Synthesis and reactions of 3,3′-dibromodihydrodipyrrins

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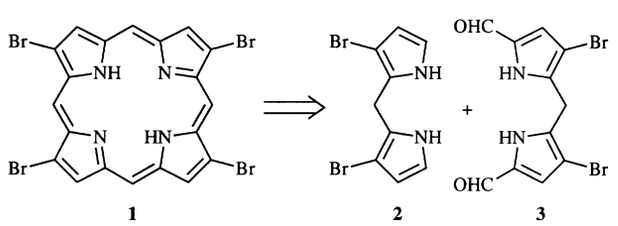
1 PERKIN

The dibromodihydrodipyrrin diester 7 was prepared by reaction of the corresponding pyrrole 6 with dimethoxymethane and BF_3·Et_2O. Subsequently 7 was converted into the dibromodihydrodipyrrin 2 in moderate yield. The diformyldihydrodipyrrin 3 was readily prepared by methylenation of the pyrrole 9 with BF_3·Et_2O, followed by deprotection. Attempted synthesis of the porphyrin 1 from 2 and 3 was unsuccessful because of the low reactivity of 2. The reaction of 7 or 11 with hexabutylditin in the presence of a Pd catalyst produced a new type of tin complex 12 in low yield. This complex was also readily obtained by an alternative procedure and found to revert to 7 upon reaction with TFA.

Introduction

Porphyrins are of considerable importance and interest and in recent years their functionalization has attracted much attention. However, most of the porphyrins prepared so far are *meso*-substituted compounds, the corresponding functionalized β-substituted *meso*-non-substituted porphyrins having been scarcely reported other than for β-alkyl derivatives; this is because of limitations and difficulties in their synthesis. The synthesis of such compounds is therefore a challenge. Recently, some β- and *meso*-substituted porphyrins have been synthesized utilizing cross-coupling reactions of β-halogeno derivatives.[1] Of such reactions, that of Stille and Suzuki[2] is excellent for the formation of carbon–carbon bonds, and we thought that it might be applied to the synthesis of β-substituted *meso*-non-substituted porphyrins. To test this, we attempted to prepare β-bromoporphyrin **1** using the '2 + 2' MacDonald method[3] (Scheme 1). Although the plan was unsuccessful, we learned



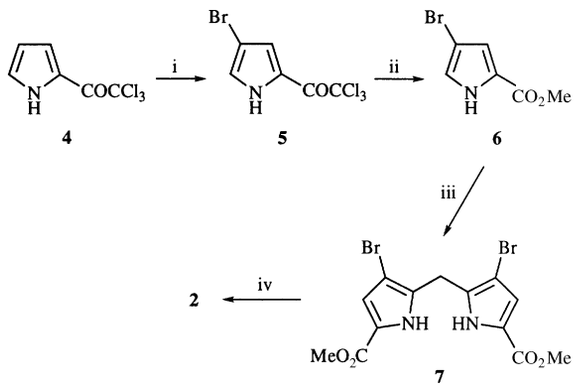
1 **2** **3**

Scheme 1

something of β-substituted dihydrodipyrrin compounds, the properties of which are unknown; we report here their preparation and reactivity.

Results and discussion

The bromopyrrole ester **6**[4] was easily prepared (57%) in a two-step reaction by bromination of trichloroacetylpyrrole **4**,[5] and subsequent ester formation from the trichloroacetyl group[6] (Scheme 2). Because of its two electron-withdrawing groups however, compound **6** was very stable and, therefore, it was difficult to prepare the dihydrodipyrrin **7** from it; thus, every combination of protic acid (*e.g.* HCl, HBr, TFA and *p*-TsOH) and methylene source (*e.g.* formaldehyde and dimethoxymethane) failed in this respect. However an earlier report[7] suggested that BF_3·Et_2O was useful for the synthesis of a dihydrodipyrrin from a pyrrole ester with an electron-withdrawing β-substituent. By this technique the pyrrole **6** with BF_3·Et_2O in

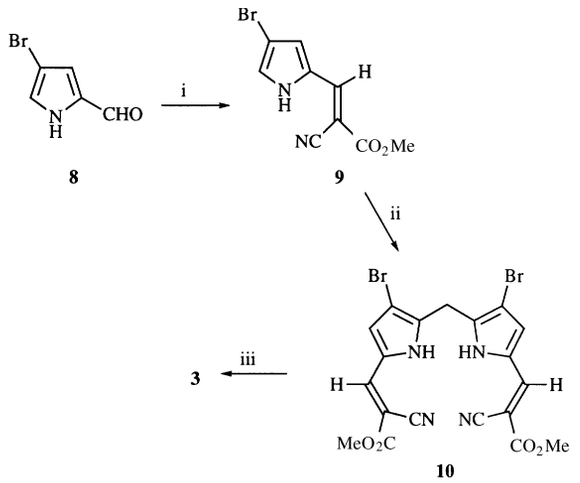


4 **5** **6** **7**

Scheme 2 *Reagents and conditions*: i, Br_2, $CHCl_3$, RT, 10 min; ii, NaOMe, MeOH, RT, 20 min; iii, $CH_2(OMe)_2$, BF_3·Et_2O, CH_2Cl_2, RT, 24 h; iv, KOH, $(CH_2OH)_2$, 120 °C, 15 min and 150 °C, 30 min

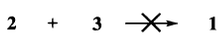
CH_2Cl_2 gave the dihydrodipyrrin diester **7** in 59% yield (Scheme 2). Although the pyrrole **6** has two reaction points, cross-linking occurred only at the α-position as confirmed by X-ray analysis of the derivatives of **7**. We next attempted saponification and subsequent decarboxylation of **7** to give **2**. The decarboxylation step was difficult, pyrolysis of the carboxylic acid resulting only in blackening; the acid unreactive in the presence of TFA. This behaviour resembles the unsuccessful attempts to decarboxylate 4-bromopyrrole-2-carboxylic acid.[8] By a careful study of the experimental conditions we succeeded in the preparation of the dihydrodipyrrin in 47% yield by heating **7** at 150 °C in ethylene glycol under basic conditions for 30 min (Scheme 2). Careful purification of **2** was necessary since in the presence of impurities it increasingly blackened with time. When pure, **2** was white, stable at room temperature under normal conditions for several hours and slightly light-sensitive; after 3 days, 90% of **2** survived.

The synthesis of diformyldihydrodipyrrin **3** was much easier than that of **2**. Protection of formylpyrrole **8**[9] by reaction[10] with cyanoacetic acid ester and methylamine in methanol for 1 h afforded the vinylpyrrole **9** (89%) which by methylenation with BF_3·Et_2O in CH_2Cl_2 at 30 °C for 11 h gave the dihydrodipyrrin **10** (86%) (Scheme 3). We were unable to recognize spectroscopically the geometrical isomers that should result statistically: either *E* or *Z* derivatives for **9** and either *E*,*E*, *E*,*Z* or *Z*,*Z* derivatives for **10**. When heated with conc. aqueous KOH for 30 min **10** was deprotected to give the dihydrodipyrrin **3** (72%) (Scheme 3). The dihydrodipyrrin **10** has a low solubility in common organic solvents.



Scheme 3 *Reagents and conditions*: i, $CH_2(CN)CO_2Me$, $MeNH_2$, MeOH, RT, 1 h; ii, $CH_2(OMe)_2$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 30 °C, 11 h; iii, KOH, H_2O, 110 °C, 30 min

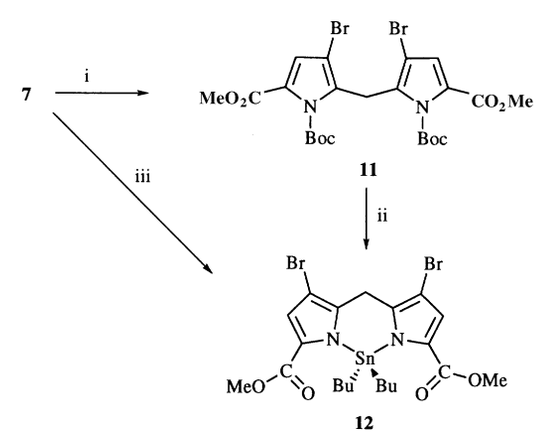
Attempted synthesis of the porphyrin **1** from the dihydrodipyrrins **2** and **3** (Scheme 4), with an acid catalyst such as *p*-



Scheme 4

TsOH and $BF_3{\cdot}Et_2O$ in CH_2Cl_2 in the dark failed to give detectable amounts of product. In fact the reactivity of the dihydrodipyrrin **2** was poor, in that it failed to react with Ehlrich's reagent, 4-dimethylaminobenzaldehyde, and other aldehydes. This unexpected result is explicable in terms of a reduction of the π-electron density on the pyrrole ring as the result of the electron-withdrawing bromo substituent. This suggests that it is necessary to have an electron-donating β-substituent on the pyrrole ring to ensure the success of the porphyrin synthesis.

Next, in order to examine the reactivity of the two bromo substituents of the dihydrodipyrrin diester, we attempted its conversion into a tributyltin compound. First, the *N*-Boc-protected dihydrodipyrrin **11** was synthesized in 89% yield by reaction [11] of the dihydrodipyrrin **7** with Boc_2O in the presence of 4-dimethylaminopyridine (DMAP) in CH_2Cl_2 (Scheme 5).



Scheme 5 *Reagents and conditions*: i, Boc_2O, DMAP, CH_2Cl_2, RT, 1 h; ii, $Bu_3SnSnBu_3$, $Pd(OAc)_2$, PPh_3, DMF, 120 °C, 2 h; iii, $Bu_3SnSnBu_3$, $Pd(PPh_3)_4$, DMF, 80 °C, 6 h

The structure of **11** was confirmed by X-ray analysis (Fig. 1), showing a dihedral angle of 82.76° between the two pyrrole rings. Subsequently, reaction [12] of **11** with hexabutylditin in the presence of a Pd catalyst gave, unexpectedly, the dihydrodipyrrin–dibutyltin complex **12** (28%) (Scheme 5), the structure of which was also determined by X-ray analysis (Fig. 2). The

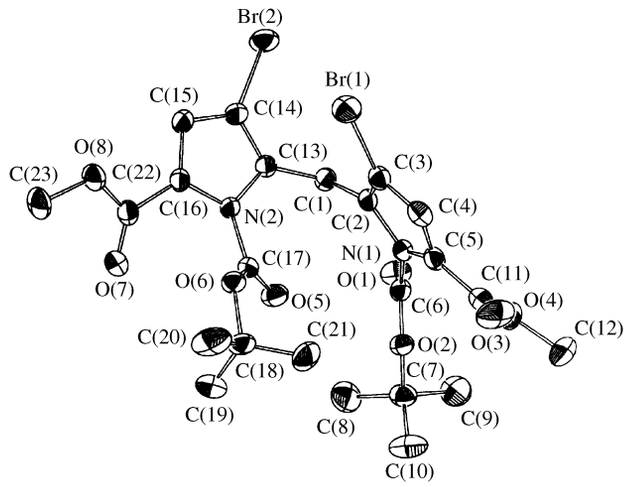


Fig. 1 ORTEP view of *N*-Boc-protected dihydrodipyrrin **11** showing 25% thermal ellipsoids with crystallographic numbering scheme

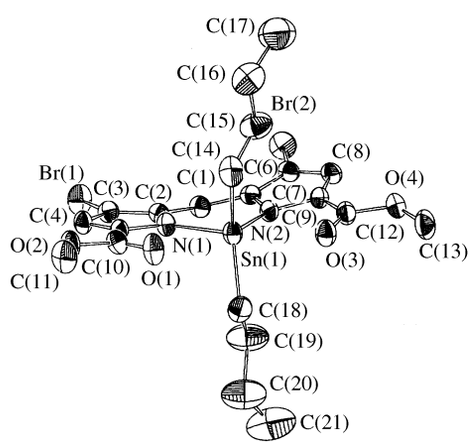


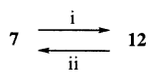
Fig. 2 ORTEP view of dihydrodipyrrin–tin complex **12** showing 30% thermal ellipsoids with the crystallographic numbering scheme

dihydrodipyrrin moiety in this is nearly coplanar with a dihedral angle of 18.42° between the two pyrrole rings. The tin atom of **12** has a distorted tetrahedral geometry (Table 1). Noteworthy are the relatively short intramolecular distances between the tin and oxygen atoms on the carbonyl groups (Table 1). In addition, it was found that **12** was stable under normal conditions, soluble in non-polar organic solvents such as hexane and almost insoluble in polar solvents such as methanol. At present, we have no reaction mechamism which satisfactorily explains the formation of **12**. Since the partial formation of **7** was detected by TLC analysis in the reaction of **12** with a Pd catalyst in DMF when heated, we allowed **7** to react directly with hexabutylditin in the presence of a Pd catalyst; complex **12** was obtained in 14% yield (Scheme 5). Therefore, the reaction of **7** with the tin reagent may be the key step for the formation of **12** from **11**. In this reaction the dibromo substituents remained unchanged. In order to replace the dihalogen substituents by tributyltin ones, the diiodo dihydrodipyrrin would be required.[13]

Since the dihydrodipyrrin–tin complex **12** seemed to result from reaction of a dianion of the dihydrodipyrrin **7** with dibutyltin dichloride, we attempted to optimize the conditions for this. The ready synthesis of complex **12** in 93% yield by a reaction with trimethylamine as base in CH_2Cl_2 for 1 h (Scheme 6) suggests that the facility with which this occurs is a result of the reduction of the pK_a of the dihydrodipyrrin by the presence of the two electron-withdrawing groups per pyrrole ring.[14] Furthermore, we found that the conversion of **12** to **7** with TFA readily occurred. The dihydrodipyrrin **7** precipitated upon reaction of **12** with TFA (2 equiv.) in hexane for 20 min was

Table 1 Selected bond lengths (Å) and angles (°) for **12**

Sn(1)–N(1)	2.164(6)
Sn(1)–N(2)	2.144(6)
Sn(1)–C(14)	2.049(7)
Sn(1)–C(18)	2.065(7)
Sn(1)···O(1)	2.629(5)
Sn(1)···O(3)	2.519(5)
N(1)–Sn(1)–N(2)	83.2(2)
N(1)–Sn(1)–C(14)	103.8(3)
N(1)–Sn(1)–C(18)	105.3(3)
N(2)–Sn(1)–C(14)	107.4(2)
N(2)–Sn(1)–C(18)	110.7(3)
C(14)–Sn(1)–C(18)	134.0(3)
N(1)–Sn(1)···O(1)	70.2(2)
N(1)–Sn(1)···O(3)	153.8(2)
N(2)–Sn(1)···O(1)	153.2(2)
N(2)–Sn(1)···O(3)	70.6(2)
C(14)–Sn(1)···O(1)	77.1(2)
C(14)–Sn(1)···O(3)	85.8(3)
C(18)–Sn(1)···O(1)	80.3(3)
C(18)–Sn(1)···O(3)	83.5(3)
O(1)···Sn(1)···O(3)	136.0(2)



Scheme 6 *Reagents and conditions*: i, Bu_2SnCl_2, (5:1) CH_2Cl_2–Et_3N, RT, 1 h; ii, TFA, hexane, RT, 20 min

collected easily (Scheme 6). Such an interconversion is unprecedented and may be useful for synthesis of dihydrodipyrrin derivatives.

Experimental

Mps were measured on a Yanaco MP-500D or a Büchi 535 melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1640 FT-IR spectrometer as KBr pressed pellets. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX270 FT spectrometer; *J* values are in Hz. Mass spectra were obtained on a Shimadzu QP-1000EX (EI) or a Shimadzu Kratos Concept 1s mass spectrometer (FAB). Elemental analyses were carried out on a Yanaco MT-3 CHN Corder. Commercially available reagents were used as supplied unless otherwise stated. All reactions were carried out under argon. Column chromatography was performed on silica gel (Wakogel C-300). Compounds **4**[5] and **8**[9] were prepared as previously described.

4-Bromo-2-trichloroacetylpyrrole 5[4]

Bromine (17.06 g, 107 mmol) was added dropwise to a solution of 2-trichloroacetylpyrrole **4**[5] (21.26 g, 100 mmol) in $CHCl_3$ (100 cm^3) cooled in an ice-bath. The resulting solution was stirred at room temperature for 10 min and then poured into water. The organic phase was separated, washed with aq. $NaHCO_3$ and water, dried ($MgSO_4$) and evaporated under reduced pressure. Recrystallization of the residue from hexane gave the product **5** (20.00 g, 69%) as a white solid, mp 136–138 °C (lit.,[4] 134–136 °C).

4-Bromo-2-methoxycarbonylpyrrole 6[4]

A solution of NaOMe (1.00 mol dm^{-3} in methanol; 25 cm^3, 25.0 mmol) was added slowly to a solution of 4-bromo-2-trichloroacetylpyrrole **5** (14.58 g, 50.0 mmol) in methanol (60 cm^3). The mixture was then stirred at room temperature for 20 min after which it was diluted with water (200 cm^3) and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layer and extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. Recrystallization of the residue from hexane gave the product **6** (8.35 g, 82%) as a white solid, mp 106–106.5 °C (lit.,[4] 98.5–100 °C).

Bis(3-bromo-5-methoxycarbonylpyrrol-2-yl)methane 7

BF_3·Et_2O (2.84 g, 20.0 mmol) was added dropwise to a solution of 4-bromo-2-methoxycarbonylpyrrole **6** (4.08 g, 20.0 mmol) and dimethoxymethane (7.61 g, 100 mmol) in CH_2Cl_2 (50 cm^3). After agitation of the mixture for several minutes, a white solid was precipitated. The reaction mixture was stirred at room temperature for 24 h, after which it was concentrated with a rotary-evaporator under reduced pressure. The resulting reddish solid was filtered off, washed with a small volume of CH_2Cl_2 and recrystallized from $CHCl_3$–toluene (5:1) to give the title compound **7** (2.48 g, 59%) as a white solid, mp 223–226 °C (decomp.) (Found: C, 37.33; H, 2.71; N, 6.69. Calc. for $C_{13}H_{12}N_2O_4Br_2$: C, 37.17; H, 2.88; N, 6.67%); δ_H(270 MHz, $CDCl_3$) 3.78 (6 H, s, 2 × OCH_3), 4.05 (2 H, s, CH_2), 6.75 (2 H, d, $J_{1,4}$ 2.6, 2 × 4-H) and 10.55 (2 H, br s, 2 × NH); δ_C(67.8 MHz, $CDCl_3$) 23.97, 52.27, 97.90, 116.95, 121.71, 131.64 and 161.51; ν_{max}/cm^{-1} 3229 (NH), 3137, 1684 (C=O), 1489, 1440, 1327, 1277, 1251, 1211, 1005 and 766; *m/z* (EI) 422 (M^+, 48%), 420 (M^+, 100) and 418 (M^+, 50).

Bis(3-bromopyrrol-2-yl)methane 2

In the dark, a suspension of the dihydrodipyrrin **6** (212 mg, 0.50 mmol) and 85% KOH (152 mg, 2.30 mmol) in ethylene glycol (2 cm^3) was stirred first at 120 °C for 15 min and then at 150 °C for 30 min to give a black reaction mixture; this was then immediately poured onto ice. After neutralization with AcOH (0.2 cm^3), the resulting solid was extracted with CH_2Cl_2. The organic phase was washed with water, dried ($MgSO_4$) and evaporated in the dark under reduced pressure. Purification of the crude product by column chromatography with CH_2Cl_2–hexane (3:1) as eluent gave the title compound **2** as a white solid (72 mg, 47%), mp 84.5–87 °C (decomp.) (Found: C, 35.71; H, 2.61; N, 9.03. Calc. for $C_9H_8N_2Br_2$: C, 35.56; H, 2.65; N, 9.22%). The presence of trace impurities damaged the product; δ_H(270 MHz, $CDCl_3$) 3.89 (2 H, s, CH_2), 6.17 (2 H, dd, *J* 2.6 and 3.0), 6.60 (2 H, AA′BB′, *J* 3.0 and 3.0) and 7.89 (2 H, br s, 2 × NH); δ_C(67.8 MHz, $CDCl_3$) 23.04, 95.64, 110.93, 117.65 and 126.31; ν_{max}/cm^{-1} 3358 (NH), 3131, 1560, 1267, 1081, 1006, 885 and 725; *m/z* (EI) 306 (M^+, 27%), 304 (M^+, 53), 302 (M^+, 27) and 143 (100).

3-Bromo-2-(2-cyano-2-methoxycarbonylvinyl)pyrrole 9

40% $MeNH_2$ in methanol (0.2 cm^3) was added dropwise to a solution of pyrrole-2-carbaldehyde **8**[9] (3.49 g, 20.0 mmol) and methyl cyanoacetate (2.08 g, 20.8 mmol) in methanol (60 cm^3). The mixture was stirred at room temperature for 1 h, after which it was evaporated under reduced pressure. Recrystallization of the residue from methanol gave the title compound **9** as a yellow solid (4.56 g, 89%), mp 179–180.5 °C (decomp.) (Found: C, 42.38; H, 2.72; N, 10.97. Calc. for $C_9H_7N_2O_2Br$: C, 42.38; H, 2.77; N, 10.98%); δ_H(270 MHz, [$^2H_6$]-DMSO) 3.80 (3 H, s, OCH_3), 7.34 (1 H, s), 7.60 (1 H, s), 8.90 (1 H, s, CH=C) and 12.39 (1 H, br s, NH); δ_C(67.8 MHz, [$^2H_6$]-DMSO) 52.83, 93.01, 99.80, 116.52, 117.09, 126.78, 127.48, 142.01 and 163.16; ν_{max}/cm^{-1} 3359 (NH), 3120, 3030, 2950, 2217 (C≡N), 1715 (C=O), 1605, 1383, 1261, 1229, 1125 and 918; *m/z* (EI) 256 (M^+, 78%), 254 (M^+, 78) and 224 (100).

Bis[3-bromo-5-(2-cyano-2-methoxycarbonylvinyl)pyrrol-2-yl]-methane 10

BF_3·Et_2O (2.84 g, 20.0 mmol) was added slowly to a solution of the vinylpyrrole **9** (2.56 g, 10.0 mmol) and dimethoxymethane (3.61 g, 47.5 mmol) in CH_2Cl_2 (250 cm^3). The mixture was stirred at 30 °C for 11 h, and then cooled in an ice-bath and allowed to stand for 30 min. The resulting yellow solid was filtered off, washed with a small volume of CH_2Cl_2 and collected. Vacuum drying of the residue afforded the analytically pure dihydrodipyrrin **10** as a yellow powder (2.26 g, 86%), mp 242–244 °C (decomp.) (Found: C, 43.41; H, 2.87; N, 10.72. Calc. for $C_{19}H_{14}N_4O_4Br_2$: C, 43.71; H, 2.70; N, 10.73%); δ_H(270

MHz, [$^2H_6$]-DMSO) 3.79 (6 H, s, 2 × OCH_3), 4.11 (2 H, s, CH_2), 7.39 (2 H, d, $J_{1,4}$ 2.0, 2 × 4-H), 8.08 (2 H, s, 2 × CH=C) and 12.35 (2 H, br s, 2 × NH); δ_C(67.8 MHz, [$^2H_6$]-DMSO) 24.08, 52.80, 92.17, 100.74, 116.66, 117.88, 125.97, 134.14, 141.65 and 163.27; ν_{max}/cm^{-1} 3258 (NH), 3132, 2956, 2217 (C≡N), 1718 (C=O), 1693, 1602, 1430, 1284, 1218, 1148 and 825; *m/z* (EI) 524 (M^+, 27%), 522 (M^+, 53), 520 (M^+, 27) and 330 (100).

Bis(3-bromo-5-formylpyrrol-2-yl)methane 3

A suspension of the dihydrodipyrrin **10** (1.05 g, 2.00 mmol) and 85% KOH (8.02 g, 121 mmol) in water (20 cm^3) was stirred in an oil-bath held at 110 °C for 30 min. After cooling to room temperature, the mixture was poured onto ice and neutralized with conc. HCl (*ca.* 11.5 cm^3). The product was extracted with AcOEt, and the organic solution was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. Recrystallization of the residue from ethanol yielded the title compound **3** as a fine white solid (518 mg, 72%), mp 251–254 °C (decomp.) (Found: C, 36.82; H, 2.37; N, 7.84. Calc. for $C_{11}H_8N_2O_2Br_2$: C, 36.70; H, 2.24; N, 7.78%); δ_H(270 MHz, [$^2H_6$]-DMSO) 4.01 (2 H, s, CH_2), 7.06 (2 H, d, $J_{1,4}$ 2.3, 2 × 4-H), 9.39 (2 H, s, 2 × CHO) and 12.33 (2 H, br s, 2 × NH); δ_C(67.8 MHz, [$^2H_6$]-DMSO) 23.13, 97.20, 121.71, 131.73, 133.96 and 178.75; ν_{max}/cm^{-1} 3307 (NH), 3087, 1661 (C=O), 1634, 1428, 1407, 1118 and 753; *m/z* (EI) 362 (M^+, 50%), 360 (M^+, 100) and 358 (M^+, 52).

Bis[3-bromo-1-(*tert*-butoxycarbonyl)-5-(methoxycarbonyl)-pyrrol-2-yl]methane 11

4-Dimethylaminopyridine (48 mg, 0.40 mmol) was added to a suspension of the dihydrodipyrrin **7** (1.68 g, 4.00 mmol) and Boc_2O (2.61 g, 12.0 mmol) in CH_2Cl_2 (40 cm^3). Within a few minutes there was liberation of CO_2 and dissolution of **7** started. The reaction mixture was stirred at room temperature for 1 h after which excess of Boc_2O was removed by addition of 2-diethylaminoethylamine (463 mg, 3.99 mmol); the solution was then stirred for an additional 10 min. It was then washed with aq. $KHSO_4$, water, aq. $NaHCO_3$ and brine, dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography of the residue with CH_2Cl_2 as eluent and recrystallization of the product from ethanol gave the title compound **11** as white crystals (2.21 g, 89%), mp 153–157 °C (decomp.) (Found: C, 44.47; H, 4.40; N, 4.52. Calc. for $C_{23}H_{28}N_2O_8Br_2$: C, 44.54; H, 4.54; N, 4.52%); δ_H(270 MHz, $CDCl_3$) 1.49 [18 H, s, 2 × $(CH_3)_3C$], 3.81 (6 H, s, 2 × OCH_3), 4.42 (2 H, s, CH_2) and 6.77 (s, 2 H, 2 × 4-H); δ_C(67.8 MHz, $CDCl_3$) 24.00, 27.28, 51.88, 85.84, 100.23, 120.64, 124.19, 131.97, 148.30 and 160.13; ν_{max}/cm^{-1} 3128, 2989, 1766 (C=O), 1703 (C=O), 1484, 1369, 1297, 1212, 1162, 1133 and 847; *m/z* (EI) 422 ($M^+ - 2 \times CO_2 - 2 \times C_4H_8$, 52%), 420 ($M^+ - 2 \times CO_2 - 2 \times C_4H_8$, 100) and 418 ($M^+ - 2 \times CO_2 - 2 \times C_4H_8$, 50).

Preparation of the dihydrodipyrrin–tin complex 12

Method A. A suspension of *N*-Boc-protected dihydrodipyrrin **11** (100 mg, 0.16 mmol), hexabutylditin (197 mg, 0.34 mmol), $Pd(OAc)_2$ (8 mg, 0.2 equiv.) and PPh_3 (18 mg, 0.4 equiv.) in dry DMF (2 cm^3) was stirred at 120 °C for 2 h. The resulting mixture was poured into brine and extracted with AcOEt. The extract was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography with hexane–AcOEt (2:1) as eluent gave a colourless solid **12** (29 mg, 28%), mp 118–118.5 °C (from methanol) (Found: C, 38.68; H, 4.27; N, 4.28. Calc. for $C_{21}H_{28}N_2O_4Br_2Sn$: C, 38.75; H, 4.34; N, 4.30%); δ_H(270 MHz, $CDCl_3$) 0.75 [6 H, t, *J* 6.9, 2 × $(CH_2)_3CH_3$], 1.14–1.55 (12 H, m), 3.90 (6 H, s, 2 × OCH_3), 4.06 (2 H, s, CH_2) and 7.02 (2 H, s, 2 × 4-H); δ_C(67.8 MHz, $CDCl_3$) 13.44, 24.32, 25.38, 25.95, 26.97, 52.40, 98.64, 118.06, 124.08, 139.19 and 166.41; ν_{max}/cm^{-1} 2960, 1637 (C=O), 1509, 1435, 1363, 1224, 1049 and 762; *m/z* (FAB) 651 ($M^+ + 1$).

Method B. A suspension of the dihydrodipyrrin **7** (70 mg, 0.17 mmol), hexabutylditin (199 mg, 0.34 mmol) and $Pd(PPh_3)_4$ (38 mg, 0.2 equiv.) in dry DMF (2 cm^3) was stirred at 80 °C for 6 h. The above described work-up afforded the dihydrodipyrrin–tin complex **12** (15 mg, 14%).

Facile conversion of the dihydrodipyrrin 7 into the dihydrodipyrrin–tin complex 12

To a suspension of the dihydrodipyrrin **7** (1.26 g, 3.01 mmol) and dibutyltin dichloride (915 mg, 3.01 mmol) in CH_2Cl_2 (30 cm^3), triethylamine (6 cm^3) was added at once. The mixture was stirred at room temperature for 1 h after which it was washed with aq. citric acid, aq. $NaHCO_3$ and water, dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography with CH_2Cl_2–hexane (1:1) as eluent gave the dihydrodipyrrin–tin complex **12** (1.83 g, 93%).

Facile conversion of the dihydrodipyrrin–tin complex 12 into the dihydrodipyrrin 7

TFA (24 mg, 0.21 mmol) was added to a solution of complex **12** (67 mg, 0.10 mmol) in hexane (3 cm^3). Within a few minutes, a white solid was precipitated. The mixture was stirred for 20 min, after which the product was filtered off and washed with hexane to afford the dihydrodipyrrin **7** as a spectroscopically pure white solid (37 mg, 85%).

X-Ray crystal structure determination of compound 11

Recrystallization of the compound from hexane gave colourless needles suitable for X-ray analysis.

Crystal data. $C_{23}H_{28}H_2O_8Br_2$, $M = 620.29$. Triclinic, $a = 11.151(3)$, $b = 12.256(3)$, $c = 11.113(4)$ Å, $\alpha = 95.76(2)$, $\beta = 114.28(2)$, $\gamma = 73.75(2)°$, $V = 1329.0(7)$ Å^3 (by least-squares refinement on diffractometer angles for 21 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P\bar{1}$ (#2), $Z = 2$, $D_x = 1.550$ g cm^{-3}. Colourless, prism crystals. Crystal dimensions: 0.35 × 0.30 × 0.10 mm, μ(Mo-Kα) 31.06 cm^{-1}.

Data collection and processing. Rigaku AFC7R diffractometer, $\omega/2\theta$ mode with ω scan width (1.63 + 0.30 tan θ)°, ω scan speed 4.0° min^{-1}, graphite-monochromated Mo-Kα radiation; 6417 reflections measured ($0 < 2\theta < 55°$, $+h$, $\pm k$, $\pm l$); 6099 unique; 3698 with $I > 3\sigma(I)$ which were retained in all calculations. A linear correction factor was applied to the data for crystal decay, *ca.* 17%. An empirical absorption correction was applied (transmission factors: 0.67–1.00). The data were corrected for Lorentz and polarization factors.

Structure analysis and refinement. Direct methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The maximum peak in the final ΔF map was 0.79 e Å^{-3}. Refinement with 3698 independent reflections and 316 variable parameters gave $R = 0.047$ and $R_w = 0.044$. The X-ray molecular structure is shown in Fig. 1. Programs and computers used and sources of scattering factor data are given in ref. 15. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

X-Ray crystal structure determination of compound 12

Recrystallization of the compound from methanol gave colourless needles suitable for X-ray analysis.

Crystal data. $C_{21}H_{28}N_2O_4Br_2Sn$, $M = 650.96$. Monoclinic, $a = 9.853(5)$, $b = 18.322(4)$, $c = 13.948(4)$ Å, $\beta = 97.40(3)°$, $V = 2497(1)$ Å^3 (by least-squares refinement on diffractometer angles for 16 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/C$ (#14), $Z = 4$, $D_x = 1.731$ g cm^{-3}. Colourless,

† For details see Instructions for Authors (1997), *J. Chem Soc., Perkin Trans 1*, 1997, Issue 1. All requests for this information should be accompanied by a full bibliographic citation together with the reference number CCDC 207/103.

prismatic crystals. Crystal dimensions: 0.30 × 0.25 × 0.20 mm, μ(Mo-Kα) 42.60 cm^{-1}.

Data collection and processing. Rigaku AFC7R diffractometer, $\omega/2\theta$ mode with ω scan width (1.73 + 0.30 tan θ)°, ω scan speed 6.0° min^{-1}, graphite-monochromated Mo-Kα radiation; 6235 reflections measured ($0 < 2\theta < 55°$, $+h$, $+k$, $\pm l$); 5907 unique; 2928 with $I > 3\sigma(I)$ which were retained in all calculations. An empirical absorption correction was applied (transmission factors: 0.87–0.99). The data were corrected for Lorentz and polarization factors.

Structure analysis and refinement. Direct methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions. The maximum peak in the final ΔF map was 0.56 e Å^{-3}. Refinement with 2928 independent reflections and 271 variable parameters gave $R = 0.045$ and $R_w = 0.045$. C(15)–C(17) and C(19)–C(20) in the butyl groups were refined as riding atoms with C–C distances of 1.54 Å and C–C–C angles of 111.0° in order to find the best placement of the carbon atoms in alkyl chains. The X-ray molecular structure is shown in Fig. 2. Programs and computers used and sources of scattering factor data are given in ref. 15. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

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