyl)-3-thienyl]methylene}-*N*-methyl-*N*-phenylammonium tetrafluoroborate 11** (108 mg, 100%): pale yellow oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 2975, 2930 and 2860 (CH), 1550 (C=N⁺), 1450, 1390, 1365, 1240, 1165, 1110–1000, 945, 870, 845, 775, 765, 730 and 700; $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 283 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.32); $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.22, 1.24, 1.35, 1.40, 1.50, 1.54, 1.57 and 1.60 (each 3 H, d, *J* 6.7, SCHMeMe), 3.20, 3.47 and 3.76 (each 1 H, sep, *J* 6.7, SCHMe₂), 3.85 (3 H, s, Me), 4.17 (1 H, sep, *J* 6.7, SCHMe₂) and 7.33–7.72 (5 H, m, Ph); $\delta_{\text{C}}(270 \text{ MHz}; \text{CDCl}_3)$ 21.08, 21.16, 22.25, 22.95, 23.40, 23.58, 23.74, 25.08, 42.60, 43.63, 43.82, 45.17, 49.07, 123.56, 130.40, 131.45, 131.75, 141.58, 141.66, 145.86, 188.76 (C=N⁺) and 217.36 (C=S) (Found: C, 48.0; H, 5.9; N, 2.5. C₂₅H₃₆BF₄NS₆ requires C, 47.7; H, 5.8; N, 2.2%).

Reaction of the Dication 9 with Isopropyl Alcohol.—Isopropyl alcohol (50 mg, 0.82 mmol) was added under nitrogen to a solution of **9** (50 mg, 0.082 mmol) in MeCN (5 cm³) at -30 °C and the mixture was stirred for 24 h. The solvent was removed under reduced pressure. Column chromatography of the residue with dichloromethane-hexane (1:1) as eluent yielded *S*-isopropyl 2,5-bis(isopropylthio)-4-(isopropylthio)thiocarbonylthiophene-3-carbodithioate **12** as an orange oil (28 mg, 75%), $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2960, 2925 and 2875 (CH), 1690 (C=O), 1450, 1390, 1370, 1245, 1200, 1160, 1085, 1050, 985, 960, 880, 825 and 760; $\lambda_{\max}(\text{MeCN})/\text{nm}$ 253 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.09) and 323 (4.01); $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.28, 1.33, 1.34 and 1.44 (each 6 H, d, *J* 6.7, SCHMe₂) and 3.32, 3.38, 3.78 and 4.07 (each, 1 H, sep, *J* 6.7, SCHMe₂); $\delta_{\text{C}}(270 \text{ MHz}; \text{CDCl}_3)$ 21.04, 22.66, 23.18, 35.83, 42.07, 42.34, 42.55, 134.44, 138.67, 141.55, 148.37, 188.29 (C=O) and 221.09 (C=S); *m/z* 452 (M⁺) (Found: C, 47.9; H, 6.5. C₁₈H₂₈OS₆ requires C, 47.75; H, 6.2%).

Reaction of the Dication 9 with Water.—A solution of **9** (50 mg, 0.082 mmol) in MeCN (5 cm³) was poured into water (50 cm³) at room temperature. The mixture was extracted with dichloromethane and the extract dried (Na₂SO₄) and evaporated under reduced pressure. The residue was chromatographed

on silica gel with dichloromethane-hexane (1:1) as eluent to give **12** (36 mg, 98%).

Reaction of the Dication 9 with Methanol.—Methanol (26 mg, 0.82 mmol) was added under nitrogen to a solution of **9** (50 mg, 0.082 mmol) in MeCN (5 cm³) at -30 °C and the mixture was stirred for 5 min. The solvent was then evaporated under reduced pressure to give the reddish oil **13**; $\delta(270 \text{ MHz}; \text{CDCl}_3)$ 1.28 (12 H, d, *J* 6.7, 2 \times SCHMe₂), 1.43 and 1.71 (each 6 H, d, *J* 6.7, SCHMe₂), 3.51 (2 H, sep, *J* 6.7, 2 \times SCHMe₂), 3.57 (3 H, s, OMe) and 3.80 and 4.13 (each 1 H, sep, *J* 6.7, SCHMe₂). As this spectrum changed gradually to that of the compound **12** by reaction with moisture, compound **13** could not be isolated in a pure form. The reaction mixture was poured into water, without removal of the solvent, and extracted with dichloromethane. The extract was dried (Na₂SO₄) and evaporated under reduced pressure. Column chromatography of the residue on silica gel with dichloromethane-hexane (2:3) gave *methy*l 2,5-bis(isopropylthio)-4-(isopropylthio)thiocarbonylthiophene-3-carboxylate **14** as orange oil (33 mg, 99%), $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2950, 2920 and 2860 (CH), 1700 (C=O), 1430, 1390, 1360, 1245, 1230, 1140, 1040, 985, 945, 780 and 700; $\lambda_{\max}(\text{MeCN})/\text{nm}$ 260 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.00) and 311 (4.08); $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.27, 1.41 and 1.45 (each 6 H, d, *J* 6.7, SCHMe₂), 3.28 and 3.48 (each 1 H, sep, *J* 6.7, SCHMe₂), 3.73 (3 H, s, OMe) and 4.10 (1 H, sep, *J* 6.7, SCHMe₂); $\delta_{\text{C}}(270 \text{ MHz}; \text{CDCl}_3)$ 21.12, 23.16, 40.54, 41.76, 42.70, 51.68, 129.35, 130.23, 147.52, 150.61, 162.82 (C=O) and 223.56 (C=S); *m/z* 408 (M⁺) (Found: C, 47.1; H, 6.0. C₁₆H₂₄O₂S₅ requires C, 47.0; H, 5.9%).

Reaction of the Dication 9 with Thiols.—Benzenethiol (19 mg, 0.18 mmol) or benzene-1,2-dithiol (14 mg, 0.098 mmol) was added under nitrogen to a solution of **9** (50 mg, 0.082 mmol) in MeCN (5 cm³) at -30 °C and the mixture was stirred for 2 h. The solvent was evaporated under reduced pressure and column chromatography of the residue with dichloromethane-hexane (1:1) as eluent gave the adducts **23** or **24**.

cis- and trans-1,3-Dihydro-1,3,4,6-tetrakis(isopropylthio)-1,3-bis(phenylthio)thieno[3,4-c]thiophene 23 (48 mg, 95%): white solid; m.p. 110–115 °C (Found: C, 55.2; H, 6.0. C₃₀H₃₈S₈ requires C, 55.0; H, 5.8%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2960, 2920 and 2860 (CH), 1440, 1385, 1365, 1245, 1155, 1120, 1050, 830 and 755; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.07, 1.15, 1.24, 1.29 and 1.32 (each 6 H, d, *J* 6.7, 2 \times SCHMeMe), 1.42 (12 H, d, *J* 6.7, 4 \times SCHMeMe), 1.43 (6 H, d, *J* 6.7, 2 \times SCHMeMe), 2.98 (2 H, sep, *J* 6.7, 2 \times SCHMe₂), 3.28 (2 H, sep, *J* 6.7, 2 \times SCHMe₂), 3.45 (2 H, sep, *J* 6.7, 2 \times SCHMe₂), 3.46 (2 H, sep, *J* 6.7, 2 \times SCHMe₂) and 7.20–7.50 (20 H, m, 4 \times Ph); *m/z* 655 (M⁺).

4,11-Dihydro-1,3,4,11-tetrakis(isopropylthio)-4,11-epithiothieno[3,4-h][5,10]benzodithiocine 24 (30 mg, 63%): colourless oil, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2925 (CH), 1430, 1385, 1370, 1250, 1160, 1055 and 755; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 1.33 (6 H, d, *J* 6.7, 2 \times SCHMeMe), 1.34 (12 H, d, *J* 6.7, 2 \times SCHMe₂), 1.45 (6 H, d, *J* 6.7, 2 \times SCHMeMe), 3.33 and 3.39 (each 2 H, sep, *J* 6.7, 2 \times SCHMe₂) and 7.17–7.15 (4 H, m, Ph); $\delta_{\text{C}}(270 \text{ MHz}; \text{CDCl}_3)$ 23.32, 23.80, 24.96, 39.09, 41.53, 69.71, 126.72, 128.84, 135.67, 140.58 and 147.48; *m/z* 500 (M⁺ - C₆H₄) (Found: C, 50.2; H, 5.7. C₂₄H₃₂S₈ requires C, 49.95; H, 5.6%).

Reaction of the Dication 9 with NaBH₄.—NaBH₄ (31 mg, 0.82 mmol) was directly added under nitrogen to a solution of **9** (50 mg, 0.082 mmol) in MeCN (5 cm³) at -30 °C. After being stirred for 0.5 h, the mixture was poured into water and extracted with dichloromethane. The extract was dried (Na₂SO₄) and evaporated under reduced pressure and the residue was chromatographed on silica gel with dichloromethane-hexane (1:1) to give *cis*-1,3-dihydro-1,3,4,6-tetrakis(isopropylthio)thieno[3,4-c]thiophene **25** as colourless oil (34 mg, 95%),

$\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2950, 2920 and 2855 (CH), 1460, 1380, 1365, 1245, 1155, 1050 and 805; $\delta_{\text{H}}(270 \text{ MHz, CDCl}_3)$ 1.30 (6 H, d, J 6.7, $2 \times \text{SCHMeMe}$), 1.32 (12 H, d, J 6.7, $2 \times \text{SCHMe}_2$), 1.36 (6 H, d, J 6.7, $2 \times \text{SCHMeMe}$), 3.55 and 3.37 (each 2 H, sep, J 6.7, $2 \times \text{SCHMe}_2$) and 5.46 (2 H, s, 1- and 3-H); $\delta_{\text{C}}(270 \text{ MHz; CDCl}_3)$ 23.50, 23.60, 23.75, 37.23, 41.88, 51.66, 128.44 and 150.17; m/z 438 (M^+) (Found: C, 49.4; H, 6.9. $\text{C}_{18}\text{H}_{30}\text{S}_6$ requires C, 49.2; H, 6.9%).

Reduction of 1 by Catalytic Hydrogenation.—The reaction was carried out according to the method described in the literature.⁴ A solution of **1** (100 mg, 0.23 mmol) in benzene (100 cm^3) was vigorously stirred for 12 h under hydrogen in the presence of 5% palladium–charcoal (1 g) at room temperature. The catalyst was filtered off and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel to give **25** (80 mg, 80%).

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Area No. 03214103 from the Ministry of Education, Science and Culture, Japanese Government.

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Paper 1/03910E

Received 29th July 1991

Accepted 8th August 1991