Syntheses and chemical and physical properties of thiophenetriptycenes[1]

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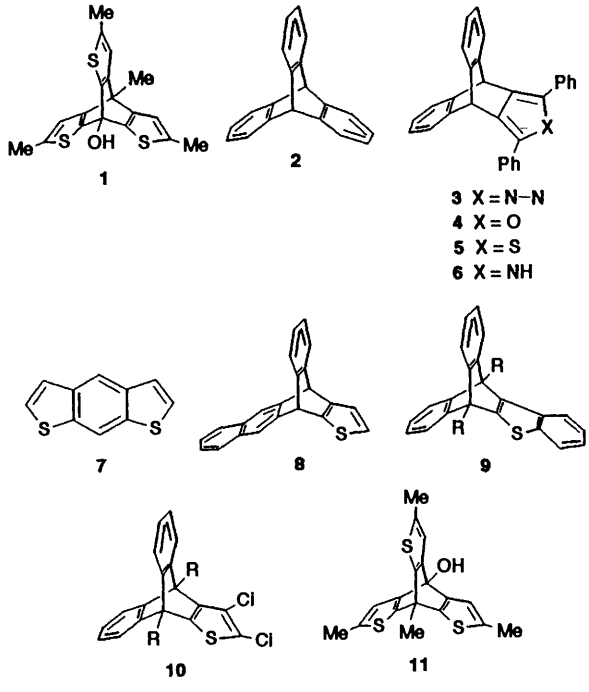
Synthesis of 8-hydroxy-4-methylthiophenetriptycene 1 was performed by treatment of the trilithium salt, prepared from 1,1,1-tris(2-bromo-4-methyl-3-thienyl)ethane 13, with diethyl carbonate. In a similar manner, the 8-hydroxy-4-ethylthiophenetriptycene 27 was prepared. The isomeric 4-hydroxy-8-methyl derivative 11 was also obtained by reaction of the trilithium salt, derived from 1,1,1-tris(3-bromo-5-methyl-2-thienyl)ethane 40, with dimethyl carbonate. Attempts to prepare 8-hydroxy-4-*tert*-butyl- 31 and 8-hydroxy-4-unsubstituted thiophenetriptycenes resulted in the formation of ketone 29 and hydroperoxide 32, respectively. The 8-hydroxy-4-methylthiophenetriptycene 1 decomposed to the corresponding ketone 26 on heating. Attempts to generate the carbocation at the bridgehead of compound 1 by dissolution in conc. H_2SO_4 or by acetolysis of methanesulfonate 44 were unsuccessful. 8-Acetoxy (45) and 8-methoxy (46) derivatives of compound 1 were prepared by treatment of compound 1 with acetic anhydride in triethylamine in the presence of DMAP and by methylation of the lithium salt of compound 1 with trimethyloxonium tetrafluoroborate, respectively. Comparison of IR spectra of regioisomers 1 and 11 indicated that hydrogen bonding of the bridgehead hydroxy group in compound 1 is somewhat hampered by the steric hindrance of the sulfur atoms of the three thiophene rings.

Introduction

Recently we reported the preparation of '8-hydroxy-4-methylthiophenetriptycene' **1**†[1] being the first example of a heteroaromatic triptycene[2] where three benzeno groups of triptycene **2** are replaced by heteroaromatic rings. Before then, in connection with previous interest on the through-space interaction between the benzene rings in triptycene **2**,[3-7] heteroaromatic triptycenes such as 4,5-pyridazino (**3**),[8,9] 3,4-furano (**4**),[8,9] 3,4-thiopheno (**5**)[10] or 3,4-pyrrolo derivatives (**6**)[10] were prepared by heteroaromatization of Diels–Alder adducts of anthracene with dibenzoylacetylene and (*E*)-dibenzoylethylene. On the other hand, it is well recognized that the Diels–Alder reaction between anthracenes and benzynes is an outstanding method giving triptycenes directly.[11,12] However, the preparation of heteroaromatic triptycenes using a similar method is limited to a few cases because of the low reactivity of benzodiheteroaromatics or naphthoheteroaromatics as well as the difficulty of generating didehydroheteroarenes (hetarynes):[13] for example, attempts to prepare the 2,3-thiopheno analogues of triptycenes **2** by the reaction of naphtho[2,3-*b*]thiophene or benzo[1,2-*b*:5,4-*b*']dithiophene **7** with benzyne were unsuccessful,[5,14] while compounds **8**–**10** were prepared by using a Diels–Alder reaction as a key step.[5,15-17] Thus, there had been no report on the preparation of a heteroaromatic triptycene comprising two or more heteroaromatic groups in it until our preliminary report on compound **1**, which was prepared by a stepwise method.

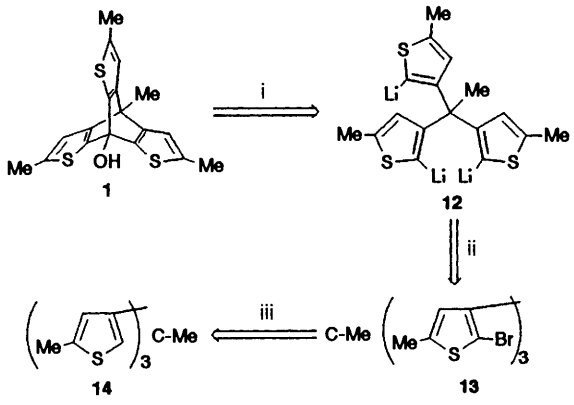
It is of interest to investigate the chemical and physical properties of compound **1** and related compounds because of their unique skeleton consisting of three 2,3-thiophene rings oriented in the same direction and two bridgehead carbons situated in distinct environments. Here we report the preparation of 4-alkyl-8-hydroxythiophenetriptycenes and an isomer, the 4-hydroxy-8-methyl derivative **11**, their reactivities, comparison of physical properties between 8-hydroxy and 4-hydroxy derivatives, and an X-ray structure analysis of 8-methoxy derivative **46**.



Results and discussion

A straightforward way to construct the thiophenetriptycene skeleton might be the Diels–Alder reaction of benzodithiophene **7** with 2,3-didehydrothiophene[18] apart from the regioselectivity of addition. However, the unreactive character of compound **7** toward benzyne[14] implies the difficulty of the route. Therefore, we planned a two-step procedure where two bridgehead carbon atoms are introduced step by step.[2] As shown in Scheme 1, the

† We call 2,5',6-trimethyl-4,8-dihydro-4,8[3',2']thiophenobenzo[1,2-*b*:5,4-*b*']dithiophene 'thiophenetriptycene' for convenience.

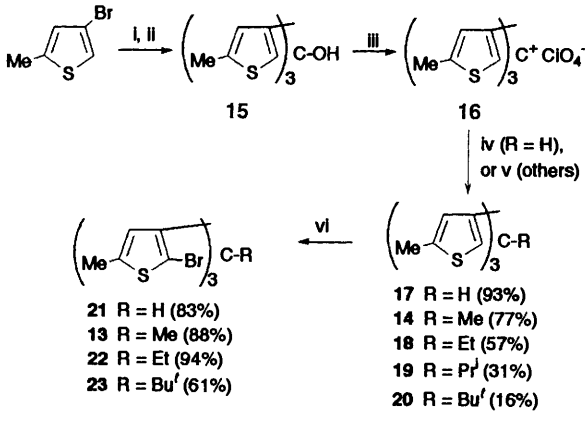


Scheme 1 *Reagents:* i, $(RO)_2C{=}O$; ii, R'Li; iii, Br_2

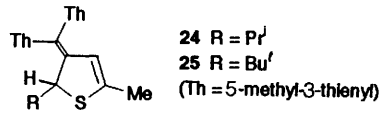
final step for the preparation of 8-hydroxy-4-methylthiophenetriptycene **1** is a reaction of trilithium salt **12** with a dialkyl carbonate. The precursor of compound **12**, tribromide **13** is prepared by bromination of 1,1,1-tris-(5-methyl-3-thienyl)-ethane **14**. The 5-methyl group in compound **14** is necessary for the regioselective bromination at the 2-position. According to this scheme we investigated the preparation of 8-hydroxy-4-alkyl (Me, Et, Pr^i, Bu^t) and 4-unsubstituted thiophenetriptycenes and also compound **11** with a similar strategy.

Preparation and attempted preparation of 8-hydroxythiophenetriptycenes

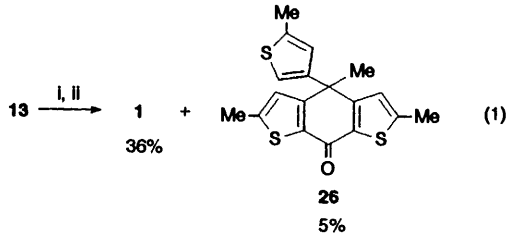
Lithiation of 4-bromo-2-methylthiophene with Bu^sLi followed by treatment with diethyl carbonate yielded tris(5-methyl-3-thienyl)methanol **15**. The alcohol **15** was converted into carbenium perchlorate **16** by treatment with $HClO_4$ in Ac_2O. Reduction of compound **16** in diethyl ether with $LiAlH_4$ gave trithienylmethane **17** in high yield (93%). Treatment of compound **16** with MeMgI, EtMgBr, Pr^iMgBr and Bu^tMgCl provided compound **14** (77%), **18** (57%), **19** (31%) and **20** (16%), respectively.[19] Reaction of compound **16** with EtMgBr gave a reduction product **17** as a by-product in 21% yield. In the case of the reaction of compound **16** with Pr^iMgBr, a mixture of the desired compound **19** and a 3-methylene-2,3-dihydrothiophene derivative **24** was obtained. Unfortunately, it was so difficult to separate this mixture by chromatographic means that we abandoned the preparation of 8-hydroxy-4-isopropylthiophenetriptycene in this stage. Incidentally, the reaction of compound **16** with Bu^tMgCl yielded the desired compound **20** and an inseparable mixture of compounds **17** and **25**. Bromination of compounds **14** and **17–20** with molecular bromine in CCl_4 gave tribromides **13** and **21–23**, respectively, in satisfactory yields (Scheme 2).



Scheme 2 *Reagents and conditions:* i, Bu^sLi, Et_2O, −78 °C; ii, $(EtO)_2C{=}O$ (0.3 mol equiv.), −78 °C; then room temp.; iii, 60% $HClO_4$, Ac_2O, −30 to −40 °C; iv, $LiAlH_4$, Et_2O, room temp.; v, RMgX, Et_2O, 0 °C; vi, Br_2, CCl_4, 0 °C



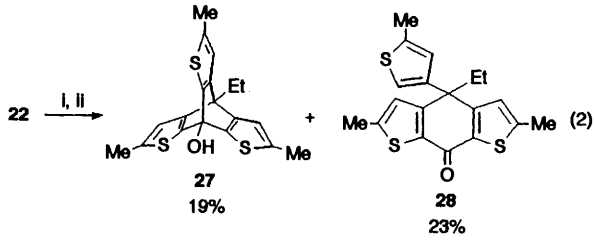
8-Hydroxy-4-methylthiophenetriptycene **1** was successfully synthesized by reaction of the corresponding trilithium salt, prepared by treatment of tribromide **13** with Bu^tLi, with diethyl carbonate [eqn. (1)]. The yield of compound **1** was improved



Reagents and conditions: i, Bu^tLi, THF–Et_2O (1:2), −78 °C; ii, $(EtO)_2C{=}O$ (1 mol equiv.), −78 °C; then room temp.

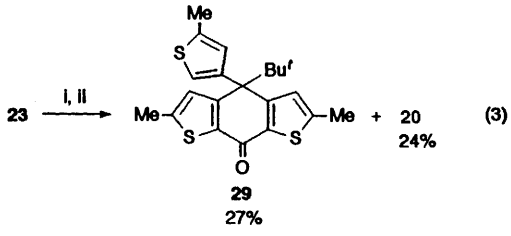
from 14% in our preliminary result[1] to 36% yield by use of a mixed solvent of tetrahydrofuran (THF) and diethyl ether instead of THF.

In a similar manner, 8-hydroxy-4-ethylthiophenetriptycene **27** could be obtained in 19% yield along with a ketone **28** (23%) [eqn. (2)].



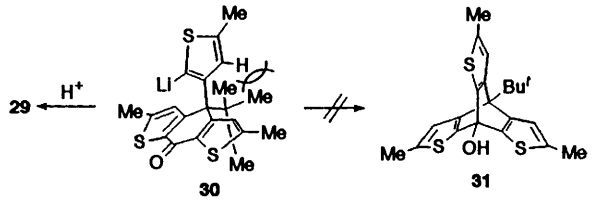
Reagents and conditions: i, Bu^tLi, Et_2O, −78 °C; ii, $(EtO)_2C{=}O$ (1 mol equiv.), −78 °C; then room temp.

An attempt to prepare 8-hydroxy-4-*tert*-butylthiophenetriptycene **31** resulted in the formation of ketone **29** in 27% yield along with debrominated product **20** [eqn. (3)]. The formation



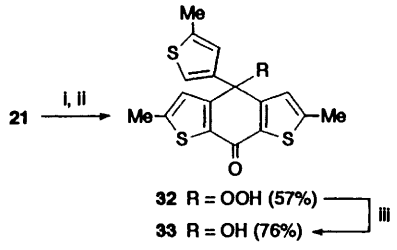
Reagents and conditions: i, Bu^tLi, Et_2O, −78 °C; ii, $(EtO)_2C{=}O$ (1 mol equiv.), −78 °C; then room temp.

of ketone **29** undoubtedly indicates the intervention of an intermediate **30**. However, large steric hindrance between the *tert*-butyl group and the 4-hydrogen atom of the 2-lithio-5-methyl-3-thienyl group in **30** would interrupt the 3-thienyl group in taking an appropriate conformation for the final ring closure (Scheme 3).



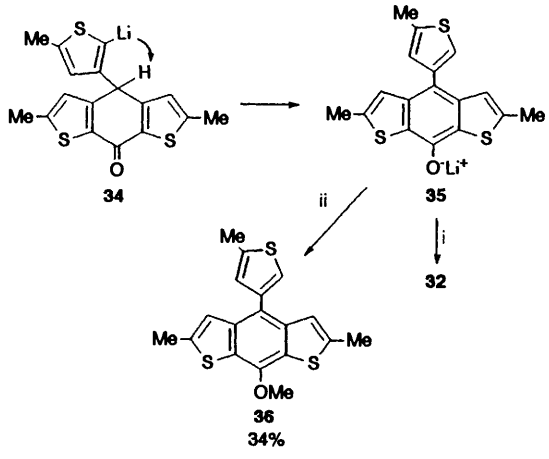
Scheme 3

We also attempted the preparation of 8-hydroxy-4-unsubstituted thiophenetriptycene. Tribromide **21** was lithiated with BuLi and the resulting trilithium salt was treated with diethyl carbonate to give unexpected hydroperoxide **32** in 57% yield (Scheme 4). The structure of compound **32** was elucidated by



Scheme 4 *Reagents and conditions:* i, BuLi, THF, −78 °C; ii, $(EtO)_2C{=}O$ (1 mol equiv.), −78 °C; then room temp.; iii, $NaBH_4$, EtOH–THF, room temp.

analysis of its spectroscopic data and chemical transformation. In the ^1H NMR spectrum of compound **32**, the hydroperoxy proton appeared at δ 8.16 and was exchanged with deuteron by shaking with D_2O. Reduction of compound **32** with $NaBH_4$ in EtOH–THF gave alcohol **33** in 76% yield. A plausible mechanism for the formation of compound **32** is shown in Scheme 5. Thus, the highly acidic, benzylic proton in

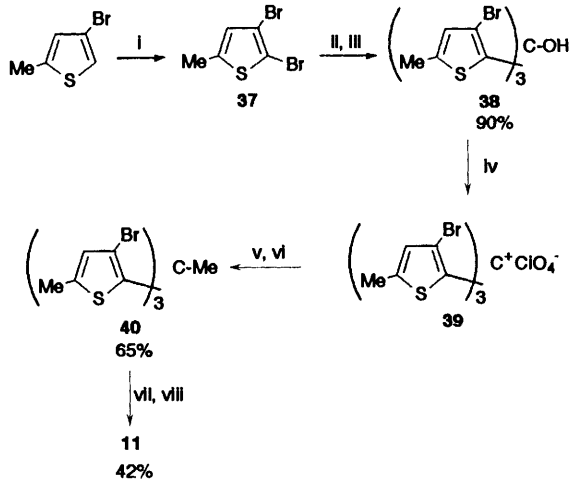


Scheme 5 *Reagents:* i, H^+, O_2; ii, Me_3O^+ BF_4^-

compound **34** is abstracted intramolecularly to give a benzo[1,2-*b*:5,4-*b*′]dithiophene derivative **35**. When the reaction is quenched, compound **35** is protonated and then reacts with atmospheric oxygen to yield hydroperoxide **32**. It has been reported that 10-substituted anthranols showed similar reactivities toward atmospheric oxygen.[20] The intervention of species **35** was confirmed by the formation of the methoxybenzo[1,2-*b*:5,4-*b*′]dithiophene **36** when it was quenched with Me_3O^+ BF_4^-.

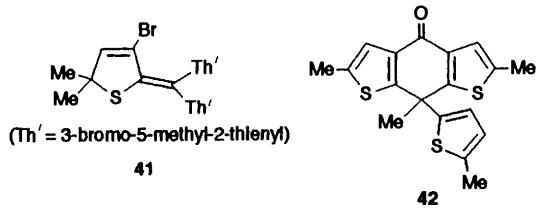
Preparation of 4-hydroxy-8-methylthiophenetriptycene 11

3-Bromo-5-methyl-2-thienyllithium, prepared from 2,3-dibromo-5-methylthiophene **37**, was allowed to react with diethyl carbonate to provide alcohol **38** in 90% yield. The alcohol **38** was converted into the corresponding perchlorate **39** by treatment with 60% $HClO_4$ in Ac_2O. The perchlorate **39** was treated with MeMgI to give a mixture of the desired adduct **40** and a small amount of a by-product, the 2-methylene-2,5-dihydrothiophene **41**. Separation of the mixture was so difficult by chromatographic means that the mixture was treated with *m*-chloroperbenzoic acid (MCPBA) to convert the contaminant **41** into the corresponding sulfoxide and then the resulting mixture was subjected to silica gel chromatography to give pure compound **40** in 65% yield based on alcohol **38**. The tribromide **40** was lithiated with Bu^{t}Li and the trilithium salt was allowed to react with dimethyl carbonate to provide the desired 4-hydroxy-8-methylthiophenetriptycene **11** in 42% yield (Scheme 6). When diethyl carbonate was employed in the place of



Scheme 6 *Reagents and conditions:* i, Br_2, CCl_4; ii, Bu^{s}Li, Et_2O, −78 °C; iii, $(EtO)_2C{=}O$ (1 mol equiv.), −78 °C; then room temp.; iv, 60% $HClO_4$, Ac_2O, −40 °C; v, MeMgI, Et_2O, −30 °C; vi, MCPBA; vii, Bu^{t}Li, THF, −78 °C; viii, $(MeO)_2C{=}O$; then room temp.

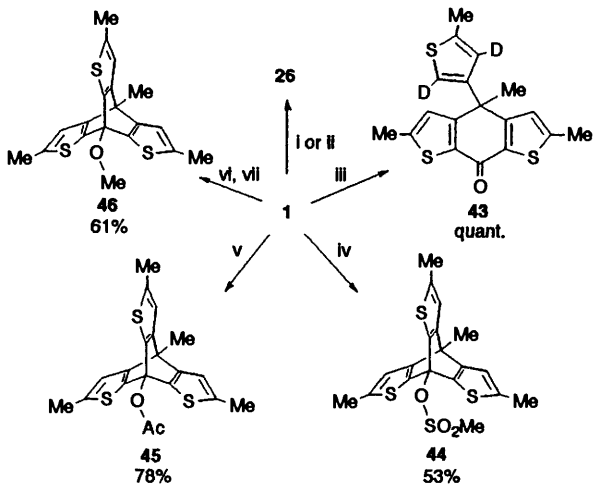
dimethyl carbonate, the yield of compound **11** decreased to ~ 10% along with the isolation of a small amount of ketone **42**.



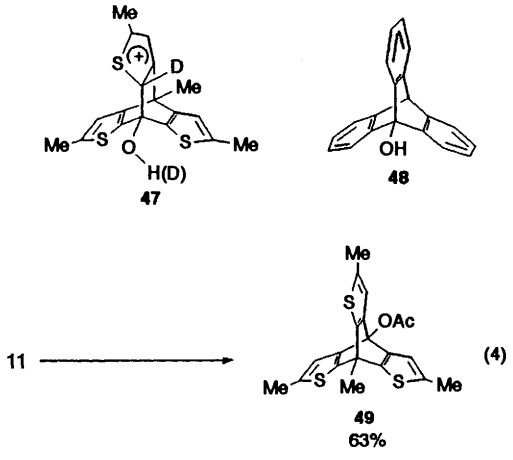
Reactivities

Crystalline 8-hydroxy-4-methylthiophenetriptycene **1** decomposed to ketone **26** when heated near its melting point (203–204 °C). Although compound **1** was expected to generate 5-methyl-2,3-didehydrothiophene by a thermal retro-Diels–Alder reaction, there was observed no evidence for the intervention of such a species when compound **1** was heated in refluxing *o*-dichlorobenzene in the presence of anthracene. Ring opening of compound **1** to ketone **26** was also induced by treatment of a THF solution of compound **1** with butyllithium at room temperature followed by stirring of the solution. The readily occurring ring-opening of compound **1** would be mainly dependent upon the large ring strain inherent in compound **1** (*vide infra*).

Another point of interest with compound **1** is whether its bridgehead can generate a carbocation. When compound **1** was dissolved in D_2SO_4 at room temperature, deuteriated ketone **43** was formed immediately. The ring-opening reaction would proceed through a deuteriated intermediate **47**. Bartlett and Greene reported that hydroxytriptycene **48** was thermally stable and recovered unchanged from its hot H_2SO_4 solution.[21] We next attempted acetolysis of 8-methanesulfonate **44** prepared by treatment of compound **1** with methanesulfonyl chloride in pyridine. Heating of mesyl ester **44** in acetic acid at 93 °C for 1 day, however, resulted in decomposition of substrate **44** into unidentified materials with 53% of recovery. Incidentally, 8-acetoxy derivative **45** was prepared by acetylation of alcohol **1** with acetic anhydride in the presence of triethylamine and 4-(dimethylamino)pyridine (DMAP) in 78% yield (Scheme 7).[22] 4-Acetoxy-8-methylthiophenetriptycene **49** could be also prepared in a similar manner [eqn. (4)].



Scheme 7 *Reagents and conditions:* i, BuLi, room temp., 1.5 h; ii, *o*-dichlorobenzene, reflux; iii, D_2SO_4; iv, $MeSO_2Cl$, pyridine, room temp.; v, Ac_2O, Et_3N, DMAP, 0 °C; vi, Bu^{s}Li, THF, −78 °C; vii, Me_3O^+ BF_4^-, −78 °C; then room temp.



Reagents and conditions: Ac_2O, Et_3N, DMAP, 70 °C, 5 h

Methylation of compound **1** was performed by O-lithiation of alcohol **1** with *sec*-butyllithium at −78 °C followed by treatment with Me_3O^+ BF_4^- in 61% yield. When iodomethane was used as a methylating agent, 8-methoxy-4-methylthiophenetriptycene **46** was formed in lower yields (30–40%). Treatment of alcohol **1** with diazomethane did not yield the ether **46**.

Physical properties

In ^1H and ^{13}C NMR spectra, 8-hydroxy-4-methyl- and 4-hydroxy-8-methyl-thiophenetriptycenes, **1** and **11**, exhibit simple patterns in harmony with C_{3v} symmetry of the thiophenetriptycene skeleton. In the ^{13}C NMR spectrum of compound **1**, two bridgehead carbons appear at δ_C 49.8 and 83.8 and the latter is assignable to the hydroxy-attached carbon. Two bridgehead carbons of compound **11** resonate in similar regions (δ_C 49.4 and 84.0).

In IR spectra (KBr) of isomers **1** and **11**, absorptions due to O–H stretching occur at 3512 and 3370 cm^{-1}, respectively. Interestingly, the absorption in compound **1** appears at higher wavenumber and more sharply than that in compound **11** (Fig. 1), which implies that the hydrogen bonding of the 8-hydroxy group of **1** is somewhat hampered by the steric hindrance caused by sulfur atoms of the thiophene rings. We have observed similar steric effects in competitive oxidation, sulfurization, and selenation between 8-phospha- and 4-phospha-thiophenetriptycenes (**50** and **51**, respectively).[23]

In the UV–VIS spectra (acetonitrile) of thiophenetriptycenes, the longest absorption maxima characteristically appear around 300 nm with log ε 3.58–3.76. Since the bathochromic effect due to three methyl substituents was estimated to be ~ 12 nm from the comparison of diphospha analogues **52** and **53** (λ_{max} in dichloromethane: 322 and 310 nm, respectively),[24] it can be said that the absorptions of thiophenetriptycenes move to slightly longer-wave regions compared with triptycene (λ_{max} 278.5 nm) and reported heterotriptycenes.[6]

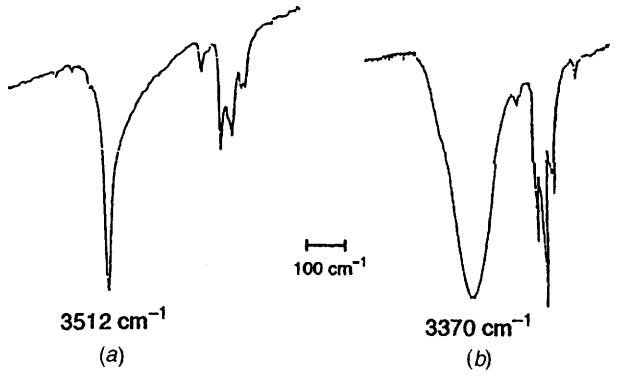


Fig. 1 Absorptions due to OH stretching of (*a*) 8-hydroxy-4-methyl- (**1**) and (*b*) 4-hydroxy-8-methyl- (**11**) thiophenetriptycenes in IR spectra

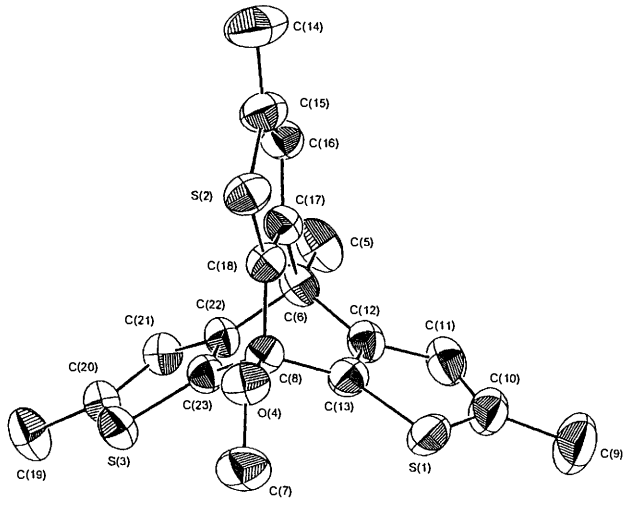
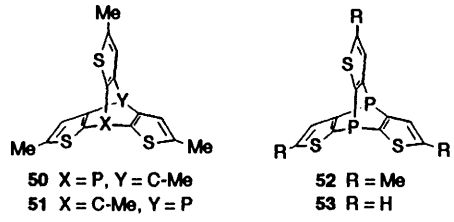


Fig. 2 ORTEP drawing of 8-methoxy-4-methylthiophenetriptycene **46**. Selected bond lengths (Å) and bond angles (°): S(1)–C(10) 1.737(6); C(9)–C(10) 1.505(8); S(2)–C(15) 1.727(5); C(14)–C(15) 1.494(9); S(3)–C(20) 1.731(4); C(19)–C(20) 1.502(7); C(6)–C(12) 1.534(6); C(6)–C(17) 1.541(6); C(6)–C(22) 1.543(6); C(8)–C(13) 1.532(6); C(8)–C(18) 1.521(6); C(8)–C(23) 1.536(5); C(6)–C(12)–C(13) 115.0(4); C(8)–C(13)–C(12) 115.6(4); C(6)–C(17)–C(18) 113.6(4); C(8)–C(18)–(17) 116.4(4); C(6)–C(22)–C(23) 114.5(4); C(8)–C(23)–C(22); 115.5(4); C(12)–C(6)–C(17) 103.7(3); C(12)–C(6)–C(22) 104.1(3); C(17)–C(6)–C(22) 102.8(3); C(13)–C(8)–C(18) 102.9(3); C(13)–C(8)–C(23) 103.0(3); C(18)–C(8)–C(23) 103.4(3).



X-Ray single-crystal structure analysis of 8-methoxy-4-methylthiophenetriptycene 46

An ORTEP drawing of compound **46** is depicted in Fig. 2. Since the three thiophene rings in compound **46** are equivalent in solution as shown by NMR spectroscopy, we can use average values for the following discussion. The average values of bond

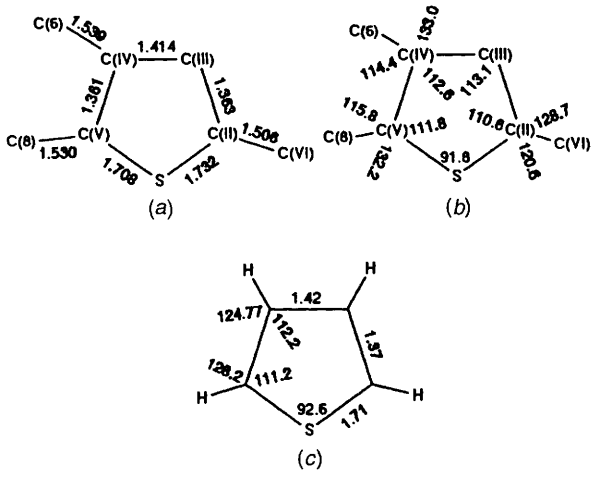


Fig. 3 (*a*) Average bond lengths (Å) and (*b*) bond angles (°) of the three thiophene rings of compound **46**. (*c*) Reported geometry of thiophene (microwave).

lengths and bond angles of the thiophene moieties are summarized in Fig. 3 with the reported geometry of thiophene as a reference.[25]

As to bond lengths, abnormal values are not observed except for a little elongation of S–C(II) (1.73 Å) and C(6, 8)–C(IV, V) (1.539, 1.530 Å) in comparison with the corresponding bond length in thiophene (1.71 Å) and that of C(sp^3)–C(thiophene) just like C(II)–C(VII) (1.506 Å), respectively. Remarkable deviations of the thiophene moieties of compound **46** from thiophene are observed in bond angles around carbons C(IV) and C(V). Thus, average bond angles of C(6)–C(IV)–C(V) and C(8)–C(V)–C(IV) are 114.4 and 115.8°, respectively, being up to 10–12° narrower than the corresponding values of thiophene. These deviations from unstrained thiophene would contribute to the chemical behaviour of compound **1** such as the relatively easy ring opening to compound **29**. Incidentally, the corresponding value for triptycene **2** is ~113°.[26] In addition, average bond angles of C(thiophene)–C(bridgehead)–C(thiophene) are 103.5 and 103.1° around C(6) and C(8), respectively, which are a little smaller than the corresponding value for compound **2** (105.3).

Experimental

General procedures

Mps were determined on a Mel-Temp capillary tube apparatus and are uncorrected. NMR spectra were determined on a JEOL PMX-60SI (at 60 MHz for ^{1}H), a JEOL FX-90Q (at 90 MHz for ^{1}H and at 22.5 MHz for ^{13}C), or on a Bruker AM-400 spectrometer (at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C) with $CDCl_3$ as the solvent. *J* Values are given in Hz and Th denotes thienyls. Low- and high-resolution mass spectra were obtained at 70 eV in the EI mode on a JEOL JMS-DX303 or a Shimadzu QP-1000 spectrometer. For compounds containing bromine, *m/z* values refer to only the ^{79}Br isotope, and the number of bromines is given in brackets. IR spectra were measured on a Hitachi Model 270-50 spectrometer and UV–VIS absorption spectra on a Hitachi 340 spectrometer. Elemental analyses were performed by the Analytical Center of Saitama University.

Extracts were dried over anhydrous $MgSO_4$. Column chromatography was performed with Merck Kieselgel 60 (70–230 mesh) and the eluent is given in parentheses.

Tris(5-methyl-3-thienyl)methanol 15

To a solution of 4-bromo-2-methylthiophene[27] (7.76 g, 43.8 mmol) in diethyl ether (40 cm^3) was added *sec*-butyllithium (1.08 mol dm^{-3}; 39.3 cm^3, 42.5 mmol) at −78 °C under argon. The mixture was stirred for 1 h at this temperature and then was treated with diethyl carbonate (1.56 cm^3, 12.9 mmol). The mixture was allowed to warm to room temperature and was stirred for 1 h. The mixture was quenched with aq. ammonium chloride and extracted with diethyl ether three times. The combined extracts were washed with water and dried. The solvent was removed under reduced pressure to give a brown oil, which was subjected to column chromatography (benzene) to give compound **15** (3.83 g, 93%) as an orange oil, δ_H(60 MHz) 2.43 (9 H, s, Th-CH_3), 2.45 (1 H, s, OH), 6.67 (3 H, br s, Th 4-H) and 6.78 (3 H, d, *J* 1.2, Th 2-H); ν_{max}(neat)/cm^{-1} 3436 (OH); *m/z* 320 (M^+, 38%) and 302 (100). The alcohol **15** was used without further purification.

1,1,1-Tris(5-methyl-3-thienyl)ethane 14

Alcohol **15** (3.83 g, 12.0 mmol) was dissolved in acetic anhydride (40 cm^3) and the solution was cooled to −40 to −50 °C on a solid CO_2–acetone-bath. To the solution was added 60% perchloric acid (10.1 g, 60 mmol) dropwise over a period of 20 min. The resulting dark-brown mixture was stirred for 1.5 h at −30 to −40 °C and subsequently diethyl ether (200 cm^3) was added slowly to precipitate perchlorate **16**. The cold bath was removed and the mixture was kept for 15 min at room temperature. The dark-brown supernatant was pipetted off and the red residue was washed with diethyl ether (10 cm^3) several times until the washings were almost colourless. The residue was dried under reduced pressure and then *in vacuo* to give perchlorate **16** as a red powder (2.86 g, 60%), mp 98–103 °C (decomp.).

To a suspension of the perchlorate **16** (2.86 g, 7.10 mmol) in diethyl ether (20 cm^3) was added MeMgI, prepared from iodomethane (2.2 cm^3, 38 mmol) and magnesium (902 mg, 37.1 mmol) in diethyl ether (20 cm^3), at 0 °C. The reaction occurred quickly and the mixture soon turned clear. The mixture was stirred for 10 min at 0 °C and for 20 min at room temperature, poured into ice–water, and extracted with diethyl ether three times. The combined extracts were dried and evaporated to dryness. The residue was purified by column chromatography (hexane) to give compound **14** (1.74 g, 77%) as crystals, mp 94.5–95.5 °C (from MeOH) (Found: C, 64.0; H, 5.7. $C_{17}H_{18}S_3$ requires C, 64.1; H, 5.7%); δ_H(400 MHz) 1.92 (3 H, s, Th_3C-CH_3), 2.41 (9 H, d, *J* 0.7, Th-CH_3), 6.50 (3 H, d, *J* 1.1, Th 2-H) and 6.56 (3 H, br s, Th 4-H); δ_C(100.6 MHz) 15.5 (q), 29.4 (q), 45.9 (s), 118.8 (d), 126.3 (d), 139.0 (s) and 149.5 (s); *m/z* 318 (M^+, 42%) and 303 (100).

Tris(5-methyl-3-thienyl)methane 17

A suspension of perchlorate **16** (428 mg, 1.06 mmol) in diethyl ether (20 cm^3) was treated with $LiAlH_4$ (123 mg, 3.25 mmol) at room temperature. The red suspension turned to a colourless, clear solution within 1 min. The mixture was quenched with EtOH (3 cm^3). The work-up described above gave compound **17** (300 mg, 93%) as crystals, mp 63.5–64.0 °C (from EtOH) (Found: C, 62.9; H, 5.2. $C_{16}H_{16}S_3$ requires C, 63.1; H, 5.3%); δ_H(400 MHz) 2.40 (9 H, s, Th-CH_3), 5.23 (1 H, s, Th_3C-*H*), 6.57 (3 H, s, ThH) and 6.59 (3 H, s, ThH); δ_C(100.6 MHz) 15.4 (q), 44.2 (d), 119.4 (d), 126.5 (d), 139.6 (s) and 144.2 (s); *m/z* 304 (M^+, 100%) and 289 (88).

1,1,1-Tris(5-methyl-3-thienyl)propane 18

In a similar way to that for compound **14** the reaction of perchlorate **16** (1.10 g, 2.74 mmol) with ethylmagnesium bromide, prepared from bromoethane (1.00 cm^3, 1.46 g, 13.4 mmol) and magnesium (333 mg, 13.7 mmol) in diethyl ether at 0 °C, gave compounds **18** (521 mg, 57%) and **17** (178 mg, 21%). Compound **18** was obtained as crystals, mp 68–69 °C (from MeOH) (Found: C, 65.1; H, 6.1. $C_{18}H_{20}S_3$ requires C, 65.0; H, 6.1%); δ_H(400 MHz) 0.86 (3 H, t, *J* 7, CH_2CH_3), 2.34 (2 H, q, *J* 7, CH_2CH_3), 2.41 (9 H, s, Th-CH_3), 6.55 (3 H, br s, Th 4-H)

and 6.65 (3 H, d, *J* 1.3, Th 2-H); δ_C(100.6 MHz) 10.2 (q), 15.5 (q), 33.7 (t), 50.6 (s), 119.1 (d), 126.9 (d), 136.5 (s) and 147.7 (s); *m/z* 332 (M^+, 8%) and 303 (100).

2-Methyl-1,1,1-tris(5-methyl-3-thienyl)propane 19

A suspension of perchlorate **16** (1.211 g, 3.01 mmol) in diethyl ether (20 cm^3) was treated with isopropylmagnesium bromide, prepared from 2-bromopropane (1.2 cm^3, 12.8 mmol) and magnesium (284 mg, 11.7 mmol) in diethyl ether (5 cm^3), at 0 °C. After the work-up described above, a mixture (500 mg) of the desired compound **19** and a 3-methylene-2,3-dihydrothiophene derivative **24** and compound **17** (146 mg, 16%) were obtained. The mixture could not be separated completely by chromatography. Compound **19**, δ_H(60 MHz) 0.85 [6 H, d, *J* 7, $CH(CH_3)_2$], 2.35 (9 H, s, Th-CH_3), 2.70–3.35 [$CH(CH_3)_2$ overlapping with that of compound **24**] and 6.50 and 6.69 (ThHs overlapping with those of **24**); 2-isopropyl-5-methyl-3-[bis(5-methyl-3-thienyl)methylene]-2,3-dihydrothiophene **24**, δ_H(60 MHz) 1.19 [6 H, d, *J* 7, $CH(CH_3)_2$], 2.35 (Th-CH_3 and vinylic CH_3 overlapping with Th-CH_3 of **19**), 2.70–3.35 [$CH(CH_3)_2$, overlapping with that of **19**], 5.23 [1 H, br s, $CHCH(CH_3)_2$], 6.28 (1 H, br s, vinyl H) and ThHs overlapping with those of compound **19**. The yields of compounds **19** and **24** estimated from the integral ratios of their ^{1}H NMR spectra were 31 and 17%, respectively.

2,2-Dimethyl-1,1,1-tris(5-methyl-3-thienyl)propane 20

A suspension of perchlorate **16** (1.57 g, 3.89 mmol) in diethyl ether (20 cm^3) was treated with *tert*-butylmagnesium chloride, prepared from 2-chloro-2-methylpropane (2.5 cm^3, 23 mmol) and magnesium (797 mg, 32.8 mmol) in diethyl ether (18 cm^3), at 0 °C. The mixture was stirred for 15 min at 0 °C and for 30 min at room temperature. After the work-up as described above, compound **20** (223 mg, 16%) and a mixture (813 mg) of a 3-methylene-2,3-dihydrothiophene derivative **25** and compound **17** were obtained. The yields of compounds **25** and **17** were estimated from the integral ratio of the ^{1}H NMR spectrum to be 51 and 9%, respectively. For compound **20**: crystals, mp 203–203.5 °C (from hexane) (Found: C, 66.7; H, 6.7. $C_{20}H_{24}S_3$ requires C, 66.6; H, 6.7%); δ_H 1.16 (9 H, s, Bu^t), 2.44 (9 H, d, *J* 1.5, Th-CH_3), 6.47 (3 H, q-like, *J* 1.5, Th 4-H) and 6.73 (3 H, s, Th 2-H); δ_C 15.6 (q), 30.4 (q), 36.6 (s), 58.8 (s), 121.6 (d), 126.6 (d), 137.1 (s) and 147.3 (s); *m/z* 360 (M^+, 0.06%) and 303 (100). 2-*tert*-Butyl-5-methyl-3-[bis(5-methyl-3-thienyl)methylene]-2,3-dihydrothiophene **25** δ_H(60 MHz) 0.78 (9 H, s, Bu^t), 2.00 (3 H, d, *J* 1, vinylic CH_3), 2.40 (6 H, s, Th-CH_3), 4.60 (1 H, s, CHBu^t), 6.15 (1 H, q-like, *J* 1, vinyl H) and ThHs overlapping with those of compound **17**.

1,1,1-Tris(2-bromo-5-methyl-3-thienyl)ethane 13

Trithienylethane **14** (1.74 g, 5.46 mmol) was dissolved in CCl_4 (35 cm^3) in a round-bottomed flask and the flask was shielded from light. A solution of bromine (2.70 g, 16.9 mmol) in tetrachloromethane (5 cm^3) was added to the solution dropwise over a period of 15 min at 0 °C. After being stirred for 1 h, the mixture was quenched with 2 mol dm^{-3} KOH and extracted with CH_2Cl_2 three times. The combined extracts were washed with water, dried and evaporated to dryness. The residue was purified by column chromatography (hexane). The eluent containing compound **13** was concentrated to ~ 50 cm^3 and the precipitate was collected by filtration to give tribromide **13** (2.67 g, 88%) as needles, mp 182–183 °C (from EtOH) (Found: C, 36.7; H, 2.7. $C_{17}H_{15}Br_3S_3$ requires C, 36.8; H, 2.7%); δ_H(400 MHz) 2.34 (9 H, d, *J* 0.7, Th-CH_3), 2.39 (3 H, s, Th_3C-CH_3) and 6.27 (3 H, q-like, *J* 0.8, ThH); δ_C(100.6 Mz) 15.5 (q), 27.7 (q), 46.8 (s), 105.6 (s), 128.6 (d), 138.1 (s) and 143.8 (s); *m/z* 552 (M^+, 9%, [Br_3]), 473 (35, [Br_2]) 394 (100, [Br]), 379 (79, [Br]) and 315 (83).

1,1,1-Tris(2-bromo-5-methyl-3-thienyl)methane 21

In a similar way to that for compound **13**, the reaction of trithienylmethane **17** (771 mg, 2.53 mmol) with bromine (1.23 g, 7.70 mmol) in CCl_4 at 0 °C gave tribromide **21** (1.13g, 83%) as crystals, mp 171–172.5 °C (from EtOH) (Found: C, 35.7; H, 2.4. $C_{16}H_{13}Br_3S_3$ requires C, 35.5; H, 2.4%); δ_H(400 MHz) 2.36 (9 H, d, *J* 0.7, Th-CH_3), 5.38 (1 H, s, Th_3C-*H*) and 6.31 (3 H, q-like, *J* 0.7, ThH); δ_C(100.6 MHz) 15.7 (q), 41.4 (d), 107.0 (s), 125.7 (d), 139.7 (s) and 140.4 (s); *m/z* 538 (M^+, 11%, [Br_3]), 459 (19, [Br_2]), 380 (100, [Br]) and 301 (69).

1,1,1-Tris(2-bromo-5-methyl-3-thienyl)propane 22

In a similar way to that for compound **13**, the reaction of trithienylpropane **18** (573 mg, 1.72 mmol) with bromine (922 g, 5.77 mmol) in CCl_4 at 0 °C gave tribromide **22** (921 mg, 94%) as crystals, mp 179.0–179.5 °C (from EtOH) (Found: C, 37.9; H, 3.1. $C_{18}H_{17}Br_3S_3$ requires C, 38.0; H, 3.0%); δ_H(60 MHz) 0.83 (3 H, t, *J* 7, CH_2CH_3), 2.37 (9 H, s, Th-CH_3), 2.93 (2 H, q, *J* 7, CH_2CH_3) and 6.60 (3 H, s, ThH); *m/z* 566 (M^+, 3%, [Br_3]), 537 (9, [Br_3]), 487 (16, [Br_2]), 408 (42 [Br]) and 379 (100, [Br]).

1,1,1-Tris(2-bromo-5-methyl-3-thienyl)-2,2-dimethylpropane 23

In a similar way to that for compound **13**, treatment of compound **20** (111 mg, 0.308 mmol) in CCl_4 (13 cm^3 and acetic acid (5 cm^3) with bromine (335 mg, 2.09 mmol) in CCl_4 (2 cm^3) at room temperature gave tribromide **23** (113 mg, 61%) as crystals, mp 105–123 °C (decomp.) (from hexane) (Found: C, 40.3; H, 3.5. $C_{20}H_{21}Br_3S_3$ requires C, 40.2; H, 3.5%); δ_H(400 MHz) 1.24 (9 H, s, Bu^t), 2.44 (9 H, s, Th-CH_3) and 7.27 (3 H, s, ThH); δ_C(100.6 MHz) 15.8 (q), 30.1 (q), 43.5 (s), 59.7 (s), 130.8 (d), 136.1 (s) and 139.8 (s) (only three peaks were observed in the aromatic region); *m/z* 537 (M^+ − Bu^t, 21%, [Br_3]), 458 (14, [Br_2]), 379 (100, [Br]) and 301 (33).

2,4,5′,6-Tetramethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-ol(8-hydroxy-4-methylthiophenetriptycene) 1

To a solution of tribromide **13** (2.26 g, 4.07 mmol) in THF (10 cm^3)–diethyl ether (20 cm^3) was added *tert*-butyllithium (1.44 mol dm^{-3}) 15.6 cm^3, 22.4 mmol) at −78 °C and the mixture was stirred at this temperature for 1 h. Diethyl carbonate (0.49 cm^3, 4.07 mmol) was added to the resulting trilithium salt and the mixture was stirred for 30 min at −78 °C and then for 30 min at room temperature. The mixture was quenched with aq. ammonium chloride and extracted with diethyl ether three times. The combined extracts were washed with water, dried and evaporated to dryness. The residue was subjected to column chromatography [CH_2Cl_2–hexane (3:1)]. After the completion of elution of thiophenetriptycene **1**, the solvent was changed to diethyl ether to elute ketone **26**. The crude thiophenetriptycene **1** was further purified by column chromatography (benzene) to give pure compound **1** (506 mg, 36%). The crude ketone **26** was purified by column chromatography twice (benzene the first time and CH_2Cl_2 the second time) to give pure compound **26** (63 mg, 5%).

8-Hydroxy-4-methylthiophenetriptycene **1**, powder, mp 203–204 °C (decomp.) (from CCl_4) (Found: C, 62.0; H, 4.6%; M^+, 344.0382. $C_{18}H_{16}OS_3$ requires C, 62.8; H, 4.7%; M, 344.0363); δ_H(400 MHz) 2.15 (3 H, s, bridgehead-CH_3), 2.33 (9 H, s, Th-CH_3), 3.18 (1 H, s, OH) and 6.62 (3 H, s, ThH); δ_C(100.6 MHz) 14.9 (q), 15.3 (q), 49.8 (s), 83.8 (s), 119.9 (d), 134.2 (s), 151.2 (s) and 155.7 (s); ν_{max}(KBr)/cm^{-1} 3512 (OH); *m/z* 344 (M^+, 100%), 329 (35), 327 (4) and 285 (46); λ_{max}(MeCN)/nm 303 (log ε, 3.70).

2,4,6-Trimethyl-4-(5-methyl-3-thienyl)-4,8-dihydrobenzo-[1,2-*b*:5,4-*b*′)dithiophen-8-one **26**, pale yellow crystals, mp 209.5–210.5 °C (from EtOH) (Found: C, 62.6; H, 4.8. $C_{18}H_{16}OS_3$ requires C, 62.8; H, 4.7%); δ_H(400 MHz) 1.87 (3 H, s, 4-CH_3), 2.31 (3 H, s, Th-CH_3), 2.49 (6 H, d, *J* 0.8, 2- and

6-CH_3), 6.12 (1 H, br s, ThH), 6.58 (2 H, d, *J* 0.8, 3- and 5-H) and 6.99 (1 H, d, *J* 1.5, ThH) δ_C(100.6 MHz) 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) and 173.3 (s); ν_{max}(KBr)/cm^{-1} 1636 (C=O); *m*/*z* 344 (M^+, 96%) and 329 (100).

4-Ethyl-2,5′,6-trimethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo-[1,2-*b*:5,4-*b*′]dithiophen-8-ol(4-ethyl-8-hydroxythiophenetriptycene) 27

To a solution of tribromide **22** (789 mg, 1.38 mmol) in diethyl ether (40 cm^3) was added *tert*-butyllithium (1.49 mol dm^{-3}; 6.50 cm^3, 9.69 mmol) at −40 °C. The mixture was stirred for 1 h at this temperature and treated with diethyl carbonate (0.25 cm^3, 2.06 mmol) at −78 °C. After being stirred for 10 min at −78 °C and for 1 h at room temperature, the mixture was quenched with aq. ammonium chloride. The mixture was extracted with diethyl ether and the extract was washed with water, dried and evaporated to dryness. The residue was subjected to column chromatography [CH_2Cl_2–CCl_4 (1:1)] to give the trithienylpropane **18** (117 mg, 26%) and a mixture of thiophenetriptycene **27** and ketone **28**. The mixture was separated by column chromatography (benzene) to give products **27** (94 mg, 19%) and **28** (113 mg, 23%).

4-Ethyl-8-hydroxythiophenetriptycene **27**, crystals, mp 141–143 °C (decomp.) (from hexane) (Found: C, 63.4; H, 5.0. $C_{19}H_{18}OS_3$ requires C, 63.7; H, 5.1%); δ_H(100 MHz) 1.51 (3 H, t, *J* 7.4, CH_2CH_3), 2.34 (9 H, d, *J* 0.7, Th-CH_3), 2.65 (2 H, q, *J* 7.4, CH_2CH_3), 3.14 (1 H, s, OH) and 6.68 (3 H, q-like, *J* 0.7, ThH); δ_C(100.6 MHz) 10.5 (q), 15.4 (q), 22.5 (t), 55.2 (s), 83.5 (s), 120.6 (d), 133.9 (s), 151.9 (s) and 154.5 (s); ν_{max}(KBr)/cm^{-1} 3500 (OH); *m*/*z* 358 (M^+, 100%), 343 (60) and 329 (65); λ_{max}(MeCN)/nm 300 (log ε 3.76).

4-Ethyl-2,6-dimethyl-4-(5-methyl-3-thienyl)-4,8-dihydrobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-one **28**, crystals, mp 182–183.5 °C (from EtOH) (Found: C, 63.1; H, 5.2%; M^+, 358.0516. $C_{19}H_{18}OS_3$ requires C 63.7; H, 5.1%; M, 358.0520); δ_H(400 MHz) 0.42 (3 H, t, *J* 7.3, CH_2CH_3), 2.31 (3 H, s, Th-CH_3), 2.46 (2 H, q, *J* 7.3, CH_2CH_3), 2.49 (6 H, s, 2- and 6-CH_3), 6.15 (1 H, s, ThH), 6.53 (2 H, s, 3- and 5-H) and 6.99 (1 H, d, *J* 1.2 ThH); δ_C(100.6 MHz) 8.4 (q), 15.4 (q), 16.4 (q), 33.6 (t), 49.3 (s), 117.5 (d), 125.54 (d), 125.59 (d), 135.0 (s), 140.2 (s), 144.8 (s), 146.6 (s), 155.8 (s) and 173.6 (s); ν_{max}(KBr)/cm^{-1} 1646 (C=O); *m*/*z* 358 (M^+, 27%) 343 (9) and 329 (100); λ_{max}(MeCN)/nm 332 (log ε 3.97) and 274 (3.98).

Attempted preparation of 4-*tert*-butyl-2,5′,6-trimethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-ol 31

To a solution of tribromide **23** (185 mg, 0.309 mmol) in ether (10 cm^3) was added *tert*-butyllithium (1.50 mol dm^{-3}; 1.4 cm^3, 2.1 mmol) at −40 °C. The mixture was stirred for 1 h at −30 to −40 °C and treated with diethyl carbonate (0.06 cm^3, 0.50 mmol) at −78 °C. After being stirred for 10 min at −78 °C and for 1 h at room temperature, the mixture was quenched with aq. ammonium chloride and extracted with diethyl ether. The ethereal layer was washed with water, dried and evaporated to dryness. The residue was subjected to column chromatography [CH_2Cl_2–CCl_4 (1:1)] to give compound **20** and ketone **29**. Each of the crude products **20** and **29** was purified by column chromatography (hexane and benzene, respectively) to give compound **20** (26 mg, 24%) and ketone **29** (32 mg, 27%), respectively.

4-*tert*-Butyl-2,6-dimethyl-4-(5-methyl-3-thienyl)-4,8-dihydrobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-one **29**, crystals, mp 145–147 °C (decomp.) (from hexane) (Found: M^+, 386.0887. $C_{21}H_{22}OS_3$ requires M, 386.0833); δ_H(400 MHz) 1.10 (9 H, s, Bu^t) 2.31 (3 H, s, Th-CH_3), 2.48 (6 H, s, 2- and 6-CH_3), 6.07 (1 H, br s, ThH), 6.48 (2 H, q-like, *J* 0.9, 3- and 5-H) and 7.19 (1 H, d, *J* 1.6, ThH); δ_C(100.6 MHz) 15.2 (q), 16.3 (q), 26.6 (q), 39.5 (s), 57.2 (s), 119.6 (d), 126.5 (d), 129.5 (d), 135.4 (s), 138.4 (s), 141.6 (s), 145.7 (s), 156.1 (s) and 173.9 (s); *m*/*z* 386 (M^+, 4%) and 330 (100).

Attempted preparation of 2,5′,6-trimethyl-4,8-dihydro-4,8[3′,2′]-thiophenobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-ol

To a solution of tribromide **21** (409 mg, 0.755 mmol) in THF (10 cm^3) was added butyllithium (1.68 mol dm^{-3}; 1.40 cm^3, 2.35 mmol) at −78 °C. After being stirred for 1 h at −78 °C, the mixture was treated with diethyl carbonate (0.1 cm^3, 0.825 mmol) and was then allowed to warm to room temperature. The mixture was quenched with aq. ammonium chloride and extracted with diethyl ether. The ethereal layer was washed with water, dried and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2) to give hydroperoxide **32** (156 mg, 57%) and trithienylmethane **17** (34 mg, 15%).

4-Hydroperoxy-2,6-dimethyl-4-(5-methyl-3-thienyl)-4,8-dihydrobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-one **32**, grey powder, mp 142–147 °C (decomp.) (washed with EtOH) (Found: C, 56.1; H, 4.1. $C_{17}H_{14}O_3S_3$ requires C, 56.3; H, 3.9%); δ_H(400 MHz) 2.39 (3 H, d, *J* 0.6, Th-CH_3), 2.53 (6 H, s, 2- and 6-CH_3), 6.47 (1 H, s, ThH), 6.88 (2 H, d, *J* 0.8, 3- and 5-H), 6.96 (1 H, d, *J* 1.3, ThH) and 8.16 (1 H, br s, OOH); δ_C(100.6 MHz) 15.3, 16.4, 119.9, 123.6, 125.7, 136.3, 139.3, 140.6, 149.4, 151.0 and 172.7; *m*/*z* 362 (M^+, 10%), 346 (63) and 330 (100); ν_{max}(KBr)/cm^{-1} 3326 (OOH) and 1627 (C=O).

Reduction of hydroperoxide 32 to 4-hydroxy-2,6-dimethyl-4-(5-methyl-3-thienyl)-4,8-dihydrobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-one 33 with $NaBH_4$

To a solution of hydroperoxide **32** (42 mg, 0.12 mmol) in EtOH (6 cm^3)–THF (6 cm^3) was added $NaBH_4$ (7.0 mg, 0.18 mmol) at room temperature. After being stirred for 20 h at room temperature, the mixture was diluted with aq. ammonium chloride and extracted with diethyl ether. The organic layer was washed with water, dried and evaporated to dryness. The residue was purified by column chromatography (CH_2Cl_2) to give alcohol **33** (30 mg, 76%) as light brown crystals, mp 194–197 °C (decomp.) (from EtOH) (Found: C, 59.0; H, 4.1. $C_{17}H_{14}O_2S_3$ requires C, 58.9; H, 4.1%); δ_H(400 MHz) 2.35 (3 H, d, *J* 0.8, Th-CH_3), 2.50 (6 H, d, *J* 0.8, 2- and 6-CH_3), 2.84 (1 H, s, OH), 6.31 (1 H, s, ThH), 6.61 (2 H, d, *J* 0.9, 3- and 5-H) and 7.17 (1 H, d, *J* 1.4, ThH); *m*/*z* 346 (M^+, 100%), 331 (36), 330 (40) and 317 (21); ν_{max}(KBr)/cm^{-1} 3408 (OH) and 1616 (C=O).

8-Methoxy-2,6-dimethyl-4-(5-methyl-3-thienyl)benzo[1,2-*b*:5,4-*b*′]dithiophene 36

To a solution of tribromide **21** (394 mg, 0.727 mmol) in THF (10 cm^3) was added butyllithium (1.68 mol dm^{-3}; 1.4 cm^3, 2.4 mmol) at −78 °C. After being stirred for 1 h at −78 °C, the mixture was treated successively with diethyl carbonate (0.09 cm^3, 0.74 mmol) and trimethyloxonium tetrafluoroboranuide (5 mol equiv.). The mixture was allowed to warm to room temperature, and was quenched with aq. ammonium chloride and extracted with diethyl ether. The ethereal layer was washed with water, dried and evaporated to dryness. The residue was subjected to column chromatography (hexane–CH_2Cl_2) to give the methoxy derivative **36** (85 mg, 34%) and trithienylmethane **17** (89 mg, 40%). Compound **36** was obtained as crystals, mp 123.5–124.5 °C (from MeOH) (Found: M^+, 344.0361. $C_{18}H_{16}OS_3$ requires M, 344.0363); δ_H(400 MHz) 2.54 (6 H, s, 2- and 6-CH_3), 2.58 (3 H, s, Th-CH_3), 4.16 (3 H, s, OCH_3), 6.93 (1 H, s, ThH), 7.02 (2 H, s, 3- and 5-H) and 7.11 (1 H, s, ThH); δ_C(100.6 MHz) 15.4 (CH_3), 16.4 (CH_3), 59.3 (OCH_3), 120.9 (C), 121.46 (CH), 121.65 (CH), 126.54 (C), 127.8 (CH), 139.43 (C), 139.49 (C), 139.55 (C), 140.0 (C) and 146.8 (C); *m*/*z* 344 (M^+, 100) and 329 (83).

Tris(3-bromo-5-methyl-2-thienyl)methanol 38

To a solution of 2,3-dibromo-5-methylthiophene **37**[28] (10.5 g, 40.9 mmol) in diethyl ether (40 cm^3) was added *sec*-butyllithium

(1.07 mol dm $^{-3}$; 37.0 cm^3, 39.6 mmol) at −78 °C and the mixture was stirred for 1 h at this temperature. The mixture was treated with diethyl carbonate (1.50 cm^3, 12.4 mmol) and stirred for 20 min at −78 °C and for 1 h at room temperature. The mixture was quenched with aq. ammonium chloride and extracted with diethyl ether three times. The extracts were combined, washed with water, dried and evaporated to dryness. To the viscous oil was added hexane to precipitate a powder, which was collected by filtration. The powder was washed with hexane several times to give alcohol **38** (6.21 g, 90%) as a powder, mp 83 °C (decomp.) (Found: C, 34.7; H, 2.4. $C_{16}H_{13}Br_3OS_3$ requires C, 34 5; H, 2.35%); δ_H(60 MHz) 2.42 (9 H, s, Th-CH_3), 4.43 (1 H, s, OH) and 6.63 (3 H, br s, ThH); *m/z* 554 (M$^+$, 6%, [Br_3]), 536 (22, [Br_2]), 521 (5, [Br_3]) and 378 (100, [Br]).

1,1,1-Tris(3-bromo-5-methyl-2-thienyl)ethane 40

Alcohol **38** (1.60 g, 2.87 mmol) was dissolved in acetic anhydride (20 cm^3) and the mixture was cooled to −40 to −50 °C. To the mixture was added 60% $HClO_4$ (1.60 g, 9.55 mmol) dropwise with a glass pipette over a period of 20 min and then diethyl ether (5 cm^3) was added. The mixture was stirred for 1 h at −30 to −40 °C and diethyl ether (200 cm^3) was added to the mixture held at −30 to −40 °C to precipitate perchlorate **39**. The suspension was kept for 40 min and the dark brown supernatant was removed through Teflon tubing. The residue was washed with diethyl ether (10 cm^3) several times until the washings were almost no longer coloured. Throughout the above manipulations the temperature was maintained within the range −30 to −40 °C. The perchlorate **39** was suspended in diethyl ether (25 cm^3) and was treated with methylmagnesium iodide, prepared from iodomethane (1.04 cm^3, 16.7 mmol) and magnesium (404 mg, 16.6 mmol) in diethyl ether (20 cm^3), at −30 °C. After being stirred for 30 min at −30 °C and for 1 h at room temperature, the mixture was quenched with aq. ammonium chloride and extracted with benzene three times. The combined extracts were washed with water and dried. The solid was removed by filtration and the filtrate was cooled over an ice–water-bath, treated with MCPBA (>70%; 150 mg, >0.61 mmol), and stirred for 30 min. To the mixture was added an appropriate amount of silica gel and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (CCl_4) to give compound **40** (1.03 g, 65%) as crystals, mp 259.5–260.5 °C (from CCl_4) (Found: C, 36.4; H, 2.8. $C_{17}H_{15}Br_3S_3$ requires C, 36.8; H, 2.7%); δ_H(400 MHz) 2.39 (9 H, d, *J* 0.8, Th-CH_3), 2.65 (3 H, s, Th_3C-CH_3) and 6.66 (3 H, q-like, *J* 0.8, ThH); δ_C(100.6 MHz) 15.2 (q), 27.8 (q), 46.9 (s), 107.6 (s), 130.5 (d), 136.5 (s) and 141.4 (s); *m/z* 552 (M$^+$, 27%, [Br_3]), 537 (55, [Br_3]) and 379 (100, [Br]).

When the above work-up was carried out without treatment with MCPBA, a yield of 4–5% of 4-bromo-5-[bis(3-bromo-5-methyl-2-thienyl)methylene]-2,2-dimethyl-2,5-dihydrothiophene **41** was obtained as yellow crystals, mp 133.5–140 °C (from EtOH) (Found: C, 36.3; H, 2.7. $C_{17}H_{15}Br_3S_3$ requires C, 36.8; H, 2.7%); δ_H(400 MHz) 1.56 (6 H, s, Bu^t), 2.40 (3 H, d, *J* 0.9, Th-CH_3), 2.41 (3 H, d, *J* 0.8, Th-CH_3), 6.45 (1 H, s, vinyl H), 6.58 (1 H, q-like, *J* 0.9, ThH) and 6.61 (1 H, q-like, *J* 0.9, ThH); δ_C(100.6 MHz) 15.6 (q), 15.7 (q), 30.1 (q), 30.3 (q), 56.7 (s), 109.0 (s), 111.6 (s), 112.7 (s), 114.1 (s), 127.3 (d), 128.2 (d), 133.1 (s), 136.9 (s), 141.1 (s), 141.5 (s), 148.3 (s) and 152.4 (d); *m/z* 552 (M$^+$, 23%, [Br_3]), 537 (24, [Br_3]), 473 (8, [Br_2]) and 379 (100, [Br]).

2,5′,6,8-Tetramethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo[1,2-*b*:5,4-*b*′]dithiophen-4-ol(4-hydroxy-8-methylthiophenetriptycene) 11

To a solution of tribromide **40** (1.614 g, 2.91 mmol) in THF (45 cm^3) was added *tert*-butyllithium (1.57 mol dm^{-3}; 11.1 cm^3, 17.4 mmol) at −78 °C. The resulting mixture was stirred for 1 h at −78 °C and then treated with dimethyl carbonate (1.22 cm^3, 14.5 mmol). After being stirred for 15 min at −78 °C and for 1.5 h at room temperature, the mixture was quenched with aq. ammonium chloride and extracted with diethyl ether three times. The combined extracts were washed with water, dried and evaporated to dryness. The residue was purified by column chromatography twice [CH_2Cl_2 for the first time and benzene–Et_2O (6:1) for the second] to give compound **11** (422 mg, 42%) as crystals, mp 170–172 °C (from hexane) (Found: C, 62.4; H, 4.75%; M$^+$, 344.0346. $C_{18}H_{16}OS_3$ requires C, 62.75; H, 4.75%; M, 344.0363); δ_H 2.10 (3 H, s, bridgehead CH_3), 2.33 (9 H, d, *J* 0.8, Th-CH_3), 3.19 (1 H, br s, OH) and 6.77 (3 H, q-like, *J* 0.8, ThH); δ_C 15.3 (q), 15.9 (q), 49.4 (s), 84.0 (s), 118.7 (d), 134.0 (s), 150.5 (s) and 156.5 (s); ν_{max}(KBr)/cm^{-1} 3370 (OH); λ_{max}(MeCN)/nm 301 (log ε 3.58) and 240 (3.79); *m/z* 344 (M$^+$, 100%), 329 (33), 311 (17), 301 (27) and 285 (51).

The crystals recrystallized from CCl_4 melted at 178–184.5 °C and included one molecule of CCl_4 (the chlorine was detected by Beilstein's method) per molecule of compound **11** (Found: C, 52.9; H, 3.9. $C_{18}H_{16}OS_3$·CCl_4 requires C, 52.7; H, 3.8%).

When diethyl carbonate was used in the place of dimethyl carbonate, the yield of alcohol **11** decreased to ~10% with formation of a small amount of 2,6,8-trimethyl-8-(5-methyl-2-thienyl)-4,8-dihydrobenzo[1,2-*b*:5,4-*b*′]dithiophen-4-one **42**, crystals, mp 197–197.5 °C (from MeOH) (Found: M$^+$, 344.0342. $C_{18}H_{16}OS_3$ requires M, 344.0363); δ_H(400 MHz) 2.16 (3 H, s, 8-CH_3), 2.38 (3 H, s, Th-CH_3), 2.46 (6 H, d, *J* 0.9, 2- and 6-CH_3), 6.55–6.56 (1 H, m, ThH), 6.76 (1 H, d, *J* 3.8, ThH) and 7.16 (2 H, q-like, *J* 1.5, 2- and 5-H); ν_{max}(KBr)/cm^{-1} 1654 (C=O); *m/z* 344 (M$^+$, 90%), 329 (100), 311 (14), 301 (110) and 285 (27).

Isomerization of 8-hydroxy-4-methylthiophenetriptycene 1 to ketone 26 by treatment with BuLi

To a solution of alcohol **1** (12 mg, 0.034 mmol) in THF (2 cm^3) was added butyllithium (1.66 mol dm^{-3}; 0.025 cm^3, 0.42 mmol) at room temperature. After being stirred for 1.5 h at room temperature, the mixture was quenched with aq. ammonium chloride and extracted with diethyl ether. The extract was washed with water, dried and evaporated to dryness. The ^{1}H NMR spectrum of the residue showed the formation of ketone **26** in more than 95% yield.

2,4,5′,6-Tetramethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo[1,2-*b*′:5,4-*b*′]dithiophen-8-yl methanesulfonate 44

To a solution of alcohol **1** (38 mg, 0.11 mmol) in pyridine (3 cm^3) was added methanesulfonyl chloride (0.5 cm^3) and the mixture was stirred for 9 h at room temperature. The mixture was quenched with water and extracted twice with diethyl ether. The combined extracts were washed successively with 1.2 mol dm^{-3} HCl, aq. $NaHCO_3$, and water, dried and evaporated to dryness. The residue was separated by column chromatography [CCl_4–CH_2Cl_2 (1:1)] to give methanesulfonate **44** (25 mg, 53%) and alcohol **1** (5 mg, 13%). Ester **44** was obtained as crystals, mp 203–204.5 °C (decomp.) (from EtOH) (Found: M$^+$, 422.0151. $C_{19}H_{18}O_3S_4$ requires M, 422.0139); δ_H(400 MHz) 2.14 (3 H, s, bridgehead CH_3), 2.32 (9 H, s, Th-CH_3), 3.45 (3 H, s, SO_2CH_3) and 6.60 (3 H, br s, ThH); δ_C(100.6 MHz) 14.8 (q), 15.1 (q), 40.5 (q), 49.4 (s), 91.5 (s), 119.3 (d), 135.5 (s), 146.8 (s) and 155.5 (s); *m/z* 422 (M$^+$, 87%), 343 (100), 328 (24) and 315 (93).

Attempted solvolysis of methanesulfonate 44 in acetic acid

A solution of methanesulfonate **44** (8.0 mg) in acetic acid (2 cm^3) was heated at 93 °C for 1 day. To the mixture were added water and diethyl ether and the ethereal layer was separated, washed with aq. $NaHCO_3$, dried and evaporated to dryness.

The residue was subjected to column chromatography [CCl_4–CH_2Cl_2 (1:1)] to give the starting material (4.2 mg, 53% recovery).

2,4,5′,6-Tetramethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo[1,2-*b*:5,4-*b*′]dithiophen-8-yl acetate 45

To a mixture of compound **1** (94.3 mg, 0.274 mmol), triethylamine (1 cm^3) and acetic anhydride (0.7 cm^3) was added DMAP (167 mg, 1.37 mmol). After the mixture had been stirred for 1.5 h at 0 °C, triethylamine (0.7 cm^3) and acetic anhydride (0.5 cm^3) were added to the mixture. After being stirred for another 1 h at 0 °C, the mixture was quenched with 1.2 mol dm^{-3} HCl, and extracted with diethyl ether three times. The combined extracts were washed successively with 1.2 mol dm^{-3} HCl, water, aq. Na_2CO_3 and water in this order, dried and evaporated to dryness. The residue was purified by column chromatography [CH_2Cl_2–hexane (3:1)] to give the acetoxy derivative **45** (83 mg, 78%) as crystals, mp 243.5–247.5 °C (from hexane) (Found: C, 62.1; H, 4.7. $C_{20}H_{18}O_2S_3$ requires C, 62.1; H, 4.7%); δ_H(90 MHz) 2.14 (3 H, s, bridgehead CH_3), 2.30 (9 H, d, *J* 1, Th-CH_3), 2.41 (3 H, s, OAc) and 6.58 (3 H, q-like, *J* 1, ThH); δ_C(22.5 MHz) 15.0 (q), 20.9 (q), 49.4 (s), 86.6 (q), 119.0 (d), 134.8 (s), 147.6 (s), 155.2 (s) and 168.4 (s); ν_{max}(KBr)/cm^{-1} 1770, 1761 and 1202; *m*/*z* 386 (M^+, 80%), 344 (99) and 315 (100).

8-Methoxy-2,4,5′,6-tetramethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo[1,2-*b*:5,4-*b*′]dithiophene 46

To a solution of alcohol **1** (996 mg, 2.89 mmol) in THF (25 cm^3) was added *sec*-butyllithium (1.08 mol dm^{-3}; 3.2 cm^3, 3.5 mmol) at −78 °C. After being stirred for 40 min at −78 °C, the mixture was treated with trimethyloxonium tetrafluoroboranuide (670 mg, 4.53 mmol). The mixture was allowed to warm to room temperature slowly over a period of 12 h, quenched with aq. ammonium chloride, and extracted three times with diethyl ether. The combined extracts were washed with water (×3), dried and evaporated to dryness. The residue was purified by column chromatography [CH_2Cl_2–hexane (1:2)] to give the methoxy derivative **46** (672 mg, 61%) and the starting compound **1** (176 mg, 18% recovery). Compound **46** was obtained as pale yellow plates, mp 199–200 °C (from hexane) (Found: C, 63.4; H, 5.1. $C_{19}H_{18}OS_3$ requires C, 63.65; H, 5.1%); δ_H(90 MHz) 2.14 (3 H, s, bridgehead CH_3), 2.32 (9 H, d, *J* 1, Th-CH_3), 4.05 (3 H, s, OCH_3) and 6.60 (3 H, q-like, *J* 1, ThH); δ_C(22.5 MHz) 15.1 (q), 49.4 (s), 55.8 (q), 89.8 (s), 119.4 (d), 134.7 (s), 148.8 (s) and 156.3 (s); λ_{max}(CH_2Cl_2)/nm 302 (log ε 3.69); *m*/*z* 358 (M^+, 100%) and 344 (45).

Crystal structure determination of compound 46

Crystal data. $C_{19}H_{18}OS_3$, *M* = 358.50. Monoclinic, *a* = 13.752(3), *b* = 14.367(2), *c* = 9.394(2) Å, β = 93.14(2)°, *V* = 1853.1(6) $Å^3$ (by least-squares refinement on diffractometer angles for 20 automatically centered reflections, λ = 1.541 78 Å), space group $P2_1/n$, *Z* = 4, D_c = 1.28 g cm^{-3}, *F*(000) = 752. Pale yellow plates. Crystal dimensions: 0.50 × 0.30 × 0.10 mm, μ(Cu-Kα) = 3.601 mm^{-1}.

Data collection and processing. Mac Science MXC18 diffractometer, ω/2θ mode with ω-scan width = 1.18 + 0.20 tan θ, ω-scan speed const. 10.0° min^{-1}, graphite-monochromated Cu-Kα radiation; 3456 reflections measured ($3.0 \leqslant 2\theta \leqslant 130°$, $+h$, $-k$, $\pm l$), 3070 unique reflections.

Structure analysis and refinement. The structure was solved by direct methods using SIR[29] in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least-squares[30] to minimize the functions $\Sigma(w|F_o| - |F_c|)^2$, where $w = \exp(5.00 \sin^2\theta/\lambda^2)/\sigma^2(F_o)$, for 2676 reflections with $I > 3\sigma I$. The final *R* and R_w values are 0.067 and 0.077, respectively. Atomic scattering factors from ref. 31. All calculations were carried out on a SUN SPARC 10 workstation. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.‡

2,5′,6,8-Tetramethyl-4,8-dihydro-4,8[3′,2′]thiophenobenzo[1,2-*b*:5,4-*b*′]dithiophen-4-yl acetate 49

To a solution of 4-hydroxy-8-methylthiophenetriptycene **11** (197 mg, 0.570 mmol) in triethylamine (5 cm^3)–acetic anhydride (3 cm^3) was added DMAP (34 mg, 0.27 mmol). The mixture was heated at 70 °C for 5 h and was then cooled to room temperature. The mixture was quenched with 1.2 mol dm^{-3} HCl, and extracted with diethyl ether (×3). The combined extracts were washed successively with 1.2 mol dm^{-3} HCl, water and aq. Na_2CO_3 in this order, dried and evaporated. The residue was purified by column chromatography [CH_2Cl_2–hexane (2:1)] to give the acetoxy derivative **49** (139 mg, 63%) as pale yellow crystals, mp 249.5–250.5 °C (Found: C, 61.9; H, 4.7. $C_{20}H_{18}O_2S_3$ requires C, 62.1; 4.7%); δ_H(400 MHz) 2.10 (3 H, s, bridgehead CH_3), 2.31 (9 H, s, Th-CH_3), 2.46 (3 H, s, OAc) and 6.59 (3 H, s, ThH); δ_C(100.6 MHz) 15.3 (CH_3), 16.0 (CH_3), 21.4 (CH_3), 49.1 (C), 87.3 (C), 120.2 (CH), 133.5 (C), 150.2 (C), 153.0 (C) and 169.2 (C); ν_{max}(KBr)/cm^{-1} 1763 and 1220; λ_{max}(CH_2Cl_2)/nm 296 (log ε 3.74); *m*/*z* 386 (M^+, 78%), 344 (91) and 315 (100).

‡ See instructions for authors (1996), January issue.

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Paper 5/06005B
Received 11*th September* 1995
Accepted 11*th December* 1995