New Stable Dication of 1,3,4,6-Tetrakis(isopropylthio)-2λ^4,δ^2-thieno[3,4-*c*]thiophene generated by its Oxidation using Nitrosonium Tetrafluoroborate

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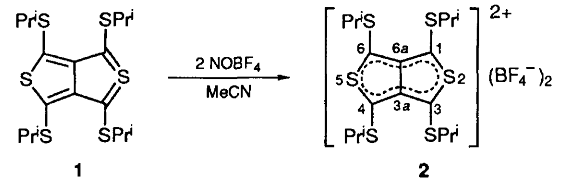
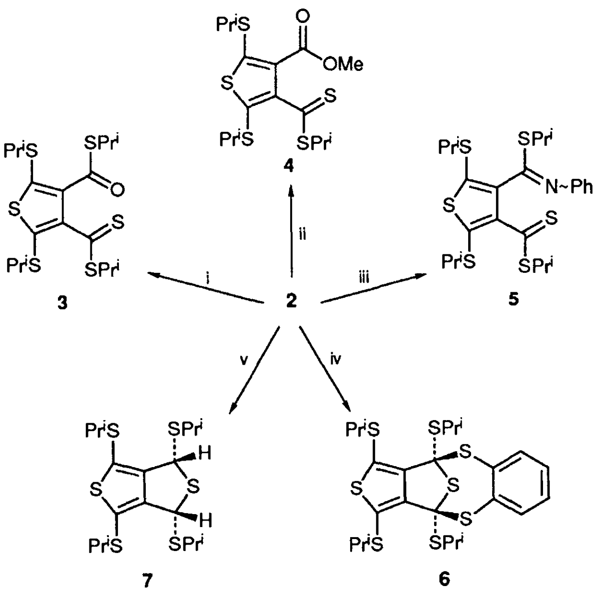
The oxidation of 1,3,4,6-tetrakis(isopropylthio)-2λ^4,δ^2-thieno[3,4-*c*]thiophene **1** by $NOBF_4$ (2 equiv.) gives the dication **2**, which reacts with H_2O, MeOH and aniline to give the thiophene derivatives **3**–**5** by fission of the C–S bond of the thieno[3,4-*c*]thiophene ring; **2** also reacts with 1,2-dimercaptobenzene and $NaBH_4$ to give the adducts **6** and **7** respectively.

1,3,4,6-Tetrakis(alkylthio)-2λ^4,δ^2-thieno[3,4-*c*]thiophenes[1] are interesting compounds which have a nonclassical structure with 10 π-electrons. Previously we have disclosed that the cyclic voltammogram of 1,3,4,6-tetrakis(isopropylthio)-2λ^4, δ^2-thieno[3,4-*c*]thiophene **1** in MeCN shows two redox waves with oxidation potentials at $E_1 = +0.19$ V and $E_2 = +0.54$ V *vs.* saturated calomel electrode (SCE) and **1** is more electron-donating than tetrathiafulvalene.[2] These findings led us to oxidise **1** chemically to its dication which is an unknown sulphur analogue of pentalene with 8 π-electrons. We now report a new stable dication, 1,3,4,6-tetrakis(isopropylthio)-thieno[3,4-*c*]thiophenium bis(tetrafluoroborate) **2**, which is prepared from **1** by a two-electron oxidation using nitrosonium tetrafluoroborate, $NOBF_4$, as the oxidant (Scheme 1). Furthermore, we describe that the reaction of **2** with H_2O, MeOH and aniline gives the thiophene derivatives **3**–**5** by the



Scheme 1



Scheme 2 *Reagents and conditions*: i, H_2O (large excess), room temp., 1 h; ii, MeOH (10 equiv.), −30 °C, 2 h; iii, $PhNH_2$ (10 equiv.), −30 °C, 0.5 h; iv, 1,2-dimercaptobenzene (1.2 equiv.), −30 °C, 1 h; v, $NaBH_4$ (10 equiv.), −30 °C, 2 h

fission of the C–S bond of the thieno[3,4-*c*]thiophene ring and that reaction with 1,2-dimercaptobenzene and $NaBH_4$ gives the adducts **6** and **7** respectively.

The reaction of **1** with $NOBF_4$ was carried out as follows. A solution of $NOBF_4$ (177 mg, 1.51 mmol) in MeCN (20 ml) was added under nitrogen to a suspended solution of **1** (300 mg, 0.688 mmol) in MeCN (7.5 ml) at −30 °C. A blue-purple colour appeared immediately and the mixture became homogeneous. After stirring for 1 h at −30 °C, dry Et_2O (200 ml) was added to the reaction mixture. The precipitate was filtered off, washed with ether and dried under vacuum to give the dication **2** (350 mg, 84%) as a reddish-purple solid [m.p. 147–148 °C (decomp.)].† The formation of the dication **2** indicates that the addition of NO^+ to the 1-position of **1** does not occur. The dication **2** was quite stable under nitrogen at room temperature. The ^1H NMR spectrum of **2** at −30 °C exhibited a doublet for methyl protons and a septet for methine protons at lower field than those of **1** by 0.42 and 0.82 ppm respectively. Furthermore, the peaks of the ring carbons of **2** in its ^{13}C NMR spectrum at −30 °C also appeared at lower field than those of **1** by 23.1 and 25.0 ppm respectively. These downfield shifts are attributable to the positive charge delocalised in a π-electron system of **2**. In the UV–VIS spectrum of **2** in MeCN, the absorption peak at the longest wavelength was shifted 84 nm to a longer wavelength than that of **1** (513 nm).

The dication **2** was reduced by *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) (2 equiv.) in MeCN to give **1** in 73% yield by the transfer of two electrons, accompanied by the formation of $TMPD^{+\cdot}$ which was confirmed by the measurement of the UV–VIS spectrum [eqn. (1)]. The

$$\mathbf{2} + 2\,\text{TMPD} \xrightarrow[\text{MeCN}]{} \mathbf{1} + 2\,\text{TMPD}^{+\cdot}\text{BF}_4^- \qquad (1)$$

reaction of **2** with various nucleophiles was carried out under nitrogen in MeCN (Scheme 2). It was found that the dication **2** reacts readily with H_2O, MeOH and aniline to give the ring-opening products **3**, **4** and **5** in 98, 99 and 88% yields respectively.† This reaction is considered to proceed by the attack of the nucleophiles on the 1-position of **2**, followed by the fission of the C(3)–S bond of the ring. When 1,2-dimercaptobenzene and $NaBH_4$ were used, the adducts **6** and **7** were obtained in 63 and 95% yields respectively.†

Thus, the present results provide evidence for the formation of the stable dication **2** in the reaction of **1** with $NOBF_4$.

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† *Selected spectroscopic data*: Compound **2**: ^1H NMR (CD_3CN, −30 °C) δ 1.71 (24H, d), 4.26 (4H, br sept.); ^{13}C NMR (CD_3CN, −30 °C) δ 22.4, 51.2, 139.5, 176.2; UV–VIS (MeCN) λ_{max} 274 (log ε 4.34), 295 (4.45), 418 (4.24), 579 nm (4.51); satisfactory elemental analysis was obtained.

Compound **3**: ^1H NMR ($CDCl_3$) δ 1.28 (6H, d), 1.33 (6H, d), 1.34 (6H, d), 1.44 (6H, d), 3.32 (1H, sept.), 3.38 (1H, sept.), 3.78 (1H, sept.), 4.07 (1H, sept.); IR ν_{max}/cm^{-1} (neat) 1690 (C=O); *m/z* 452 (M^+).

Compound **4**: ^1H NMR ($CDCl_3$) δ 1.27 (6H, d), 1.41 (6H, d), 1.45 (6H, d), 3.28 (1H, sept.), 3.48 (1H, sept.), 3.73 (3H, s), 4.10 (1H, sept.); IR ν_{max}/cm^{-1} (neat) 1700 (C=O); *m/z* 408 (M^+).

Compound **5**: ^1H NMR [$(CD_3)_2SO$, 100 °C] δ 1.23 (6H, d), 1.25 (6H, d), 1.42 (6H, d), 3.32 (1H, sept.), 3.4–3.6 (1H, br sept.), 4.01 (1H, sept.), 6.84 (2H, d), 6.99 (1H, t), 7.20 (2H, t); IR ν_{max}/cm^{-1} (neat) 1600 (C=N); *m/z* 527 (M^+).

Compound **6**: ^1H NMR ($CDCl_3$) δ 1.33 (6H, d), 1.34 (12H, d), 1.45 (6H, d), 3.33 (2H, sept.), 3.39 (2H, sept.), 7.17 (2H, dd), 7.51 (2H, dd); *m/z* 500 (M^+ − 76).

Compound **7**: ^1H NMR ($CDCl_3$) δ 1.30 (6H, d), 1.32 (12H, d), 1.36 (6H, d), 3.35 (2H, sept.), 3.37 (2H, sept.), 5.46 (2H, s); *m/z* 438 (M^+). The *cis* configuration of **7** was assigned on the basis of the fact that the ^1H NMR spectrum of **7** agreed with that of the product prepared by the hydrogenation of **1** over Pd/C catalyst.[3]