

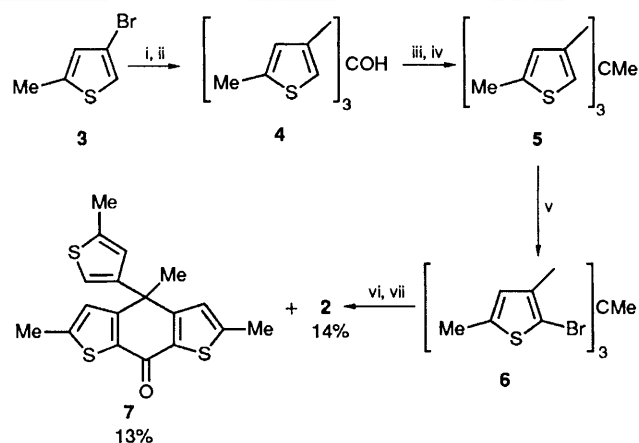
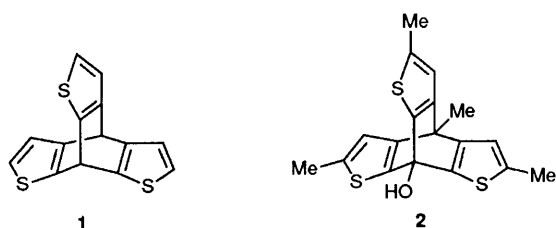
Synthesis and Isomerization of the Novel Heterotriptycene, 8-Hydroxy-2,4,5',6-tetramethyl-4,8-dihydro-4,8[3',2']-thiophenobenzo[1,2-*b*:5,4-*b'*]dithiophene

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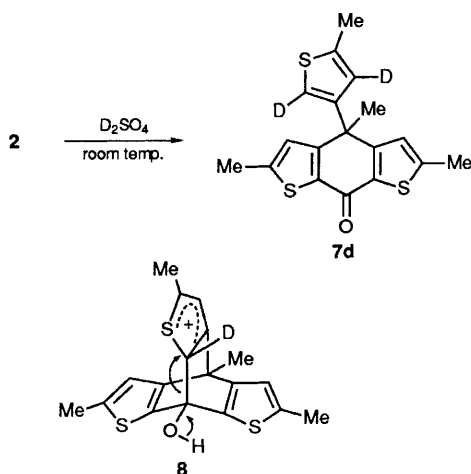
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The reaction of 1,1,1-tris(2-lithio-5-methyl-3-thienyl)ethane with diethyl carbonate yields the novel heterotriptycene **2**, which isomerizes to ketone **7** either by heating or under acidic or basic conditions.

Heterotriptycenes, which are constructed by the replacement of benzene rings of triptycene with other heteroaromatic rings, are a rare class of compound because of limitations on their synthetic methodology.¹ Heterotriptycene **1** is hitherto unknown and is of interest not only for the structure where three 2,3-thiophene rings are orientated in the same direction but also whether or not it possesses the potential to stabilize its bridgehead carbocation² with lone-pairs on sulphur atoms. Here we report the first synthesis and some reactions of the compound **2**, the hydroxytetramethyl derivative of **1**.



Scheme 1 Reagents and conditions: i, BuⁿLi, Et₂O, -78°C; ii, (EtO)₂C=O (0.3 equiv.), -78°C, then room temp.; iii, 60% HClO₄, Ac₂O; iv, MeMgI, Et₂O, 0°C; v, Br₂, AcOH-CCl₄; vi, Bu^tLi, THF, -78°C; vii, (EtO)₂C=O (0.33 equiv.), -78°C, then room temp.



The lithiation of 4-bromo-2-methylthiophene **3**³ with *n*-butyllithium followed by treatment with diethyl carbonate (0.3 mol. equiv.) gave the alcohol **4**. The crude **4** was treated with 60% perchloric acid in acetic anhydride to give rise to a carbenium salt, the reaction of which with MeMgI gave **5** in 16% yield based on diethyl carbonate.⁴ The compound **5** was brominated with bromine in acetic acid–carbon tetrachloride to give tribromide **6** in 96% yield. The tribromide **6** thus obtained was lithiated with *tert*-butyllithium in tetrahydrofuran (THF) at $-78^\circ C$ and the resulting trillithium salt was allowed to react with diethyl carbonate (0.33 mol. equiv.). Chromatographic purification gave the desired heterotriptycene **2** in 14% yield along with ketone **7**[†] in 13% yield (Scheme 1).

† All new compounds gave satisfactory analytical and spectral data. **5**: m.p. 94.5 – $95.5^\circ C$; 1H NMR δ ($CDCl_3$) 1.92 (s, 3H), 2.41 (d, J 0.7 Hz, 9H), 6.50 (d, J 1.1 Hz, 3H), 6.56 (br s, 3H); ^{13}C NMR δ ($CDCl_3$) 15.5 (q), 29.4 (q), 45.9 (s), 118.8 (d), 126.3 (d), 139.0 (s), 149.5 (s); **6**: m.p. 182 – $183^\circ C$; 1H NMR δ ($CDCl_3$) 2.34 (d, J 0.7 Hz, 9H), 2.39 (s, 3H), 6.27 (d, J 0.8 Hz, 3H); ^{13}C NMR δ ($CDCl_3$) 15.5 (q), 27.7 (q), 46.8 (s), 105.6 (s), 128.6 (d), 138.1 (s), 143.8 (s); **7**: m.p. 209.5 – $210.5^\circ C$; 1H NMR δ ($CDCl_3$) 1.87 (s, 3H), 2.31 (s, 3H), 2.49 (d, J 0.8 Hz, 6H), 6.12 (br s, 1H), 6.58 (d, J 0.8 Hz, 2H), 6.99 (d, J 1.5 Hz, 1H); ^{13}C NMR δ ($CDCl_3$) 15.3 (q), 16.3 (q), 28.2 (q), 44.4 (s), 117.8 (d), 125.4 (d), 125.9 (d), 133.4 (s), 140.6 (s), 144.6 (s), 148.8 (s), 157.5 (s), 173.3 (s).

The heterotriptycene **2** gives colourless crystals and decomposes to **7** near its melting point (203 – $204^\circ C$). The spectroscopic data are as follows: 1H NMR δ ($CDCl_3$, 400 MHz) 2.15 (s, 3H, Me), 2.33 (s, 9H, 3Me), 3.18 (s, 1H, OH), 6.62 (s, 3H, arom H); ^{13}C NMR δ ($CDCl_3$, 100.6 MHz) 14.9 (q), 15.3 (q), 49.8 (s), 83.8 (s), 119.9 (d), 134.2 (s), 151.2 (s), 155.7 (s); IR (KBr) 3512 cm^{-1} (OH); mass spectrometry m/z 344 (M^+ , 100), 329 (35), 327 (4), 285 (46). It is noteworthy that compound **2** shows the longest absorption maximum at 303 nm ($\log \epsilon$ 3.70) in the UV–VIS spectrum (acetonitrile). This bathochromic shift (*ca.* 25 nm) compared with triptycene and reported heterotriptycenes^{1c} is probably due to the effective through-space interaction between thiophene rings.⁵

When heterotriptycene **2** was dissolved in D_2SO_4 in order to observe the generation of a bridgehead carbocation, deuterated ketone **7d** was formed quantitatively. This isomerization is probably initiated by the formation of σ -complex **8** followed by ring opening. The isomerization of **2** to **7** was also observed either on treatment with *n*-butyllithium in Et_2O at room temperature or on heating in refluxing *o*-dichlorobenzene in the presence of anthracene. The isomerization of 9-hydroxytriptycene, however, was not observed.⁶

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